MODELLING MUNICIPAL WASTEWATER TREATMENT PLANTS FOR INDUSTRIAL EFFLUENT DISCHARGE PERMITTING:
FOCUSING ON HOW MODELLING CAN BE CARRIED OUT IN CASES WHERE MEASUREMENTS AND RESOURCES ARE LIMITED

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DECLARATION

I, ……..……..…….. declare that:

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As the candidate's Supervisor I have approved this thesis for submission.

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ABSTRACT

It has been shown by Mzulwini (2008) that at eThekwini Municipality, in practice, the traditional approach to trade effluent discharge permitting does not provide adequate protection to the wastewater treatment plants (WWTPs). The municipality has 27 wastewater treatment plants which discharge their final effluent into the nearest river in the respective areas. The receiving rivers are exposed to contamination. To avoid or reduce such contamination, the final treated effluent must have acceptable levels of compliance to the set quality standards. Among other factors, a more efficient permitting process will protect WWTPs from excessive pollutant loadings and improve the quality of the final treated effluent discharged to the rivers.

The search for an improved permitting system inspired a project (K5/1734) which was funded by the Water Research Commission (WRC). The aim of the project was to identify ways of improving the permitting process by developing a means of predicting the effect of a specific industrial effluent on the performance of a municipal wastewater treatment plant (WWTP) through the use of laboratory measurements on the industrial effluent and a bio-process simulation model describing both the laboratory tests and the WWTP. The deliverable of the project would be a calibrated model that could be used to simulate scenarios related to evaluations of how much pollutant load could be discharged into a WWTPs for a specified level of compliance to the treated effluent quality standards set by the authority.

The conditions in which municipalities in South Africa operate had great influence on the approach adopted in the study. Municipalities are part of local government whose operations face limited resources and skills resulting in limited service delivery in many sectors including the water and sanitation sector. In the water and sanitation sector the amount and nature of plant data collected from the municipal WWTPs is adequate for plant performance monitoring but inadequate for modelling according to good modelling guidelines. Thus, this study explores how the limited data and information available to a municipality for plant performance monitoring, can be used to develop a model for a municipal WWTP. Considering that the model development would be based on plant performance monitoring data, the model would be of limited purpose i.e. to evaluate the long term impact of industrial effluents in order to establish regulatory limits on the effluent discharged into the WWTP. In order to address some of the limitations of data the study proposes techniques of filling in the gaps where critical information is missing.

While there are established methods and approaches to modelling WWTPs for cases where the majority of the data and required information for modelling is available or can be obtained, the approach for modelling

cases with limited information is not well established. The study explores methods of closing the missing gaps in data and information available to the municipality in order to obtain a model that can predict the long term effect of industrial effluent on the performance of a WWTP. The acceptability of the model's prediction was evaluated based on the standards of compliance, similar to those used by the municipality during its evaluations of WWTP compliance to final treated effluent standards. Introducing the use of mathematical models of WWTP in the permitting process in municipal wastewater management is novel. The sample area for the study was Verulam WWTP in eThekwini Municipality.

Verulam WWTP relies on the activated sludge process to treat the incoming wastewater. Modelling of the activated sludge process was based on the IWA, ASM1 model. A crucial part of developing the model was characterisation of influent wastewater received at the WWTP. The influent characterisation required for modelling is more detailed than that routinely employed for monitoring the performance of the WWTP. ASM type models require further break down of the organic, nitrogenous and phosphorus fraction into smaller sub-fractions. While the measurement of the total organic, nitrogenous and phosphorus fractions is straight forward if standard methods (Standard Methods, 1995) are followed, the sub-fractionation of the organic, nitrogenous and phosphorus fractions, especially the organic fraction requires more extensive and sophisticated measurement techniques.

The organic fraction of municipal wastewater (measured in terms of chemical oxygen demand, COD) is divided into three main fractions, non-biodegradable, biodegradable and active biomass. To determine the amount of readily biodegradable fraction S_S and heterotrophic active biomass X_H, the batch test procedure outlined in Wentzel et al. (1995) was used. The inert soluble substrate, S_I was determined by a flocculation-filtration procedure on the wastewater collected at the end of the batch respirometric test (Wentzel et al., 1999). The autotrophic biomass was assumed to be of negligible concentration. A modelling approach was proposed to estimate the slowly biodegradable fraction X_S and the inert particulate fraction X_I.

The batch test results of the industrial effluent from Verulam WWTP confirmed the complexity of industrial effluent and its significant variation when compared to domestic effluent. The respirograms for the wastewater received by the Verulam WWTP showed characteristics very different from the typical respirogram of domestic wastewater. Furthermore, samples taken on different days differed markedly from each other. This means that for the purpose of evaluation the impact of industrial effluents over an extended period such as a year, COD fractionation has to be done more frequent, perhaps even daily, if it were to be done experimentally. The results of the study indicated that COD fractionation is more difficult in the case of a WWTP receiving industrial effluent that differs significantly with domestic wastewater.

A new approach ('the catchment balance approach') was attempted in order to determine the organic fractions in wastewater. The principle behind this approach was to review the present knowledge and measured data with respect to the characteristics and volumes of the wastewater released by the major contributors to the WWTP catchment and then come up with a reasonable estimate of the composition of the combined wastewater stream received by the WWTP with special focus on the COD fractions. The procedures used to come up with estimates were a form of probabilistic modelling based on Monte Carlo simulations. The information that is needed for estimation of the characteristics of each wastewater source stream was obtained from combining the data available from measurements made during the time to time monitoring of individual factory effluent quality undertaken by municipal inspectors and a qualitative assessment of wastewater aimed at estimating the chemical and physical properties that theoretically could be expected to be present based on the knowledge of the factory's core business. A significant feature of the catchment balance methodology is that the influence of each factory is already represented in the wastewater characterisation, albeit in a very approximate form.

The evaluation of the factory effluent for the purpose of setting the permit conditions thus becomes just a special case of the process of improving the model to represent specific issues in the catchment, rather than a separate modelling process as envisaged in the original project proposal. The catchment balance and the wastewater treatment process model, taken together, form a probabilistic model, whose evaluation was carried out on a statistical basis by comparing its outputs with measurements on a cumulative probability basis, rather than a day-by-day basis. This is consistent with the envisaged use of the model, which would be to predict the probable cumulative impact of a factory's effluent on the quality of treated wastewater being returned to the environment.

PREFACE

This thesis entitled "Modelling municipal wastewater treatment plants for industrial discharge permitting: Focusing on how modelling can be carried out in cases where measurements and resources are limited" was prepared by the candidate Mr Farai T Mhlanga, under the supervision of Professor Chris A Buckley and Mr Chris J Brouckaert. This thesis was solely prepared by the candidate. Some parts of the thesis refer to research work of others, and references for these sources have been provided to the best of the candidate's efforts.

This preface also intends to highlight that some of parts of this thesis form part of a scientific report entitled "Investigation into Methods for the Development of a Protocol for Quantitative Assessment of Industrial Effluents for Permitting of Discharge to Sewer - an eThekwini Case Study" (K5/1734) prepared for and submitted to the Water Research Commission (WRC) in South Africa who funded the research. The candidate was a co-author of the scientific report submitted to the WRC.

GLOSSARY

Activated sludge	Product that results when primary effluent is mixed with a mass of microorganism and then agitated and aerated to promote biological treatment, speeding the breakdown of organic matter in wastewater undergoing treatment.
Aerobic	The condition of living or acting in the presence of molecular oxygen.
Autotrophs	Organisms which use inorganic carbon dioxide or bicarbonate as sole carbon source for growth and development.
Bacteria	Single-cell, prokaryotic micro-organisms.
Chemical oxygen demand	A measure of the oxygen equivalent of organic matter content in a sample that is susceptible to oxidation by a strong chemical oxidant at elevated temperature and reduced pH.
Heterotrophs	Organisms that require organic substrates to obtain carbon for growth and development.
Inhibition	An impairment of bacterial function.
Kinetics	The branch of chemistry that is concerned with the rates of change in the concentration of reactants in a chemical reaction.
Pollution	The introduction of contaminants into an environment, of a substance which has harmful or poisonous effects.
Respiration	A biochemical process by which living organisms take up oxygen from the environment and consume organic matter, releasing both carbon dioxide and heat energy.
Suspended solids	Un-dissolved non-settleable solids present in wastewater.
Trade effluent	Any liquid which is given off as a result of any industrial, trade, manufacturing, mining or chemical process or any laboratory research or agricultural activity and includes any liquid other than standard domestic effluent or storm-water.
Wastewater	Water that has been used in homes, industries, and businesses that is not for reuse unless treated by a wastewater facility.

LIST OF SYMBOLS AND ABBREVIATIONS

ACRU	Agricultural Catchments Research Unit
ADMI	American Dye Manufacturers' Institute
ASM	Activated sludge model
ASM1	Activated sludge model No. 1
ASM2	Activated sludge model No. 2
ASM2d	Activated sludge model No. 2d
ASM3	Activated sludge model No. 3
ASU	Activated sludge unit
ATU	Allyl thiourea
b_A	Decay coefficient for autotrophic biomass (/d)
b_H	Decay coefficient for heterotrophic biomass (/d)
BOD	Biological oxygen demand (mg/L)
CDF	Cumulative distribution function
CFD	Computational fluid dynamics
COD	Chemical oxygen demand (mg/L)
COD_T	Total chemical oxygen demand (mg/L)
C_{TN}	Total nitrogen (mg N/L)
DNA	Deoxyribonucleic acid
DO	Dissolved oxygen (mg O_2/L)
DWAF	Department of Water Affairs and Forestry
EMC	Event mean concentration
EMS	Environmental management system
F/M	Food to micro-organism ratio (mg COD/ mg MLVSS.d)
f_E	Endogenous residue fraction (mg COD/mg COD)
f_{MA}	Maximum ratio of S_{ads}/Z_{BH} (mg COD/mg COD)
f_P	Fraction of biomass leading to particulate products (mg COD/mg COD)
f_{XI}	Fraction of particulate non-biodegradable COD (mg COD/mg COD)
GMP	Good modelling practice
HSG	Hochschulgruppe
IAWPRC	International Association on Water Pollution Research and Control
IAWQ	International Association of Water Quality

IQR	Interquartile range
IWA	International Water Association
i_{XB}	Mass of nitrogen per mass of X_B (mg N/mg COD)
i_{XE}	Mass of nitrogen per mass of COD in endogenous mass (mg N/mg COD)
i_{XP}	Mass of nitrogen per mass of X_P (mg N/mg COD)
i_{XI}	Mass of nitrogen per mass of X_I (mg N/mg COD)
K_A	S_{enm} specific adsorption rate
k_a	Ammonification rate (m^3·COD/mg·d)
k_h	Maximum specific hydrolysis rate (mg COD/mg COD·d)
K_{MP}	Heterotrophic maximum specific growth rate on SBCOD (/d)
K_{NH}	Ammonia half-saturation coefficient for autotrophic biomass (mg NH_3-N/m^3)
K_{NO}	Nitrate half saturation coefficient for heterotrophic biomass (mg NO_3-N/m^3)
K_{OA}	Oxygen half-saturation coefficient for autotrophic biomass (mg O_2/m^3)
K_{OH}	Oxygen half-saturation coefficient for heterotrophic biomass (mg O_2/m^3)
K_S	Half-saturation coefficient for heterotrophic biomass (mg COD/m^3)
K-S	Kolmogorov-Smirnov
K_{SH}	Heterotrophic half saturation coefficient on S_{bs} (mg COD/m^3)
K_{SP}	Heterotrophic half saturation coefficient on S_{ads} (mg COD/mg COD)
K_X	Half-saturation coefficient for hydrolysis of slowly biodegradable substrate (mg COD/mg COD)
LIMS	Laboratory information management system
MSL	Model Specification Language
MLE	Maximum likelihood estimation
MLSS	Mixed liquor suspended solids (mg/L)
MLVSS	Mixed liquor volatile suspended solids (mg/L)
MoM	Method of moments
N	Nitrogen
O	Oxygen
OED	Optimal experimental design
ODE	Ordinary differential equation
OP	Ortho Phosphorus
OUR	Oxygen Uptake Rate (mg/L·h)
P	Phosphorus
PAO	Phosphorus accumulating organisms

PID	Proportional integral derivative
RAS	Return activated sludge
RBCOD	Readily biodegradable COD (mg/L)
RV	Random variate
S_{ads}	Adsorbed slowly biodegradable substrate (mg/L)
S_{ALK}	Alkalinity (Mol HCO_3^-/L)
SBCOD	Slowly biodegradable COD (mg COD/L)
SBR	Sequencing batch reactor
SCADA	Supervisory control and data acquisition
SCS	Soil Conservation Services
S_{bs}	Readily biodegradable soluble substrate (mg COD/L)
S_{enm}	Enmeshed slowly biodegradable substrate (mg COD/L)
S_I	Soluble non-biodegradable COD (mg COD/L)
S_{ND}	Soluble nitrate nitrogen concentration (mg N/L)
S_{NH}	Soluble ammonia nitrogen (mg N/L)
S_{NI}	Soluble non-biodegradable organically bound nitrogen (mg N/L)
S_{NO}	Nitrate and nitrite (mg N/L)
S_O	Dissolved oxygen concentration (g O_2/m^3)
SRT	Solids retention time (h)
S_S	Readily biodegradable COD (mg COD/L)
STOWA	Stichting Toegepast Onderzoek Waterbeheer (Acronym for Foundation for Applied Waterr Research)
S_{us}	Unbiodegradable soluble COD (mg COD/L)
SWOT	Strengths, weaknesses, opportunities and threats
TKN	Total Kjeldahl Nitrogen (mg N/L)
TN	Total Nitrogen (mg N/L)
TP	Total Phosphorus (mg P/L)
TSS	Total suspended solids (mg/L)
TUDP	Technical University Delft Phosphorus model
UCT	University of Cape Town
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
VSS	Volatile suspended solids (mg/L)
WAS	Waste activated sludge

WEF	Water Environment Federation
WERF	Water Environment Research Foundation
WEST	World-wide Engine for Simulation and Training
WISA	Water Institute of South Africa
WQI	Water Quality Inspector
WRC	Water Research Commission of South Africa
WWTP	Wastewater treatment plant
X_{BA}	Autotrophic biomass (mg COD/L)
X_{BH}	Heterotrophic biomass (mg COD/L)
X_I	Inert particulate COD (mg COD/L)
X_{ND}	Particulate nitrate nitrogen (mg N/L)
X_{NI}	Particulate non-biodegradable organically bound nitrogen associated with X_I (mg N/L)
X_{NP}	Particulate non-biodegradable organically bound nitrogen associated with X_P (mg N/L)
X_S	Slowly biodegradable COD (mg COD/L)
X_P	Particulate products arising from biomass decay (mg COD/L)
Y_A	Yield for autotrophic biomass (mg COD/mg N)
Y_{ZH}	Yield of heterotrophic biomass (mg COD/mg COD)
Z_{BH}	Heterotrophic active biomass (mg COD/L)
Z_E	Endogenous mass (mg COD/L)
Z_I	Inert mass (mg COD/L)
μ_A	Autotrophic maximum specific growth rate (/d)
μ_H	Heterotrophic maximum specific growth rate (/d)
η_g	Correction factor for μ_H under anoxic conditions
η_h	Correction factor for hydrolysis under anoxic conditions

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1 INTRODUCTION

The use of mathematical models to simulate and predict the behaviour of activated sludge systems has become a key component in wastewater management in recent years (Henze, 2008; Petersen et al., 2000). Mathematical models have become an accepted tool for assessing the effect of changes in wastewater flows and loads in full scale wastewater treatment plants. Simulation exercises using mathematical models have proved valuable in training of operators (Pena-Tijerina, 2007). Furthermore the application of mathematical models is growing and now encompasses areas of research, plant design, troubleshooting and process control (Vanhooren et al., 2003). Municipalities stand to benefit from the use of mathematical models in wastewater management.

The major instruments available to municipalities for the management of wastewater are wastewater treatment plants for remediation, discharge permits for placing limits on what may be discharged, and discharge tariffs for financing the treatment and for providing incentives and penalties for users of the system (DWAF, 2001). An optimal strategy that involves all the above mentioned instruments is required for the municipality to serve all its clients while meeting the treated effluent discharge standards set by the relevant authorities. However, the presence of industrial effluent in the wastewater streams introduces a complex, and most of the time, poorly understood variability of the composition and volumes of wastewater. This complexity associated with industrial wastewater complicates the treatment process of the wastewater. The sources of the industrial wastewater are factories located in the different catchments of the municipal wastewater treatment plants (WWTPs). The factories are issued with discharge permits which allow them to discharge industrial effluent into the municipal sewer system, for treatment.

Industrial effluent can often be accommodated up to a certain point without compromising the quality of the treated water. Beyond that point it may compromise the ability to treat the wastewater to the required quality standards. In response to this challenge, the Water Research Commission (WRC) of South Africa and eThekwini Municipality initiated a research project (K5/1734) in 2007. It was proposed to develop a protocol that would enable the municipality to evaluate the ability of a receiving WWTP to adequately treat incoming influent wastewater to the required final effluent discharge standards before granting the discharge permit to the factory discharging within the catchment area of the WWTP. Since the permit is part of a regulatory process, the protocol is required to be scientifically and legally defensible. Developing a model for the wastewater treatment was proposed as a part of the protocol. The study area was eThekwini Municipality which is found in the province of KwaZulu-Natal in South Africa. EThekwini is the largest city in this province covering about 2 300 km^2 with a population of over 3 million people.

In eThekwini Municipality the eThekwini Water and Sanitation (EWS) department carries the responsibility of monitoring water pollution in four key areas; at source, at the reticulation system, at the WWTP and testing the treated effluent that is discharged to the receiving water body (Durban Metro Guide line No.6, 2001). The municipality has 27 wastewater treatment plants which discharge their final effluent into the nearest river in the respective areas. In order to protect the receiving rivers from contamination, the final effluent quality must comply to set discharge standards.

The EWS department faces significant challenges with regard to provision of the above mentioned services. One of the significant challenges is the shortage of sufficiently skilled personnel to deal with complexities of treating industrial effluents. Furthermore the shortage of skilled personnel slows down the process of introducing new tools for wastewater management such as modelling. This was the case, when this study was carried out. At the time of the study EWS did not use any WWTP modelling and as a result they had not developed the capacity to undertake measurements to support modelling.

A typical stepwise procedure for modelling WWTPs includes data collection, data reconciliation and calibration of model parameters (Gernaey et al., 2004). Since limited amounts of plant data are collected from the municipal WWTPs during plant performance monitoring, such data is the only data available for modelling purposes. Against this background, this study explores how the limited data and information available to a municipal department such as EWS can be used to develop a model for a municipal WWTP that can be used to improve the permitting process in that municipality. Hence one of the objectives of the research was to test whether modelling could be done successfully with limited measurement data. Thus, the initial approach in this study started with the assumption that using routine plant monitoring data supplemented by respirometry to determine the influent wastewater COD fractions would lead to acceptable modelling results for the permitting process. When this did not provide acceptable outcomes alternative approaches were proposed. When respirometry proved to be inadequate to determine the influent COD fractions, the catchment balance approach was proposed and probabilistic techniques of filling in the gaps where critical information is missing were used on the available data, in order to achieve the goal of having a WWTP model with predictive power of acceptable reliability for the purpose of informing the permitting process.

1.1 Motivation

Section 24 of the National Environmental Management Act No. 107 of 1998 requires environmental authorities such as EWS, to conduct a thorough assessment of the environmental impacts, and mitigation measures before issuing out a discharge permit. The effluent discharge permit consequently is a crucial interface between the local authority and the industry. Hence the permitting system has to carefully balance protection of the general public and the environment against the rights of those working in

industry and the promotion of economic activity. Furthermore, the Constitution of the Republic of South Africa No. 108 of 1996 has through section 33 of the Bill of Rights strived to ensure that everyone has a right to administrative action that is lawful, reasonable and procedurally fair. The steps taken to guarantee this right extend to the administrative process of setting standards for, and granting of industrial effluent permits. Therefore the due process to issue a permit includes very strongly the giving of reasons for decisions taken.

Predicting the effect of what a particular factory would have on the performance of the WWTP where the factory intends to discharge would address the requirements of the National Environmental Management Act of assessing the environmental effect before issuing out a discharge permit and fulfil the requirements of the local authority to give reasons for the decisions taken in the administrative process of permitting. Simulations run on a model of the WWTP can provide the required predictions.

Over the years the modelling of biological wastewater treatment processes has developed from fundamental concepts to complex mathematical models. The work of the IAWPRC, later IAWQ and now IWA (International Water Association) task groups (Henze et al., 1987, Henze et al., 2000) has introduced a suite of activated sludge models (ASM1, ASM2, ASM2d, ASM3 and other models), which provide researchers and practitioners with a set of standard basic models for biological wastewater treatment processes (Lacopozzi et al., 2007). After defining the purpose of a model, a series of steps are carried out to get to a point where simulations and model predictions can be performed using a WWTP model. The main steps that have been identified are; defining the purpose of the WWTP model, selecting the models that describe the units of the WWTP to be simulated, determining the hydraulic model of the WWTP, wastewater and biomass characterisation, data reconciliation to a steady state model, calibration of activated sludge parameters, model verification and finally scenario evaluations (Petersen et al., 2002; Hulsbeek et al., 2002).

Challenges that are faced during the modelling of WWTPs include issues related to the data available for modelling. In some cases the challenge is related to large volumes of data collected by instruments fitted around the plant. The data available may be noisy, strongly coupled, associated with uncertainty or incomplete. In order to proceed with modelling, various methods of handling the data are required. In this study, after defining the purpose of the model, in a background of limited measurement data, the aim was to determine whether the available data was adequate for the specific purpose of the model in a permitting investigation.

Another critical aspect of modelling using activated sludge models (ASM type) is influent characterisation which is more detailed than what is regularly done in WWTPs in eThekwini municipality. The influent characterisation requires further break down of the organic, nitrogenous and

phosphorus fraction into smaller sub-fractions. While the measurement of the total organic, nitrogenous and phosphorus fractions is straight forward if standard methods are followed, the sub-fractionation of the organic, nitrogenous and phosphorus fractions, especially the organic fraction is a challenge.

Chemical oxygen demand (COD) is used to measure the organic material fraction in wastewater. In a previous case of modelling a WWTP owned by eThekwini Municipality, COD fractionation of the influent wastewater was accomplished largely through the use of respirometry based experiments on the wastewater. A similar approach was attempted on the influent wastewater at the Verulam WWTP, but serious difficulties were faced. Satisfactory and consistent characterisation of the influent wastewater could not be achieved. There appeared to be two main reasons for this. The first was that the composition of the influent wastewater at Verulam WWTP was extremely variable. Such variability means that COD fractionation of influent wastewater would have to be repeated many times as necessary to establish a reliable statistical distribution for the permitting process. The observed variability indicates that the number would be too high to be feasible for the municipality to undertake. The second reason was that, it appears that measurement of oxygen utilisation rate on the respirometry apparatus that was available for this study as the main characterisation tool was seriously affected by some constituents of the wastewater. These two issues constituted a significant setback to the conceptual and experimental basis of the initial methodology. Thus it became necessary to explore an alternative approach to obtain reliable COD fractionation of influent wastewater for modelling purposes.

In order to improve the discharge permitting system for eThekwini municipality, the use of WWTP models as a tool for assessment of scenarios in which new factories are introduced into a WWTP catchment is proposed. The WWTP models would allow running of simulations that will provide information to decision-makers assessing factories for trade effluent discharge permits. However, to deliver this, the challenge of limited measurements at the WWTP to be modelled and data characterised by gaps and missing points had to be addressed. Furthermore the failure of common and established methods in COD fractionation of influent wastewater received at the WWTP necessitated a new approach for influent COD fractionation.

1.2 Objective of thesis

This study investigates if and how well, modelling of WWTP can be carried out using limited data collected for regular plant monitoring in municipalities such as eThekwini Municipality. The context in which the study is being carried out, is to further determine if a new idea (proposed in the study) of using WWTP models in the process of evaluating the impact of industrial effluent from factories, during evaluations in the effluent discharge permitting process, will be a valuable tool for municipalities.

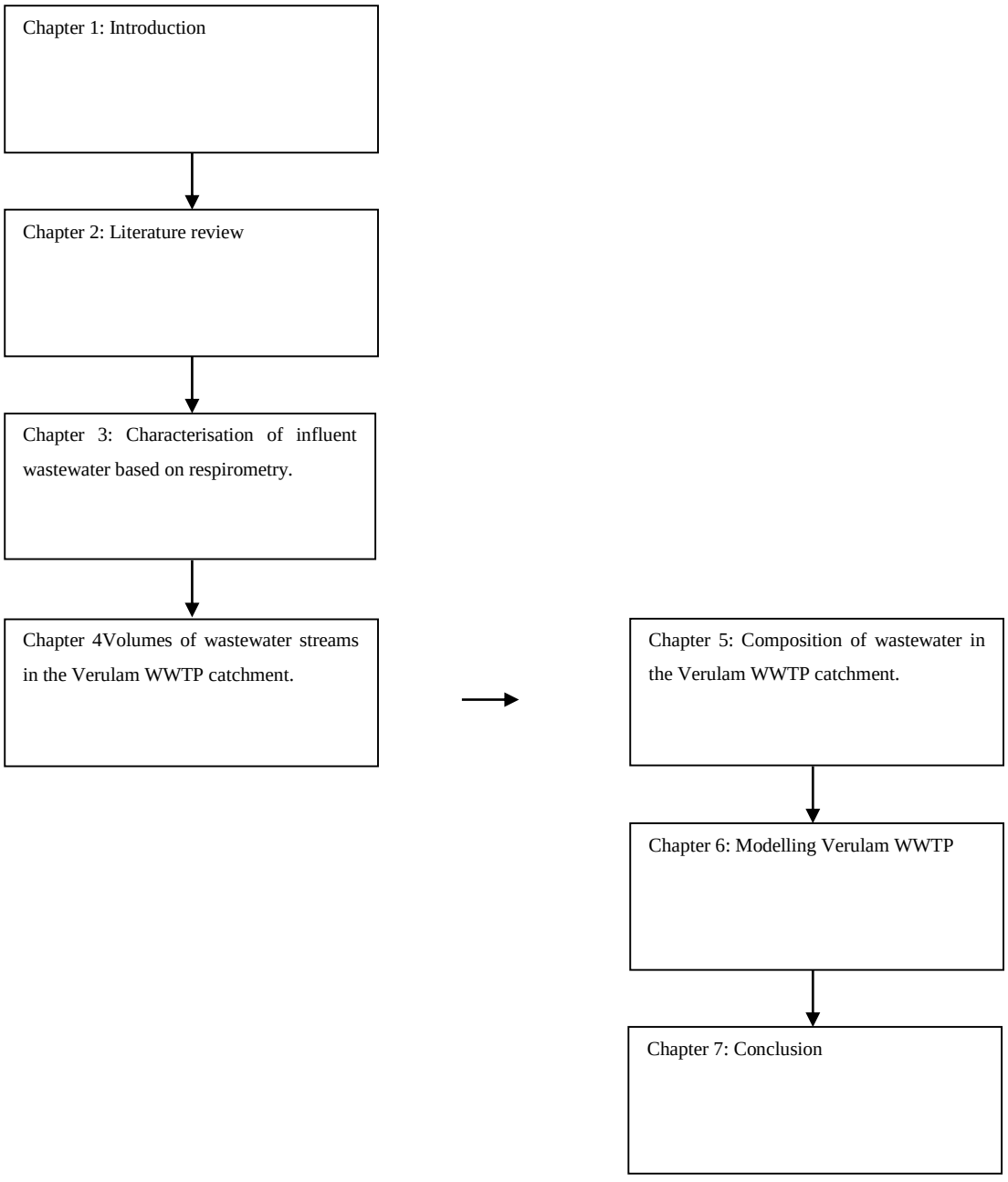
Hence the overall aim of this thesis was to develop an approach of how a WWTP model can be developed under conditions of limited measurements and available data in municipalities with limited measurement data. The purpose of the model would be to run simulations and inform the discharge permitting system for eThekwini Municipality. Furthermore the study seeks to propose a method to determine the COD fractions present in influent wastewater containing industrial effluent, after direct measurement techniques (respirometry and filtration) on influent wastewater from Verulam WWTP did not yield reliable COD fractionation. The objectives were as follows:

- To apply advanced statistical methods (distribution fitting and Monte Carlo simulations) to handle missing data and low quality data from WWTP operation and monitoring data, in order to generate missing wastewater flows and compositions in various industrial wastewater sources in the Verulam WWTP catchment.
- Use the catchment balance for the estimation of COD fractions in the combined influent wastewater received at Verulam WWTP
- To develop a model of Verulam WWTP and demonstrate how the model can be used during the evaluation process for an industrial effluent discharge permit for a new factory moving into a WWTP catchment.

This thesis presents the attempted COD fractionation based on direct measurement techniques followed by the proposed ‘catchment balance approach’ that was then used to estimate the COD fractions present in influent wastewater from the WWTP. Thereafter, a model of Verulam WWTP was developed, and used to demonstrate how the model would be used as a tool for assessment during the process of evaluating the impact on compliance of the final treated effluent from the WWTP when a factory is introduced in the WWTP catchment.

1.3 Outline of thesis

The candidate tried to the best of his ability to write the chapters such that they could be read independently. This means that some repetitions appear in the theory that is common to different chapters. However, effort was made to keep the repetitions to a minimum. The chapter headings of the thesis are as follows:



2 LITERATURE REVIEW

The review begins with an overview of wastewater management in eThekwini municipality with the aim of presenting how the trade effluent discharge system fits in the wastewater management approach in the municipality. A summary of the recommend steps and requirements for modelling WWTPs using ASM models is provided followed by a detailed description of the AMS1 model. A discussion of influent wastewater characterisation and COD fractionation for modelling is also presented.

2.1 Wastewater management in eThekwini Municipality

Formal water quality management in South Africa began as early as 1919 (Van der Merwe et al., 1990). The inception of the Union Health Act (Act 36) in 1919 assigned the responsibility to control water pollution to the Public Health Department. Under the Public Health Department, the duty of the Chief Health Officer was to ensure that the best available methods of sewage disposal were used at all times as a form of pollution control. Since then the Act has evolved. Amendments and improvements of Act 36 of 1919 brought about the South African Water Act (Act 54 of 1956) and later the National Water Act (Act 36 of 1998) (Eddy et al., 2003).

The South African Water Act (Act 54 of 1956) employed the Uniform Effluent Standards (UES) approach to control water pollution. This approach regulates the input of pollutants into receiving water bodies by setting uniform standards across the entire country of the effluent quality discharged into these water bodies. The advantages of this approach include ease of implementation, simplicity and appearance of fairness. The major drawback of the approach is the focus on the effluent quality while ignoring the effect of the effluent on the receiving water body. This results in excessive treatment in some areas and inadequate treatment in others due to factors such as the varying assimilative capacity of receiving wastewaters. The UES approach managed to limit the rate of deterioration of the water quality in South Africa while the quality of the water continued to deteriorate (Van der Merwe et al., 1990) leading to further amendments that led to the promulgation of the National Water Act (Act 36 of 1998) which adopted the Receiving Water Quality Objectives (RWQO) approach.

The RWQO approach takes into account the effect of the effluent on the receiving water body. It is based on the principle that the receiving water has a capacity to assimilate pollution without detriment to the customary uses of the water body. In this particular approach the uses of the receiving water body are defined and then the effluent standards set based on the defined use of the water concerned and requirement to ensure that the water quality of the water body is kept within the acceptable levels. Site specific effluent standards are set and then used to control pollution from point sources in the catchment area. In this way the water quality of the receiving water body is managed in a cost effective way which ensures that the adequate protection is received at all times.

In order to achieve effective wastewater collection and treatment, municipalities have to monitor and control sewage disposal and treatment. The municipality is required by the Water Services Act (WSA), 1997 (Act No. 108 of 1997) to establish and apply sewage disposal bylaws and ensure that they are observed by all water users. In eThekwini Municipality the eThekwini Water and Sanitation (EWS) department carries the responsibility of monitoring water pollution in four key areas; at source, at the reticulation system, at the WWTP and testing the treated effluent that is discharged to the receiving water body (Durban Metro Guide line No.6, 2001).

2.1.1 Monitoring water pollution at source

Monitoring water pollution at source involves regulating the volumes and strength of trade effluent discharged by industry and commerce into the municipal sewer system. The sewage disposal bylaws define trade effluent as any liquid whether or not containing matter in solution or suspension which is given off in the course of or as a result of any industrial trade, manufacturing, mining, chemical process or any laboratory research or agricultural activity. Trade effluent includes any liquid other than standard domestic effluent or storm-water (Guidelines for permit application, 2006). The municipality uses effluent discharge permits to control pollution at source. For trade effluent to be accepted into the municipal sewer system, it should comply with the standards set by the municipality for trade effluent. The duty to apply for a discharge permit for the disposal of trade effluent is set by the sewage disposal bylaws which state that no person shall discharge, cause or permit to be discharged any trade effluent except with written permission of an authorized officer and in accordance with the sewage disposal bylaws (Guidelines for permit application, 2006).

The initial step in the application process for a discharge permit is submission of requested information to the municipality by completing an application form provided by the municipality. The application form is made up of 12 Modules. Out of the 12 modules, Modules 1, 2, 8, and 10 deal with the discharge of industrial effluent. In this thesis only modules related to the discharge of industrial effluent are presented. A brief summary of the modules is presented in Appendix A. The municipality assesses the information provided by the applicants during the processing of the application for a trade effluent discharge permit.

2.1.2 Monitoring wastewater treatment plants

Each wastewater treatment plant is authorized by the Department of Water Affairs to discharge wastewater to the natural environment. The WWTP is required to treat the wastewater to meet the standards laid out in its license before discharging. To achieve this close monitoring of all WWTPs is necessary. The monitoring program of WWTPs involves regular sampling and testing the influent entering the WWTP, the water streams at different stages of the wastewater treatment process and the

final treated effluent. The results from the laboratory tests are used by operators running the WWTPs to control the treatment process in order to achieve the best quality of treated effluent. The testing of the influent wastewater provides a check on the effectiveness of the pollution control at source. Figure 2.1 shows the average compliance of WWTPs under eThekwini Water and Sanitation for the year 2011/12.

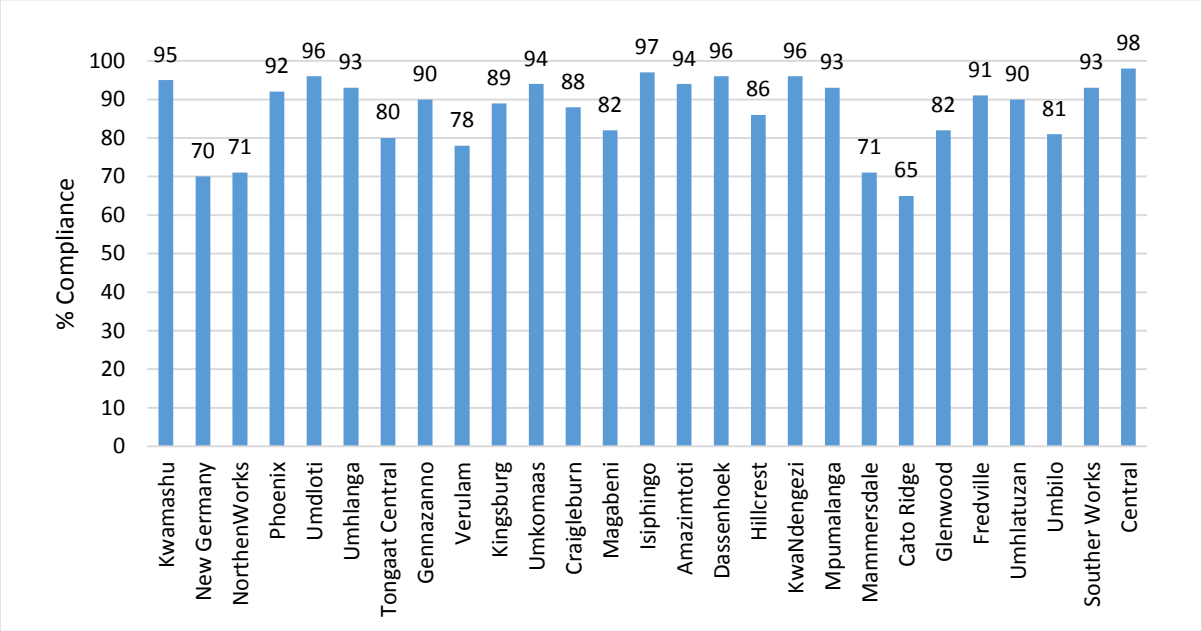


Figure 2.1 Annual average compliance of WWTPs in eThekwini municipality 2011/2012 (source: Durban Blue and Green drop annual report 2011/2012)

The average compliance of Verulam WWTP during the 2011-2012 period was 78% indication that there was room to improve the compliance at Verulam WWTP.

2.1.2.1 Monitoring receiving water bodies

The Durban Metropolitan area has 14 rivers. The largest river in the area is Umgeni River. Treated domestic and industrial wastewater is discharged into most of the rivers in the Durban Metropolitan area. The list of rivers which receive treated effluent include Umdloti, Ohlanga, Umgeni, Umbilo, Umhlatuzana, Umlaas, Isipingo and Little Amanzimtoti. These rivers are exposed to contamination. In addition to rivers receiving treated effluent, eThekwini municipality runs two deep sea sewage out falls from which settled sewage and sewage sludge are disposed of into the sea (Sludge disposal to Sea, 1983). Two sub-marine pipelines were constructed in 1968 and 1969 after extensive surveys by the National Institute for Water Research and Council of Scientific and Industrial Research (CSIR) (McGlurg et al., 1977) which endorsed the project. The sub marine pipelines transport domestic and industrial wastewater to the deep sea out falls. Figure 2.2 and Figure 2.3 respectively, show the rivers in the Durban Metropolitan Area and the location of the deep sea sewage outfalls and sampling points for beach water quality testing.

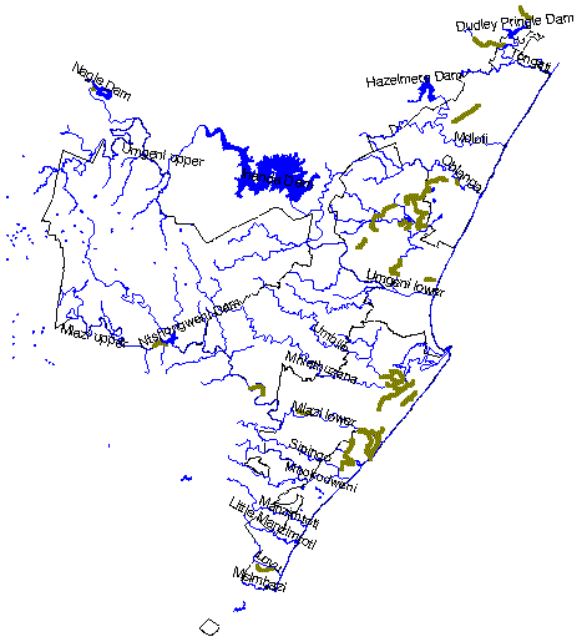


Figure 2.2 Rivers in Durban metropolitan Area (Source www.ceroi.net, 01-02-2015)

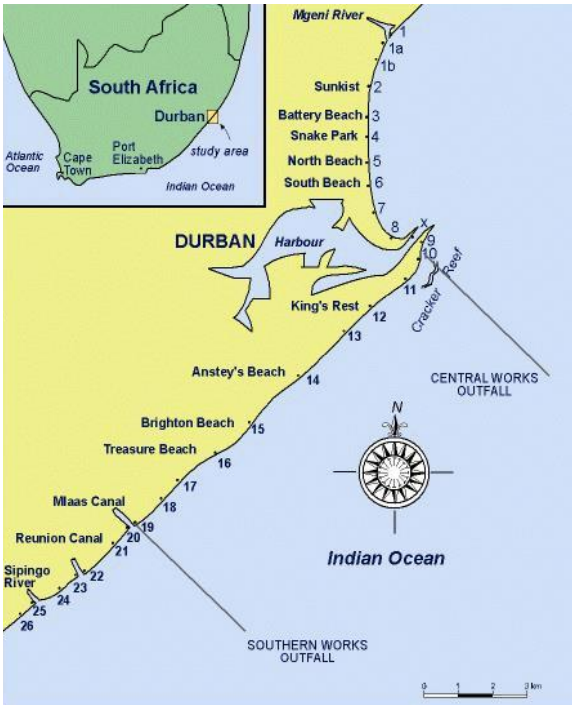


Figure 2.3 Location of deep sea sewage outfalls and sampling points for water quality assessments (Warwich, 2000)

EThekwini Water and Sanitation Scientific Services collects samples from the rivers at different points on a monthly basis and tests for a variety of parameters in order to establish the level of contamination in the rivers. The deep sea sewage out falls operate under permits that require an external agent such as the CSIR to be appointed by the municipality to conduct detailed annual surveys of the water quality and marine life along the coastline and areas next to the outfalls (Bailey et al., 2000). When pollutant concentrations exceed the specified standards for the water bodies of concern, EWS is required to implement corrective measures in the responsible problem areas. The monitoring of the deep sea sewage out falls and the rivers ensure that the environment is not compromised.

2.2 The Water Research Commission project

Industrial effluent can often be accommodated up to a certain point without compromising the quality of the treated water. Beyond that point it becomes a great challenge to treat the wastewater to the required quality standards. In response to this challenge, the Water Research Commission (WRC) of South Africa and eThekwini Municipality initiated a research project (K5/1734) in 2007. The broad aim of the project was to develop a methodology for predicting the cut-off point of industrial wastewater with sufficient reliability such that the methodology could to be useful in setting discharge limits for industrial effluents. The proposed main deliverable of the WRC project was a protocol for the quantitative assessment of industrial effluents. By protocol it is meant here, a formalised programme of laboratory testing and simulations based on mathematical modelling, which will lead to a prediction of

a particular WWTP's performance while accepting a given load of effluent including industrial wastewater. The key purpose of the protocol would be to enable the municipality to evaluate the ability of a receiving WWTP to adequately treat incoming influent wastewater to the required final effluent discharge standards before granting the discharge permit to the factory discharging within the catchment area of the WWTP. Since the permit is part of a regulatory process, the protocol is required to be scientifically and legally defensible (WRC, 2013). The overview of the project can be illustrated by Figure 2.4.

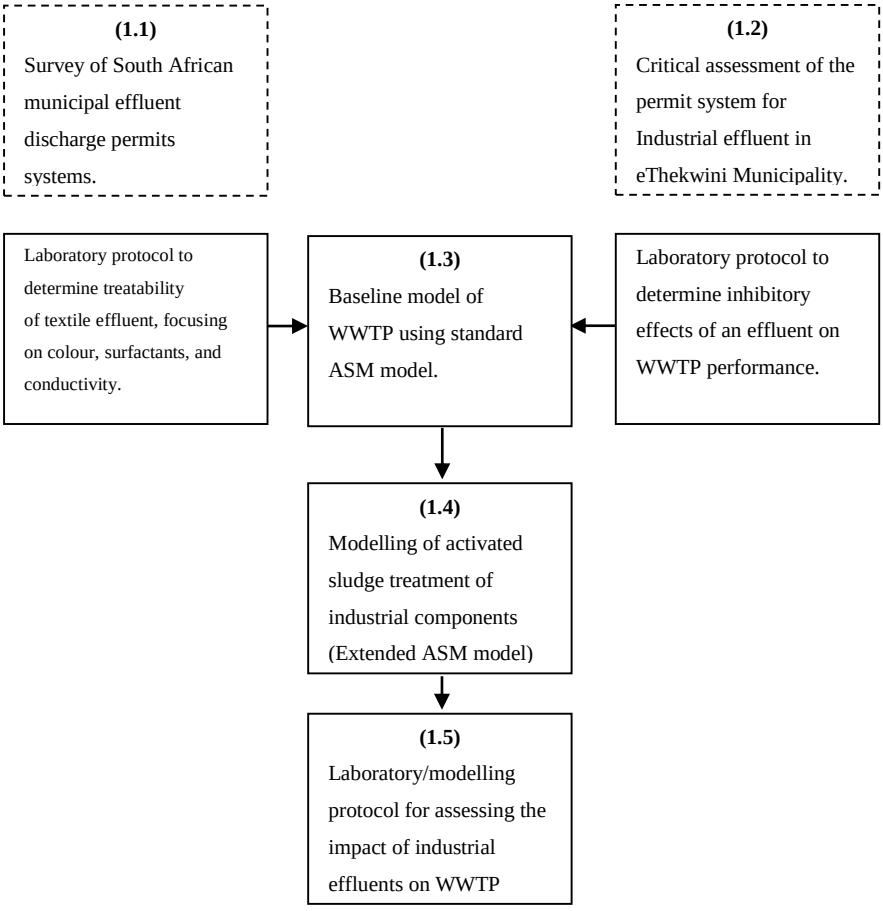


Figure 2.4 Overall structure of WRC research project

The approach to the WRC project began with a survey of the municipal effluent discharge permit systems in South Africa including the study site, eThekwini Municipality. Thereafter a baseline model of an existing WWTP for one of the WWTP's run by eThekwini Municipality was developed. The initial baseline model was based on one of the International Water Associating (IWA) activates sludge models (Henze et al., 2000). This baseline model would then be extended to account for the fate of industrial components that are present in the industrial effluent received at the WWTP. The structural extension of the activated sludge mathematical model (adding additional components, processes and provisional model parameter values) would be informed by the results obtained from the investigations of the

treatability of industrial effluent and the investigation of the inhibitory effects of industrial effluent in the activated sludge system. Due to the sustained high impact of textile effluents on several WWTPs in eThekwini Municipality, textile effluents were chosen as the subject of all the investigations related to industrial effluent. The final deliverable of the broad project would be the final synthesis of the outcomes from the different sub-projects outlining the protocol.

The results of the survey showed that eThekwini Municipality appears to have the most sophisticated system, based on the most experience of dealing with industrial effluents while the critical assessment of the permit system of eThekwini Municipality showed that the effluent discharge permits were not protecting the WWTPs as they should because their provisions were not being adequately enforced. A baseline model for a WWTP receiving a significant proportion of industrial effluent was developed. Since IWA models cannot model the fate of components such as heavy metals, surfactants and textile dyes as separate processes, investigations aimed at establishing the kinetic models for the fate of heavy metals and dyes were carried out. However the dye-house that was discharging textile effluent closed down and relocated to another catchment before the assessment of the impact of the textile effluent was completed. Since the dye-house was no longer available for the investigation it was decided to move to another study site; Verulam WWTP, which had a textile factory in the catchment area (WRC, 2013).

The project plan envisaged that the outcomes of the various project would be synthesised into an effluent evaluation protocol that would be tested in a case study involving the process of granting an actual effluent discharge permit to a textile factory. However, for reasons that were not all within the control of the research project the case study could not be completed. The factory that was originally chosen for the Marianridge WWTP closed down before the case study was completed. JMV Textiles in Verulam WWTP catchment was then chosen as a substitute, but because the pollution officer assigned to the permit investigation left the employ of the municipality, the permit was granted hurriedly, without involving the proposed protocol (WRC, 2013).

2.3 Modelling of wastewater treatment plants using ASM models

The activated sludge process was developed around 1913 by Clark and Gage in Massachusetts and by Ardern and Lockett (1914) in Manchester, England (Metcalf and Eddy, 1991). The activated sludge system involves growing an activated mass of microorganism that is capable of oxidising constituents of the wastewater under aerobic conditions in an aeration tank. Figure 2.5 shows a basic configuration of the activated sludge process.

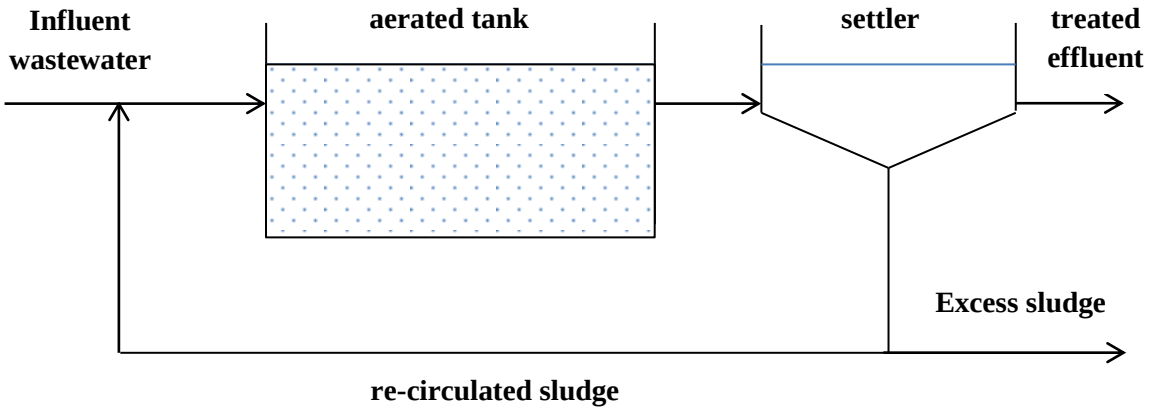


Figure 2.5 Basic configuration of an activated sludge process

The microbial suspension which is referred to as mixed liquor suspended solids (MLSS) is contacted with incoming influent wastewater in a bioreactor where mechanical equipment is used to mix and transfer oxygen into the process. The mixed liquor then flows to a settler where the suspension is thickened. The settled biomass is called activated sludge. The activated sludge is recycled back to the aeration tank to continue biodegradation of influent organic matter. A portion of the thickened activated sludge is periodically wasted from the process to prevent accumulation (Metcalf and Eddy, 1991). The control of the activated sludge process is very complex. Factors that affect the process include the changes in the bacteria population, variations in influent wastewater composition and flow rates, changes in pH and temperature. The efficiency of WWTPs based on the activated sludge process is affected by the presence of industrial effluent. In such cases, the WWTPs have to cope with recalcitrant chemicals that the biomass can at times, degrade at very slow rates and with toxic chemicals that may inhibit the activity of the biomass or even kill the biomass, thus reducing the efficiency of the process.

The knowledge of the mechanism of the processes that take place in the activated sludge process, has increased over the years making mathematical modelling of the activated sludge better. Mathematical modelling of activated sludge systems has become a widely accepted tool for research, plant design and optimisation and training of process engineers and plant operators. The mathematical models are only useful if the model predictions are reliable.

Modellers from around the world have approached the task of modelling in different ways over the years, resulting in several guidelines being developed. The variety of approaches and inadequate documentation of procedures in some cases makes it difficult to carry out quality assessments and comparison of simulation results from different modelling projects (WEF, 2014). In response to this challenge the IWA formed a task group, the GMP (Good Modelling Practice) Task Group (Rieger et al., 2012) to review the different modelling protocols in an attempt to form an internationally recognised

standard, the GMP Unified Protocol. Protocols that were considered by the GMP Task Group include the STOWA (Hulsbeek et al., 2002; Roeleveld and van Loosdrecht, 2002), Water Environment Research Foundation (WERF) (Melcer et al., 2003), BIOMATH (Vanrolleghem et al., 2003) and HSG (Langergraber et al., 2004) protocols. These protocols have been compared by different researchers including Sin et al. (2005) and Corominas (2006). The GMP Task Group analysed different protocols in an effort to identify the strengths of each protocol for inclusion in the unified protocol. All the protocols considered by the GMP Task Group had similarities in the modelling approach.

Key steps of approaching a modelling project that were identified from all the protocols and proposed for the unified protocol are as follows:

- Project definition
- Data collection and reconciliation
- Plant model set-up
- Calibration and validation
- Simulation and results interpretation

In-depth details of the key steps mentioned above are presented in Appendix D.

2.3.1 IWA activated sludge models

In 1982 the International Association on Water Pollution Research and Control (IAWPRC), later known as the International Water Quality Association (IAWQ) and now known as the International Water Association (IWA) (Henze et al., 2000), established a Task Group on Mathematical Modelling for Design and Operation of Activated Sludge Processes whose task was to develop models for nitrogen removal in the activated sludge system. The task group was appointed at a time when various models were being developed yet the application of these models was limited due to factors such as a lack of trust in the models since there was limited computing power and the presentation of the models was complicated. Against this background, the task group published ASM1 (Henze et al., 1987a, 1987b) in 1987 which was meant to come with minimum complexity and to provide a platform for future development of models for nitrogen-removal activated sludge processes.

When the IWA task group began modelling activated sludge systems they focused on systems in which carbon oxidation, nitrification and de-nitrification are accomplished in a single sludge process (Melcer et al., 2003). The distinct steps that were followed by the task group may be summarized as follows:

- The first step was to identify the fundamental processes occurring in the activated sludge system. The term “process” describes a “micro” event such as cell growth or maintenance, rather than a series of “macro” operations as in an activated sludge process.

- The second step was to characterise the kinetics and stoichiometry of the identified processes.
- The final step was to incorporate process rate expressions into mass balance equations depicting the physical configuration of the system. These equations then need to be solved.

The application of these steps during the development of IWA models can be found in several publications such as Grady et al. (1986), Gujer and Henze (1991) and Henze et al. (1987a, 1987b).

The ASM1 model was published with guidelines for wastewater characterisation, development of computer codes and default values for model parameters that can be used for running the model before model calibration is done. Some modelling projects have used the default model parameters successfully with minor adjustments of the values of the model parameters. The matrix notation of presenting activated sludge models was introduced with ASM1 to facilitate easier presentation of complex models.

The ASM1 formed the basis for the development of more activated sludge models. When the ASM1 was published, biological-phosphorus removal was already in use in a limited number of WWTPs. From the mid-1980s to the mid-1990s the use of biological phosphorus removal processes increased and the understanding of the processes was increasing. Consequently in 1995 ASM2 was published. ASM 2 included nitrogen-removal and biological phosphorus removal processes. In 1999 the ASM 2 model was expanded to ASM2d which included denitrifying phosphorus-accumulating organisms (PAOs) after it became evident that denitrifying PAOs were required for the simulation of many results from research and practice (Henze, 2000). In 1998 the task group developed the ASM3. The ASM3 was developed for biological nitrogen removal like ASM1. The improved ASM3 was developed to correct defects that have been identified by users of ASM1 (Gujer et al., 1999). The main difference between ASM1 and ASM3 is that the latter includes storage polymers in the utilisation of substrate by heterotrophic biomass in the activated sludge. The ASM3 model introduced storage of organic substrates as a new process, and replaces the death-decay process for heterotrophic organisms with an endogenous respiration process (Gujer et al., 1999).

In summary, the introduction of the IWA activate sludge models brought with it 3 major benefits for researchers and practitioners. The first was introduction of a common language for modellers dealing with modelling concepts. The publication of ASM models introduced nomenclature and the matrix notation which improved communication, encouraging fast development of models over the years. The IWA models are presented in a matrix format called the Petersen Matrix. The notation adopted for the Petersen matrix is in conformity with IAWPRC nomenclature (Grau et al., 1982). In this notation insoluble components are assigned the symbol X and the soluble components, S. Subscripts are used to specify individual components. The matrix format allows a continuity check on any component and rapid and easy recognition of the fate of each component is made possible making the preparation of

mass balance equations relatively easy. The concept of switching functions is used in IWA models to turn process rate equations on and off as environmental conditions change. The chemical oxygen demand, COD was chosen as the best measure of the concentration of organic matter in wastewater since it provides a link between electron equivalents in the organic substrate, the biomass and the oxygen utilized. Hence the concentration of all organic materials, including biomass, is expressed in COD units in IWA based models.

The second benefit is that working with models became more organised and this allowed modellers, plant operators and researchers to be more efficient in related tasks such as experimental designs, training and organising information at WWTPs. The third major benefit of the introduction of ASM models is that their introduction and development has guided research in the field. The models have highlighted where research should be focused in order to fill in the gaps in knowledge or to develop methods of acquiring required information. A good example of a subject in which research has been guided by the ASM models is wastewater characterisation.

Since the modelling of Verulam WWTP was going to be carried out without determining all the model parameters experimentally, the use of an ASM model with fewer model parameters would be ideal. Considering this factor, ASM1 was a better choice, since it has the least number of model parameters. Furthermore experimental methods (Ekama et al., 1986; Henze et al., 1987; Sollfrank and Gujer, 1991; Kappeler and Gujer, 1992; Spanjers et al., 1998; Vanrolleghem et al., 1999; and others) that are used to obtain information for modelling and calibrating ASM models are usually based on respirometric techniques developed particularly for the calibration of ASM1. The ASM1 model gives a good description of the activated sludge process provided that the wastewater has been characterised in detail and is of domestic or municipal origin. The presence of industrial effluent has effect on how well the model works (Henze et., al 1987). The ASM1 was used to model Verulam WWTP with this challenge in mind, with an expectation of being able to evaluate to what extent ASM1 could be used in modelling a WWTP treating wastewater that contains a portion of industrial effluent. A detailed description of ASM1 is provided in the following section. Detailed descriptions of other ASM models have been omitted. They can be found in Henze, (2000).

2.3.2 Activated Sludge Model No.1 (ASM1)

The ASM1 model is presented in the Petersen matrix format in Table 2.1.

Table 2.1 The ASM1 Petersen matrix

component→ **process ↓**		1 S_I	2 S_S	3 X_I	4 X_S	5 $X_{B,H}$	6 $X_{B,A}$	7 X_P	8 S_O	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}	**Process rate**, ρj
1	Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		-i_{XB}			$-\frac{i_{XB}}{14}$	$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{O,H}+S_O}\right)X_{B,H}$
2	Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86Y_H}$	-i_{XB}			$\frac{1-Y_H}{14\cdot 2.86Y_H}-\frac{-i_{XB}}{14}$	$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_g X_{B,H}$
3	Aerobic growth of autotrophs						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$\frac{i_{XB}}{14}-\frac{1}{7Y_A}$	$\mu_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{O,A}+S_O}\right)X_{B,A}$
4	Decay of heterotrophs				1-f_P	-1		f_P					i_{XB} - f_P ·i_{XP}		$b_H \cdot X_{B,H}$
5	Decay of autotrophs				1-f_P		-1	f_P					i_{XB} - f_P ·i_{XP}		$b_A \cdot X_{B,A}$
6	Ammonification of soluble organic nitrogen										1	-1		$\frac{1}{14}$	$k_a \cdot S_{ND} \cdot X_{B,H}$
7	Hydrolysis of entrapped organics		1		-1										$k_h \frac{X_S/X_{B,H}}{K_X+X_S/X_{B,H}}\left[\left(\frac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{B,H}$
8	Hydrolysis of entrapped organic nitrogen											1	-1		$\rho_7(X_{ND}/X_S)$

2.3.2.1 COD components in ASM1

In ASM1, the organic fraction in wastewater is split based on biodegradability, rate of biodegradation, solubility and viability (Petersen et al., 2000). The first level of division splits the organic matter into three sub fractions; the biodegradable, non-biodegradable and active biomass. The biodegradable substrate is further divided into readily biodegradable (S_S) and slowly biodegradable substrate (X_S). Readily biodegradable material is assumed to consist of relatively small molecules (such as volatile fatty acids and low molecular weight carbohydrates) which can be easily carried into the cell resulting in an immediate utilization of the electron acceptor (oxygen or nitrate), while the slowly biodegradable material is assumed to consist of larger and more complex molecules, which requires extra cellular breakdown before uptake and utilization (Dold et al., 1980; Dold et al., 1986). The non-biodegradable fraction which consists of material that does not react or reacts at slow rates such that any losses in the wastewater treatment process are considered negligible, has two fractions, the non-biodegradable particulate (particulate inerts) and non-biodegradable soluble (soluble inerts). The non-biodegradable soluble fraction (S_I) passes unaffected through the treatment process in liquid phase. This definition means that the concentration of the non-biodegradable soluble fraction in the influent is expected be the same as that in the final effluent at the WWTP if there is no generation of S_I in the process. The non-biodegradable particulate (X_I) material is entrapped in the activated sludge and removed with excess sludge. In addition to X_I particulate products (X_P) which come from biomass decay are considered non-biodegradable (Weddle and Jenkins, 1971). The active biomass consists of heterotrophic (X_{BH}) and autotrophic (X_{BA}) organisms (Wentzel et al, 1995). X_P is formed by the decay of heterotrophic and autotrophic biomass. Table 2.2 shows the COD fractions for ASM1.

Table 2.2 COD components in ASM1

Symbol	Components	Units
S_I	Soluble inert (non-biodegradable) substrate	g COD/m^3
S_S	Soluble readily biodegradable substrate	g COD/m^3
X_I	Particulate inert (non-biodegradable) substrate	g COD/m^3
X_S	Particulate slowly biodegradable substrate	g COD/m^3
X_{BH}	Heterotrophic active biomass	g COD/m^3
X_{BA}	Autotrophic active biomass	g COD/m^3
X_P	Particulate products formed from biomass decay	g COD/m^3

2.3.2.2 Nitrogen components in ASM1

For ASM1 the total nitrogen (C_{TN}) in influent wastewater is divided into Total Kjeldahl Nitrogen (C_{TKN}) and nitrate and nitrite (S_{NO}). This division is similar to that of the organic fraction in that the subdivision is based on solubility, biodegradation and the rate of biodegradation. The TKN is divided into free and saline ammonia (S_{NH}), organically bound nitrogen and active biomass nitrogen (a fraction of the biomass which is assumed to be nitrogen). Similar to the division of the organic material, the organically bound nitrogen is divided into biodegradable and non-biodegradable fractions which contain soluble and particulate components. Only the particulate biodegradable organic nitrogen (X_{ND}) and soluble biodegradable organic nitrogen (S_{ND}) are explicitly included in the ASM1 model (Jeppsson, 1996). The organic particulate nitrogen fractions X_{NB}, X_{NP} and X_{NI} are associated with the organic fractions X_B, X_P and X_I respectively. The active biomass nitrogen fraction (X_{NB}) is associated with the decay of biomass which results in the production of particulate biodegradable organic nitrogen (X_{ND}) (Jeppsson, 1996). These forms of organic nitrogen can be determined by multiplying X_B by i_{XB}, X_P by $i_{XP,}$ and X_I by i_{XI} where i_{XB}, i_{XP}, and i_{XI} are the respective fractions of the nitrogen present in the parent organic fractions. In ASM1 nitrate nitrogen (S_{NO}) is a result of nitrification of ammonia by a single step process. The nitrogen components used in the matrix for ASM1 are shown in Table 2.3.

Table 2.3 Nitrogen components in ASM1

Symbol	Components	Units
S_{NH}	Ammonia nitrogen	g NH_3-N/m^3
S_{ND}	Soluble organic nitrogen	g N/m^3
S_{NO}	Nitrate + nitrite nitrogen	g NO_3-N
X_{ND}	Particulate organic nitrogen	g N/m^3

2.3.2.3 Other components

The concentration of the dissolved oxygen in the system S_O, is included in the ASM1 matrix. The processes in the matrix occur and some of then use up oxygen from solution hence the inclusion of S_O in the matrix. Another component included in the ASM1 matrix is the total alkalinity S_{ALK}. Inclusion of S_{ALK} allows the prediction of pH changes in the system. Table 2.4 shows the units for S_O and S_{ALK}.

Table 2.4 Other components in ASM1

Symbol	Components	Units
S_O	Dissolved oxygen	g O_2/m^3
S_{ALK}	Alkalinity	mole HCO_3^-

2.3.2.4 Kinetic and stoichiometric coefficients in ASM1

Kinetic and stoichiometric parameters found in ASM1 are presents in Table 2.5.

Table 2.5 Kinetic and stoichiometric parameters of ASM1

Symbol	Description	Unit
	Stoichiometric parameters	
Y_A	Yield for autotrophic biomass	g cell COD formed/(g N oxidised)
Y_H	Yield for heterotrophic biomass	g cell COD formed/(g COD oxidised)
f_P	Fraction of biomass leading to particulate products	dimensionless
i_{XB}	Mass of nitrogen per mass of COD in biomass	g N/(g COD) in biomass
i_{XE}	Mass of nitrogen per mass of COD in products from biomass	g N/(g COD) in endogenous mass
	Kinetic parameters	
μ_H	Maximum specific growth rate for heterotrophic biomass	/day
μ_A	Maximum specific growth rate for autotrophic biomass	/day
K_S	Half-saturation coefficient for heterotrophic biomass	g COD/m^3
K_{OH}	Oxygen half-saturation coefficient for heterotrophic biomass	g O_2/m^3
K_{OA}	Oxygen half-saturation coefficient for autotrophic biomass	g O_2/m^3
K_{NO}	Nitrate half saturation coefficient for heterotrophic biomass	g NO_3-N/m^3
b_H	Decay coefficient for heterotrophic biomass	/day
η_g	Correction factor for μ_H under anoxic conditions	dimensionless
η_h	Correction factor for hydrolysis under anoxic conditions	
k_h	Maximum specific hydrolysis rate	g slowly biodegradable COD/ (g cell COD·day)
K_X	Half-saturation coefficient for hydrolysis of slowly biodegradable substrate	g slowly biodegradable COD/ (g cell COD·day)
K_{NH}	Ammonia half-saturation coefficient for autotrophic biomass	g NH_3-N/m^3
k_a	Ammonification rate	m^3·COD /(g·day)

2.3.2.5 Processes in ASM1

The four main processes that are considered in ASM1 are as follows:

- Growth of biomass
- Decay of biomass
- Ammonification of nitrogen
- Hydrolysis of particulate organics

The growth rates in the processes are described by Monod kinetics that is described by the following equation:

$$\mu = \mu_{max} \frac{S}{S + K_S} \qquad [2.1]$$

Where

μ is specific growth rate

μ_{max} is maximum specific growth rate

S is substrate concentration

K_S is half saturation constant

The substrate flow in ASM1 is illustrated in Figure 2.6.

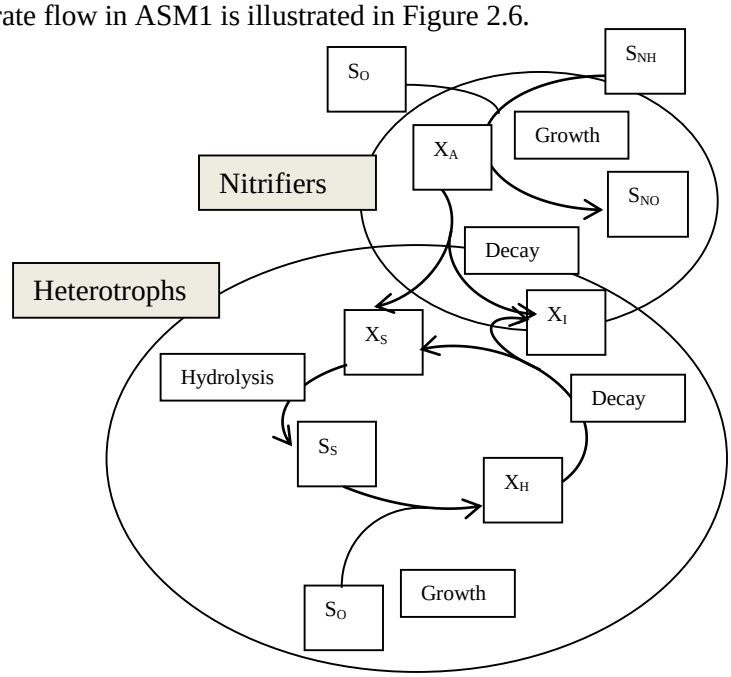


Figure 2.6 Substrate flow in ASM1 (modified from Gujer et al., 1999)

In ASM1 modelling, the readily biodegradable material S_S is considered as the only substrate for heterotrophic biomass growth. Organic slowly biodegradable material X_S is converted by hydrolysis to S_S

before utilisation. Decay of biomass is assumed to transform active biomass to inert particulate products X_P and slowly biodegradable organics X_S which re-enter the cycle of hydrolysis to S_S before use for growth by active biomass. The growth of the biomass is represented by three processes; aerobic growth of heterotrophic biomass, anoxic growth of heterotrophic biomass and aerobic growth of autotrophic biomass.

Aerobic growth of heterotrophic biomass (Process 1)

Growth of heterotrophic biomass under aerobic conditions (Process 1) results in the production of heterotrophic biomass at the expense of soluble readily biodegradable substrate S_S, and consumption of oxygen S_O. During this process, ammonia nitrogen S_{NH} is removed from solution and incorporated into cell mass. Monod kinetics are used to describe the growth of heterotrophic and autotrophic organisms.

Anoxic growth of heterotrophs (Process 2)

Anoxic growth of heterotrophic biomass occurs in the absence of oxygen. Nitrate nitrogen acts as the electron acceptor while S_S is the substrate. As in aerobic growth, ammonia nitrogen S_{NH} is converted to into organic nitrogen in the biomass. The same Monod kinetics used to model aerobic growth of heterotrophic biomass, are used to model anoxic growth of heterotrophic biomass. However since the rate of anoxic growth is lower than that for aerobic growth, the kinetic rate expression for anoxic growth is multiplied by a correction empirical coefficient (η_g<1.0) (Batchelor, 1982). Furthermore, anoxic growth is inhibited by the presence of oxygen thus a switching function in the form of the term $K_{OH}/(K_{OH} + S_O)$ is introduced to reflect this fact. The coefficient K_{OH} has the same value as in the expression for aerobic growth so that as aerobic growth declines, anoxic growth increases.

Aerobic growth of autotrophic biomass (nitrification) (Process 3)

During the aerobic growth of autotrophic biomass ammonia nitrogen S_{NH} serves as the energy source for the growth process. The end products are autotrophic cell mass and nitrate nitrogen. A small amount of ammonia is incorporated into the biomass. The aerobic growth of autotrophic biomass is influenced by the pH of wastewater in which the growth is taking place. This influence by pH is not modelled accurately in ASM1 but potential problems with pH in the bioreactor may be checked by using the alkalinity S_{ALK} term.

Decay of heterotrophic biomass (Process 4)

The decay of heterotrophic biomass is modelled using the death-regeneration concept of Dold et al. (1980). The decay process converts biomass to a combination of particulate products X_P and slowly biodegradable substrate X_S. There is no loss of COD in this process and no electron accepter is utilized. The X_S formed undergoes hydrolysis, releasing an equal amount of readily biodegradable COD. The decay process

continues at a constant rate regardless of the environmental conditions.

Decay of autotrophic biomass (Process 5)

The decay of autotrophic biomass is modelled in exactly the same way as the decay of heterotrophs.

Ammonification of organic nitrogen S_{ND} (Process 6)

In the ammonification of organic nitrogen S_{ND}, soluble organic nitrogen is converted to ammonia nitrogen S_{NH} through a first order reaction accompanied by a change in alkalinity.

Hydrolysis of entrapped organics (Process 7)

In this process slowly biodegradable substrate X_S is broken down into readily biodegradable substrate S_S. A correction factor, η_h (<1) is included to account for the reduced hydrolysis rate under anoxic conditions. The rate of this reaction appears to saturate when the amount of entrapped substrate becomes larger in proportion to the biomass hence the importance of the ratio X_S /X_{BH} in the process rate.

Hydrolysis of entrapped organic nitrogen (Process 8)

The hydrolysis of entrapped organic nitrogen is modelled in a similar way to the hydrolysis of entrapped organics.

2.3.2.6 Restrictions of ASM1

A number of assumptions and simplifications are adopted in models to make them manageable. Thus it is important to explicitly state the major assumptions, restrictions and constraints associated with a particular model. A summary of assumptions and restrictions related to the ASM1 model is presented below (Henze et al., 1987):

1) The system operates at constant temperature. A number of the coefficients in the model are functions of temperature; their functionality would have to be explicitly expressed in the rate expressions in order for time-variant temperature fluctuations to be considered.
2) The pH is constant and near neutrality. It is known that pH influences many of the coefficients in the model, however few expressions are available for expressing this influence. Hence a constant pH has been assumed. The inclusion of the alkalinity in the model allows the detection of potential problems with pH control.
3) No consideration has been given to changes in the nature of the organic matter within any given fraction (e.g. S_S). In other words, the coefficients in the rate expressions have been assumed to have

constant values. This means that while variable input loadings can be handled, changes in waste character cannot.

4) The effects of limitations of nitrogen, phosphorus, and other inorganic nutrients on the removal of organic substrate and on cell growth have not been considered. Nutrients can lead to problems in sludge settleability. Therefore, care must be taken to ensure that sufficient inorganic nutrients are present to allow balanced growth.
5) The correction factors for denitrification η_g and η_h are fixed and constant for a given wastewater even though it is possible that their values may be influenced by system configuration.
6) The coefficients for nitrification are assumed to be constant and to incorporate any inhibitory effects that other waste constituents are likely to have on them.
7) The heterotrophic biomass is homogeneous and does not undergo changes in species diversity with time. This assumption is inherent in the assumption of constant kinetic parameters. This means that the effects of substrate concentration gradients, reactor configuration, and other factors on sludge settleability are not considered.
8) The entrapment of particulate organic matter in the biomass is assumed to be instantaneous.
9) Hydrolysis of organic matter and organic nitrogen are coupled and occurs simultaneously with equal rates.
10) The type of electron acceptor does not affect the loss of active biomass by decay.
11) The type of electron acceptor does not affect the heterotrophic yield coefficient
12) ASM1 was developed for simulating the treatment of municipal wastewater. Thus it is not advised to apply the model to systems where industrial contributions dominate the characteristics of the wastewater.
13) ASM1 does not include processes that describe behaviour under anaerobic conditions. Simulations of systems with large fractions of anaerobic reactor volume may therefore result in errors.
14) ASM1 cannot deal with elevated nitrite concentrations.
15) ASM1 is not designed to deal with activated sludge systems with very high load or small sludge retention (SRT) of less than 1 day.

Assumption 12) is important in this study since there is presence of industrial effluent in the wastewater received at the WWTP. Model modifications are normally required for cases where WWTPs receive wastewater where industrial contributions dominate the wastewater characteristics (Gernaey et al., 2004). The modelling results of this study were evaluated with this fact in mind and the discussion and conclusion are presented in Chapter 5.

2.3.3 Calibration of IWA models- ASM1

Calibration of the model relies on the information gathered from the WWTP through experiments, measuring campaigns on influent and effluent wastewater streams and other parts of the WWTP. Once the information has been gathered, it is transferred to ASM model parameters during calibration. The purpose of the model determines the calibration procedure and the amount and quality of information required to achieve the calibration (Sin et al., 2005).

Numerous approaches by different modellers (Ekama et al., 1986; Henze et al.,1987; Sollfrank and Gujer, 1991; Kappeler and Gujer, 1992; Vanrilleghem et al., 1999; Petersen et al., 2003) have been used to calibrate ASM models. After transferring the information obtained from experiments (kinetic or stoichiometric parameters, wastewater characterisation results and other information), most of the calibration approaches relied on the modeller trying to manually change one model parameter at a time until a good fit to the measurement is obtained. Expert knowledge is required for this to a certain extent, ad hoc approach. A wide range of calibration approaches makes it challenging and near impossible to effectively compare and inspect the calibration of ASM models in different studies, since there is no common basis (Sin et al., 2005). In response to this lack of a standardised approach to calibration of ASM models, several systematic calibration protocols have been proposed. The proposed calibration protocols include the BIOMATH (Vanrolleghem et al., 2003), the STOWA (Hulsbeek et al., 2002), the Hochschulgruppe (HSG) (Langergraber et al., 2004) and the WERF (Melcer et al., 2003) calibration protocol. Sin et al (2005) provides a thorough review and comparison the aforementioned calibration protocols.

A summary of the four calibration protocols and their comparison and a SWOT analysis by Sin et al., (2005) is presented in Appendix D.

2.3.4 Simulation environments

Different simulators for modelling wastewater treatment plants have been developed and are commercially available. In the context of modelling wastewater treatment processes, a simulator is software that allows the modeller to simulate a wastewater treatment plant configuration (Henze, 2008). The simulators can be classified as general purpose simulators and specific wastewater treatment simulators. General purpose simulators require the modeller to provide the models that are used to model a defined plant configuration. The user of general purpose simulators must be able to fully understand the lines of code in the models. Thus this type of simulator requires more programming skills. A popular example is MATLAB^{TM}.Specific wastewater simulators require less programming skills. These simulators usually contain predefined process

unit models that can be used to build a full-scale wastewater treatment configuration. Examples of commercial wastewater simulators are presented in Table 2.6.

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Table 2.6 Examples of commercially available simulators for wastewater treatment plants

Simulator	Web address
AQUASIM	www.aquasim.eawag.ch
Bio Win	www.envirosim.com
WEST	www.hemmis.com
STOAT	www.wrcplc.co.uk/software
SIMBA	www.ifak-system.com
GPS-X	www.hydromantics.com
EFOR	www.dhisoftware.com

WEST (Worldwide Engine for Simulation, Training and automation) was the simulator available for wastewater-treatment modelling purposes in this study. WEST offers a platform for dynamic modelling and simulation of WWTPs and other types of water quality related systems. WEST is designed for plant operators, engineers and researchers studying physical, biological and chemical processes in WWTPs, sewer systems and rivers.

2.3.5 The Monte Carlo simulations

Probability distribution fitting and Monte Carlo simulations were some of the techniques that were used where appropriate; to bring the available flow and composition data to the required daily time series of flow and composition required to model Verulam WWTP. The theoretical basis behind Monte Carlo simulations is presented in Appendix D. The application of the Monte Carlo simulations in this study is discussed in the following Chapter 4.

2.4 Influent wastewater characterization for ASM1

Determining the volumes and composition of wastewater received by a WWTP is referred to as influent characterisation. It involves assessing the characteristics and quantities of the various constituents present in the particular wastewater. Since wastewater is water whose quality or composition has been adversely affected by the activity of humans in the environment, it contains a variety of organic and inorganic compounds of natural and anthropogenic origin (Metcalf and Eddy, 1991).

The constituents in wastewater can be classified as physical, chemical or biological. Chemical characterisation of municipal wastewater defines the organic, nitrogenous and phosphorus compounds present in the wastewater (Wentzel and Ekama, 2006). The organic compounds include carbohydrates, proteins and fats, while nitrogen is principally present as ammonia. In municipal wastewater, phosphorus is present in the form of phosphates mainly from domestic waste streams.

Physical characterisation determines the particulates and dissolved compounds in wastewater. Soluble, settleable and non-settleable constituents in wastewater are defined by physical characterisation. Biological characterisation identifies and quantifies the biodegradable and non-biodegradable components of the wastewater.

While the classification of wastewater constituents into physical, chemical and biological constituents includes all the material found in wastewater, it is necessary to break down this broad classification into components that can be used in chemical and mass balance equations in mathematical models. Thus, for modelling purposes the complex mixture of organic and inorganic material in wastewater is further partitioned into groups. The groups are defined according to how the material in that group behaves in the activated sludge process (Dold et al., 1980; Melcer et al., 2003).

The level to which wastewater characterisation has to be done for modelling purposes depends on the activated sludge system to be simulated (Wentzel et al., 1999). Reliable characterisation of the organic material is essential for successful prediction of oxygen demand, nitrogen removal and mixed liquor suspended solids by an activated sludge model (Wentzel and Ekama, 2006). The prediction of oxygen demand, biological nitrogen removal and phosphorus removal in the activated sludge model is strongly linked to proper characterisation of the nitrogenous material. Furthermore in activated sludge systems where low final treated effluent phosphorus concentrations are required, the correct division of phosphorus into its constituent fractions in the influent becomes important (Rieger, 2013). The importance of correct wastewater characterisation extends to beyond obtaining acceptable simulations for the activated sludge unit. In the context of modelling WWTP, wastewater characteristics not only affect the activated sludge unit but other unit operations such as solid-liquid separation in clarifiers. Hence, reliable influent wastewater characterisation is required for useful modelling results. Influent wastewater characterisation for the Activated Sludge Model No.1 (ASM1) is presented in the following sections.

2.4.1 The organic component in wastewater

In ASM1, the organic fraction in wastewater is split based on biodegradability, rate of biodegradation, solubility and viability (Petersen et al., 2000). The first level of division splits the organic matter into three sub-fractions; the biodegradable, non-biodegradable and active biomass. The biodegradable substrate is further divided into readily biodegradable (S_S) and slowly biodegradable substrate (X_S). Readily biodegradable material is assumed to consist of relatively small molecules (such as volatile fatty acids and low molecular weight carbohydrates) which can be easily carried into the cell resulting in an immediate utilisation of the electron acceptor (oxygen or nitrate), while the slowly biodegradable material is assumed to consist of larger and more complex molecule, which requires extra cellular breakdown before uptake and utilisation (Dold et al., 1980; Dold et al., 1986).

The non-biodegradable fraction which consists of material that does not react or reacts at slow rates such that any losses in the treatment process are considered negligible, has two fractions, the non-biodegradable particulate (particulate inerts) and non-biodegradable soluble (soluble inerts). The non-biodegradable soluble fraction (S_I) passes unaffected through the treatment process in liquid phase. This definition implies that the concentration of the non-biodegradable soluble fraction in the influent must be the same as that in the final effluent at the WWTP. The non-biodegradable particulate (X_I) material is entrapped in the activated sludge and removed with excess sludge. In addition to (X_I) particulate products (X_P) which come from biomass decay are considered non-biodegradable (Weddle and Jenkins, 1971). The active biomass consists of heterotrophic (X_{BH}) and autotrophic (X_{BA}) organisms (Wentzel et al, 1995). X_P is formed by the decay of heterotrophic and autotrophic biomass. Figure 2.7 shows the COD fractions for ASM1.

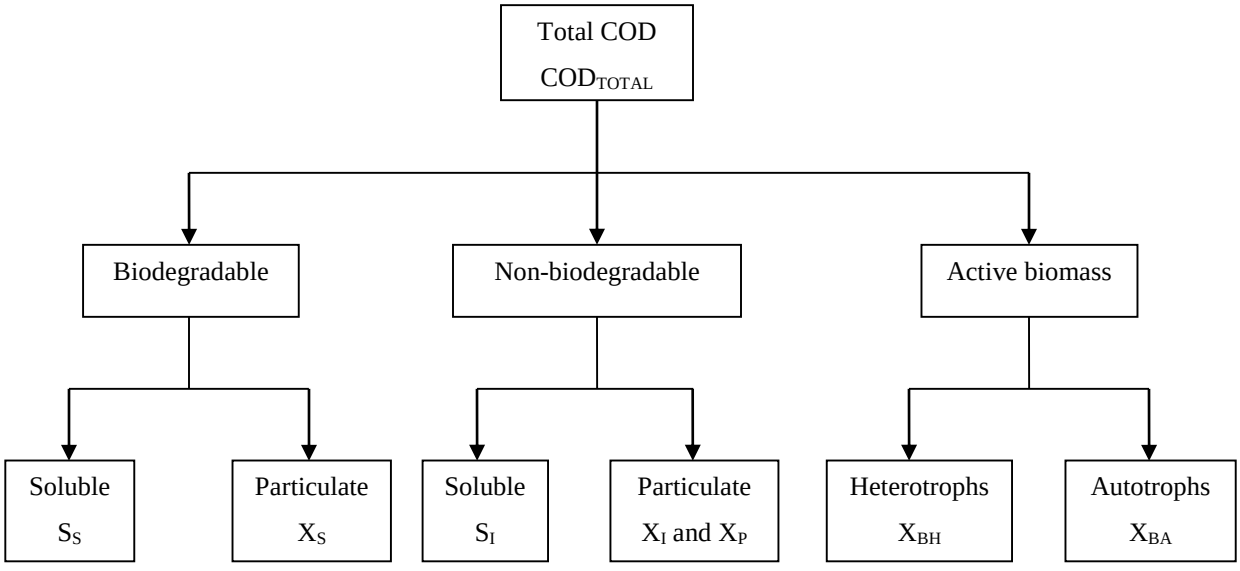

Figure 2.7 COD fractions in ASM1 (adapted from Jeppsson, 1996)

The total COD illustrated in Figure 2.7 can be summarised by Equation 2.2.

$$COD_{TOTAL} = S_S + X_S + S_I + X_I + X_P + X_{BH} + X_{BA} \quad [2.2]$$

2.4.2 The nitrogenous fraction in wastewater

The total nitrogen content in municipal wastewater is the sum of the Total Kjeldahl Nitrogen (TKN) and nitrite and nitrate. In ASM1 the nitrogenous material in the wastewater is divided as show in Figure 2.8.

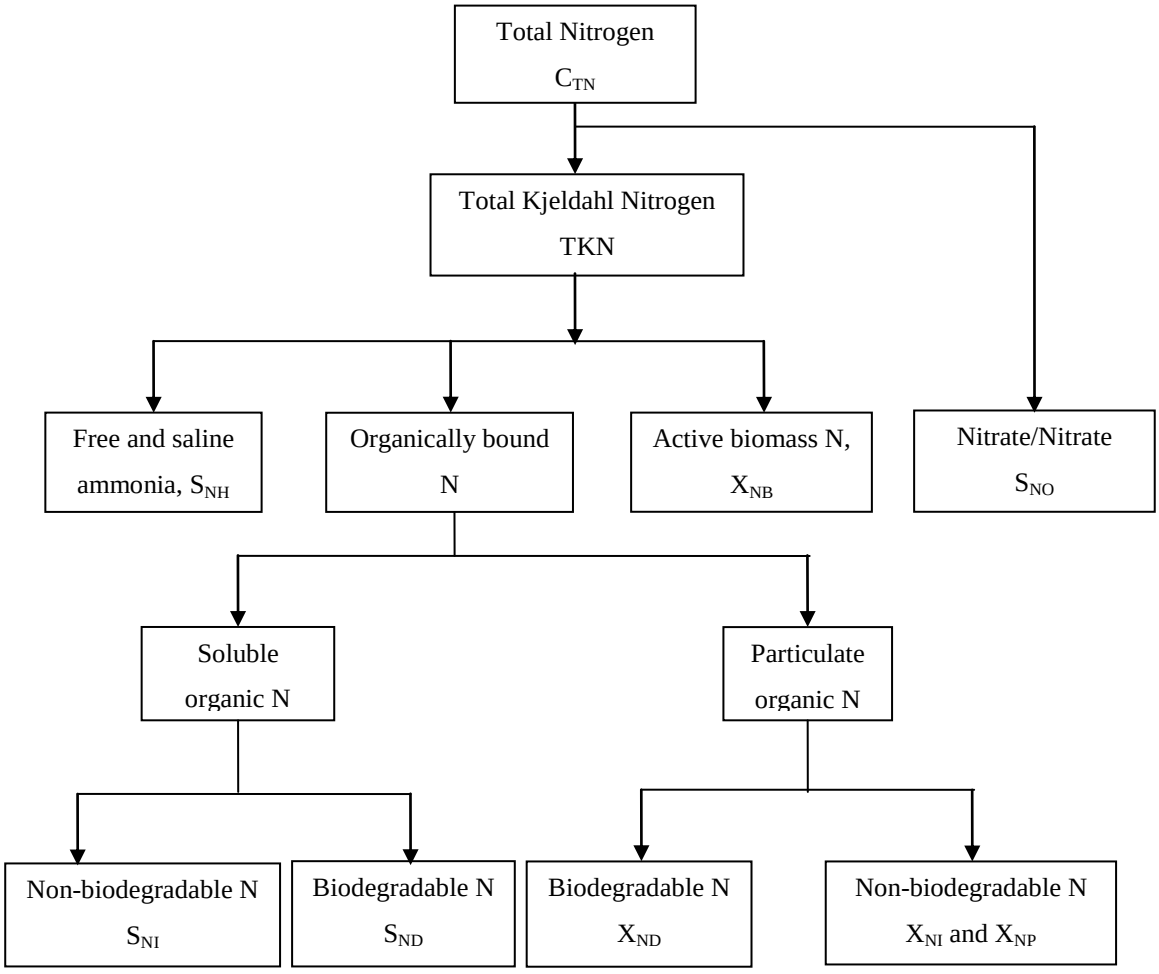

Figure 2.8 Nitrogen components in ASM1 (adapted from Jeppsson, 1996)

The division of the nitrogenous fraction is similar to that of the organic fraction in that the subdivision is based on solubility, biodegradation and the rate of biodegradation. The TKN is divided into free and saline ammonia (S_{NH}), organically bound nitrogen and active biomass nitrogen (a fraction of the biomass which is assumed to be nitrogen). Similar to the division of the organic material, the organically bound nitrogen is divided into biodegradable and non-biodegradable fractions which contain soluble and particulate components. Only the particulate biodegradable organic nitrogen (X_{ND}) and soluble biodegradable organic nitrogen (S_{ND}) are explicitly included in the ASM1 model (Jeppsson, 1996). The organic particulate nitrogen fractions X_{NB}, X_{NP} and X_{NI} are associated with the organic fractions X_B, X_P and X_I respectively. The active biomass nitrogen fraction (X_{NB}) is associated with the decay of biomass which results in the production of particulate biodegradable organic nitrogen (X_{ND}) (Jeppsson, 1996). These forms of organic nitrogen can be determined by multiplying X_B by i_{XB}, X_P by $i_{XP,}$ and X_I by i_{XI} where i_{XB}, i_{XP}, and i_{XI} are the respective fractions of the nitrogen present in the parent organic fractions. In ASM1 nitrate nitrogen (S_{NO}) is a result of nitrification of ammonia by a single step process. The total nitrogen, C_{TN} illustrated in Figure 2.8 can be summarized by Equation 2.3 as the sum of the soluble and particulate components.

$$C_{TN}= S_{NH} +S_{NI}+S_{ND} + S_{NO} + X_{NB} + X_{ND} + X_{NI} + X_{NP} \quad [2.3]$$

2.4.3 The phosphorus content in wastewater

In this study there was no need to determine the phosphorus fraction of wastewater for modelling since the WWTP to be modelled is not operated to remove phosphorus. Furthermore it is not necessary to determine the phosphorus content of wastewater when using ASM1.

2.5 COD fractionation of influent wastewater for ASM1

The total COD of wastewater for the ASM1 model is split into 7 components: S_S, X_S, S_I, X_I, X_P, X_{BH} and X_{BA} (Weddle and Jenkins, 1971; Wentzel et al, 1995), only five of these fractions are considered to be present in the influent wastewater received at a WWTP (Henze et al., 1987). Particulate products of biomass decay (X_P) and autotrophic biomass (X_{BA}) are considered to be of negligible concentration in the influent wastewater (Henze et al., 2000). Consequently the total COD is given by equation 2.4.

$$COD_{TOTAL}= S_S +X_S + S_I + X_I + X_{BH} \quad [2.4]$$

The standard COD-test is used to determine indirectly the total amount of organic matter in wastewater (Standard Methods, 1999). However, determining the constituent COD fractions is a more difficult and time-consuming task. No direct and continuous method for explicitly determining the constituent COD fractions exists (Vollerstsen et al., 2002). Quantifying the COD fractions in wastewater for modelling using ASM models can be done using different indirect methods. The methods are based on principles related to either the impact of the components on the process or the physical definition of the components or in some cases measurement methods based on a hypothesis related to a defined model structure are used (Melcer, 2003). Not all methods have been perfected to be considered as standard methods. Some of the methods used in wastewater characterisation are sourced from peer-reviewed investigations by different researchers working with different types of wastewaters. A review of the methods available for determining the COD fractions in equation 2.4 found in municipal wastewater is presented in the following sections. It is not an easy task to discuss the methods for quantifying each COD fraction separately since in practice some methods are used to estimate more than one COD fraction. At the end the methods presented are summarised and critically evaluated.

2.5.1 Determining the readily biodegradable COD (S_S)

A number of methods to quantify the readily biodegradable COD (S_S) fraction in wastewater have been proposed and investigated. The methods fall under two categories; physical and bioassay methods. In bioassay methods, the quantity of the wastewater component is derived from observations made on the biological activity in the wastewater. The biological activity in wastewater can be monitored by measuring the oxygen utilisation rate (OUR) measured in a wastewater sample placed in a bioreactor. On the other hand, physical methods are based on separating components based on particle size by using filtration.

2.5.1.1 Physical methods

The subdivision of the biodegradable COD into the S_S and slowly biodegradable COD (X_S) was initially based on the bio-kinetic response of activated sludge mixed liquor to domestic wastewater containing the biodegradable fractions (Dold et al., 1980). The observed response of the activated sludge to the two biodegradable fractions suggested a significant difference in the rates of biodegradation of S_S and X_S. To explain this difference a hypothesis was formulated (Dold et al., 1980; Dold et al., 1986).

The hypothesis suggested that the difference in activated sludge response is due to the difference in molecular size of the constituents of the S_S and X_S fractions. Each biodegradable fraction contains various compounds with a range of biodegradation rates that are consider to be relatively small when compared to the biodegradation rate difference between S_S and X_S (Dold et al., 1980). S_S consists of relatively small

molecules that are readily utilised by the microbial cells whereas X_S consists of larger and more complex molecules which need extra-cellular breakdown (hydrolysis) to smaller units before utilisation. Based on this hypothesis, physical separation of the two biodegradable COD fractions on the basis of molecular size has been proposed as a way of quantify S_S and X_S (Mbewe et al., 1995). Physical separation by filtration has been suggested and investigated (Mbewe et al., 1995).

In the filtration method, wastewater is filtered through a filter of specified pore size. Ideally X_S which consists of relatively larger molecules should be retained on the filter while the RBCOD passes through the filter with other components found in the filtrate. The COD of the filtrate is then determined. The filtrate contains both S_S and non-biodegradable soluble COD (S_I). A further separation step is required to quantify the S_S and S_I.

To quantify S_I in the influent wastewater, S_I in the final treated effluent from the activated sludge reactor is determined by filtering a sample of the final treated effluent and determining the filtrate COD. It is assumed that S_I in the final treated effluent from the activated sludge reactor is equivalent to S_I present in the influent wastewater since the S_I is inert (Henze et al., 1987). This assumption is backed by observations that all the biodegradable soluble COD in the wastewater will be removed in the activated sludge reactor, provided the sludge-age is in excess of about 3 days (Mbewe et al.,1995). If all the biodegradable soluble COD is removed, the effluent filtrate COD should give a close estimate of S_I. S_S in the influent wastewater can then be found by difference:

$$S_S = \text{Filtrate COD}_{\text{influent}} - \text{Filtrate COD}_{\text{effluent}}$$

Critical analysis of the above method identified two problems. The first problem was the selection of the correct filter pore size for filtration. The appropriate filter pore size for the method would be one that allows the passage of S_S and S_I while retaining X_S in order to give a separation that matches the bio-kinetic subdivision of the biodegradable COD.

The second was the assumption that the final effluent filtrate COD in an activated sludge system operating at sludge-ages in excess of about 3 days is closely equal to the S_I in the influent. The assumption implies that there is no substantial generation of S_I in the activated sludge system (Mbewe et al., 1995).

Several researchers (Hunter and Heukelekian, 1960; Rickert and Hunter, 1971; Levine et al., 1985; Bunch et al., 1961; Saunders and Dick, 1981; De Walle and Chian, 1974) in the past have investigated the physical methods of quantifying COD fractions in wastewater and some of the investigations were aimed at addressing the aforementioned problems in the filtration method.

On the subject of selection of filter pore size for physical methods it should be noted that the correctness of the method depends on the pore size of the filter used for separation. Selection of the correct filter pore size is not an easy task since the municipal wastewater contains a wide variety of soluble and colloidal material whose molecular sizes and weights span over a wide range (Mbewe et al., 1995). Rickert and Hunter, (1971) concluded that, wastewater-particles smaller than 1.0 µm could be approximated to be the true soluble fraction. Furthermore rapid biodegradation of particles less than 1.0 µm was observed when compared to particles larger than 1.0 µm in wastewater (Petersen, 2 000). Levine et al. (1985) concluded that filtration across a membrane with a pore size of 0.1 µm was valid to define the separation of the true soluble and particulate COD fractions.

Dold et al. (1986); Lesouef et al. (1992); Mamais et al. (1993); Bortone et al. (1994) and Torrijos et al. (1994) among others, tried different filter pore sizes and reported their findings. Dold et al. (1986) found that the S_S determined by the filtration method correlated closely with the one determined by the conventional bioassay method, when domestic wastewater was filtered through membranes with molecular weight cut-off less than 10 000 Daltons. Dold et al. (1986) also evaluated the use of 0.45 µm filters and found that a portion of X_S passed through the filter together with S_I resulting in an over estimation of S_S. This was also reported by Lesouef et al. (1992) when 7 to 8 µm glass fibre filter papers were used. Bortone et al. (1994) used industrial textile wastewater in a similar investigation and reported that membranes with molecular weight cut-off less than 10 000 Daltons gave S_S that was much lower (13% of the total COD) than that measured in bioassay batch tests (20% of the total COD).

To avoid the over estimation of S_S, Mamais et al. (1993) investigated the flocculation of colloidal material before filtration through 0.45 µm filters and reported better estimates for S_S that compared favourably with those from the conventional flow square wave bioassay test (Mbewe et al., 1995). A smaller filter pore size of 0.1 µm gave a true indication of S_S without pre-flocculation in the work of Torrijos et al. (1994) which investigated the characteristics of domestic wastewater. From the above investigations it appears that filtration using membranes with a pore size of 0.1µm would give a good separation between S_S and X_S. Pre-flocculation of the wastewater before filtration through 0.45 µm filters also seems to be a reliable method.

The assumption that the final effluent filtrate COD is closely equal to the influent S_I in activated sludge systems operating at sludge ages is in excess of about 3 days has been investigated in the past. In the review by Dold et al. (1986) of investigations done by several researchers (Hunter and Heukelekian, 1960); Bunch et al., 1961; Saunders and Dick, 1981; De Walle and Chian, 1974 and others) aimed at characterising and fractionating secondary (treated) effluents using a variety of experimental techniques, it was concluded that secondary effluents contain a wide range of organics ranging from low molecular weight volatile acids to high molecular weight polymeric compounds. Three possible sources of organics in the secondary effluent were identified as: (1) the influent COD, (2) intermediates and end products from metabolic activities of biomass, and (3) cell lysis products in the system.

The intermediate and end products from metabolic activities of biomass are present in the treated effluent even though the material is possibly degradable. The residual amount of the material present in the treated effluent depends on the rate of degradation of the material, among other things (Chudoba et al., 1969; Grady and Williams, 1975; Daigger and Grady, 1977). Furthermore researchers (Saunders and Dick, 1981; Gloor et al., 1981; Leindner et al., 1984; Chudoba, 1985; Namkung and Rittman, 1986) have proposed that cell lysis and death produce residual material adds to the soluble COD from microbial origin in the treated effluent. The lysis products can be hydrolysed and degraded to some degree (Mbewe et al., 1995).

While the review of work by the above mentioned researchers provides evidence of possible generation of non-biodegradable soluble COD in the activated sludge system that ends up in the final effluent, the review gave no clear guidance on the relative magnitude of this generation compared to the amount of S_I present in the influent wastewater. Quantifying the contribution of the two microbial sources to the effluent soluble COD would address the concern of accuracy of the proposed filtration method. A large contribution would disqualify the method because the assumption that the effluent soluble COD is equal to the influent soluble non-biodegradable COD would be incorrect. If the contribution due to microbial generation within the system is low, the error introduced in the test will be relatively small (Mbewe et al., 1995).

Chudoba (1985) reported that the effluent COD which must originate from microbial activity is 1 per cent of the influent COD while Germirli et al. (1991) and Boero et al. (1991) reported values of approximately 2.5 to 3 per cent respectively. These researchers worked with different influent feeds and used pure artificial substrates in their investigations. In comparison, influent municipal wastewater is made up of a diversity of organic material that enables the development of an assorted population of biomass. This is not the case in artificially fed systems (Mbewe et al., 1995). The conditions prevailing in municipal wastewater (presence of a wide variety of organics and the development of a diverse population of biomass) results in an increased

utilisation of the microbially generated organics in the wastewater treatment system compared to pure cultures or cultures grown on limited artificial substrates.

The work of Dold et al. (1986), Mamais et al. (1993) and Torrijos et al. (1994) using municipal wastewaters appears to confirm the above deduction and further concluded that the distribution of organic compounds after biodegradation was closely equal to that before degradation thus suggesting that there is no significant generation of S_I. Hence in conclusion, there is evidence that S_I is generated in the activated sludge system and some of the generated COD ends up in the final effluent. However, studies show that the contribution of the generated S_I to the amount initially present in the influent wastewater may not be significant. Thus, the assumption that the final effluent filtrate COD is closely equal to the influent non-biodegradable soluble COD in activated sludge systems operating at sludge ages is in excess of about 3 days can be used in the above method.

2.5.1.2 Bioassay methods

Bioassay methods are based on the biological response of active biomass to the substrate (biodegradable COD) rather than physical separation. Respirometry is a key concept in bioassay methods. Respirometry is the measurement and interpretation of the respiration rate of activated sludge (Spanjers et al., 1998). The respiration rate can be defined as the amount of oxygen per unit volume and time that is consumed by the microorganisms present in the activated sludge or wastewater (Gernaey et al., 2001). Respirometry is one of the widely used biological characterisation methods since the experimental procedures used seek to recreate the scenarios that exist in the real wastewater treatment plant (Petersen et al., 2000).

The measuring techniques in respirometers can be classified based on two criteria: 1) the phase (gas or liquid) where the oxygen is measured and 2) whether or not there are input and output streams (flowing or static) in the respirometer (Spanjers et al., 1998). The operation of respirometers can be explained in terms of these two criteria. For most applications oxygen measurements are done in the liquid phase (Gernaey et al., 2001) where a dissolved oxygen sensor is used to measure the dissolve oxygen concentration in the liquid phase. In bioassay methods the respirometer is used to measure the oxygen uptake rate (OUR) due to the utilisation of a specific substrate by biomass. The OUR test essentially consists of adding a sample to a bioreactor, placing the dissolved oxygen (DO) probe into the reactor and monitoring the decline in dissolved oxygen over time. The OUR measurements required for COD fractionation require the use of respirometers that provide continuous OUR measurement where a series of OUR points are generated in order to define a profile which is then interpreted.

To quantify S_S, an environment is created such that the difference in response of organism in activated sludge or wastewater to S_S and X_S can be monitored and separated. S_S and X_S are utilised by the active biomass at different rates and this forms the basis for separating the response of the biomass to the two COD fractions. The rate of utilisation of S_S is higher than that of X_S, by an order of magnitude (Dold et al., 1980). The proportion of S_S present in wastewater is usually much less than that of X_S (Mbewe et al., 1995) hence if the rate of utilisation of S_S is higher than that of X_S, conditions can be created whereby the S_S and X_S are utilised simultaneously and then when S_S has been depleted, X_S utilisation continues. The observed differences can then be compared and the difference between them gives the response due to the utilisation of only S_S. A number of bioassay tests have been developed to measure S_S. The bioassay tests can be divided into three groups:

- Continuous flow-through activated sludge systems
- Aerobic batch test methods
- Anoxic batch test methods

Continuous flow-through activated sludge systems

In the continuous flow-through method, a single activated sludge reactor system with a sludge recycle is operated with a daily cyclic square wave wastewater feed (12 hours with feed, 12 hours without feed) while the OUR is measured. The reactor is operated at a sludge age of about 2 to 3 days (Mbewe et al., 1995). The observed OUR profile is shown in Figure 2.9.

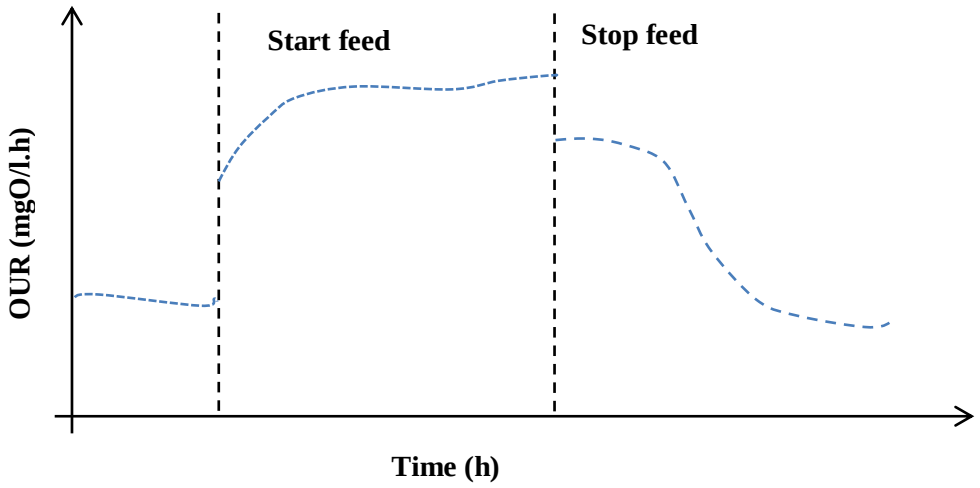

Figure 2.9 OUR response over one cycle in an aerobic activated sludge unit subjected to daily cyclic square wave feed (12h feed on, 12h feed off) (adapted from Mbewe et al., 1995)

During the feed period, the influent wastewater containing both S_S and X_S is added to the reactor. S_S and X_S are utilised simultaneously. When the feed is terminated, a precipitous drop in OUR is observed and then the OUR remains almost constant for a period before falling to a rate associated with endogenous respiration.

To explain the observed OUR profile a hypothesis was proposed (Dold et al., 1980; Ekama et al., 1986). The hypothesis suggested that for the duration of the feed period when the influent is added to the reactor, both S_S and X_S are utilised simultaneously. The rate of utilisation of S_S is system limited while that for X_S is process limited. S_S is utilised as fast as it is fed into the system. The feed rate is the limiting factor in utilisation of S_S. X_S is fed faster than the biomass can utilise it. The biomass maximum specific utilisation rate of X_S limits the rate of utilisation of the substrate, X_S resulting in accumulation of X_S in the reactor. When the influent feed is stopped, the supply of both S_S and X_S going into the reactor is cut off. Utilisation of S_S ceases since the available S_S has been essentially spent resulting in a precipitous drop in OUR. The accumulated X_S continues to be utilised at the maximum rate after the feed is terminated hence the observed plateau in the OUR profile. The utilisation continues at a maximum rate due to the conditions (high load period and short sludge age) prevailing in the reactor. If nitrification is taking place in the reactor it also continues at a maximum rate after the feed is stopped. Consequently, the precipitous drop in OUR observed after the feed is stopped is entirely due to the depletion of S_S. Thus, the drop in OUR is used to determine the S_S (Ekama et al., 1986).

The above method was investigated by Sollfrank and Gujer et al. (1991) and the investigation highlighted the difficulty in maintaining a constant temperature in the reactor when the feed was terminated. From the investigation, it was concluded that temperature variations will affect the nitrification rate, resulting in an erroneous determination of the concentration of S_S from the observed precipitous drop in OUR. Thus, Sollfrank and Gujer et al. (1991) recommended the inhibition of nitrification by addition of allyl thiourea (ATU) and that the sludge-age be increased (to approximately 5 days) in order to decrease the loading rate. The recommended changes resulted in better temperature stability. However, the suggested increase of the sludge-age resulted in an increase in biomass in the reactor which causes rapid utilisation of X_S and thus preventing sufficient accumulation of X_S during the feed period that will allow the utilisation of X_S to continue after the feed is terminated for a period sufficient to clearly recognise the OUR plateau (Mbewe et al., 1995).The continuous flow-through method has become one of the methods available for quantifying the S_S fraction in wastewater. However the method is costly and difficult to operate (Sollfrank and Gujer., 1991).

Aerobic batch method with activated sludge

In the aerobic batch method (such as in Ekama et al., 1986; Henze, 1991; 1992) a measured volume of wastewater of known total COD is mixed with a measured volume of activated sludge mixed liquor in a stirred batch bioreactor and the OUR response monitored with time. The observed OUR is then interpreted accordingly to determine the RBCOD. The ratio of wastewater to mixed liquor is important in this method. When the correct ratio of wastewater to mixed liquor is selected and the contents of the bioreactor are stirred and aerated, the observed OUR profile takes the form presented in Figure 2.10.

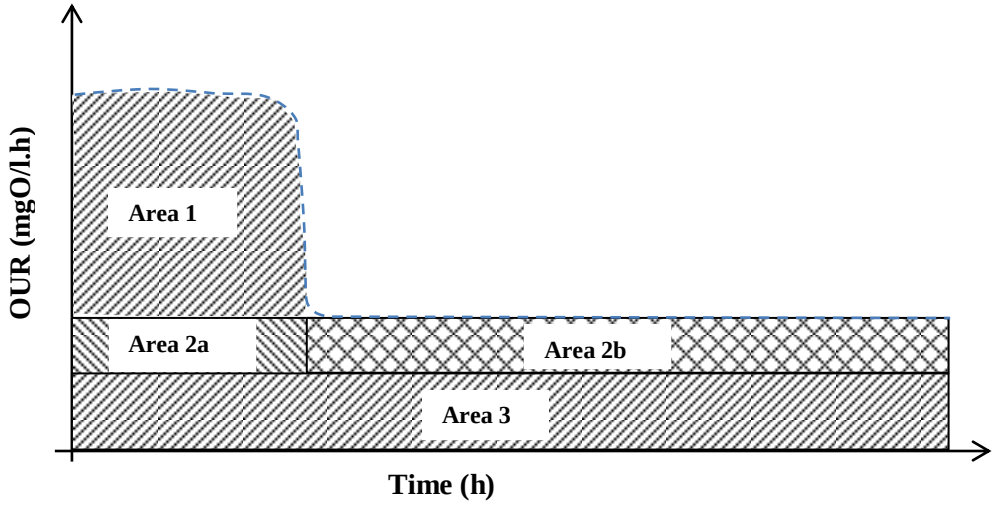

Figure 2.10 OUR response observed in an aerobic batch test (Mbewe et al., 1995)

The OUR stays constant at a plateau for a period of up to 3 hours depending on the concentration of S_S in the wastewater (Mbewe et al.,1995). After this period a precipitous drop in OUR is observed before the OUR levels off at a second plateau. The observed OUR profile is a result of nitrification and utilisation of organic material.

In order to separate the OUR due to nitrification from the OUR resulting from the utilisation of organic material the nitrification rate should be at maximum. If adequate ammonia is present at the start of the batch test and the nitrification process takes place at a maximum and constant rate over the test period, 'Area 3' in Figure 2.10 can be defined on the OUR profile. Area 1 and Area 2 relate to the OUR due to the utilisation of organic material (Mbewe et al., 1995). The OUR response due to the utilisation of organic matter is interpreted as follows:

At the beginning of the batch test both S_S and X_S are present and they are utilised independently but simultaneously by heterotrophic biomass for growth. S_S is absorbed directly and utilised. X_S is broken down to smaller units by extracellular hydrolysis. The resulting smaller units are then directly utilised by the

biomass. The observed OUR due to the utilisation of organic material is the sum of the OUR associated with utilisation of S_S and that associated with utilisation of X_S.

The observed OUR is constant over the initial period because the amounts of S_S and X_S present at the beginning of the test and during the initial period are sufficient for S_S to be utilised at the maximum rate and for X_S hydrolysis and utilisation to take place at a maximum rate. When the S_S is exhausted, the OUR falls to the second plateau shown in Figure 2.10. This plateau is the OUR response due to the maximum hydrolysis and utilisation of only X_S. The area under the OUR-time profile due to the utilisation of S_S is used to determine the wastewater S_S concentration. Ekama et al. (1986) and Dold et al. (1991) provide details of the calculations.

The ratio of wastewater to mixed liquor used in the batch test can be interpreted as a food to microorganism ratio (F/M) (Melcer et al., 2003). Altering the F/M ratio does not affect the calculated amount of S_S since Area 1 in the OUR-time profile is determined by the amount of S_S available in the wastewater. However changing the F/M ratio affects the shape of the OUR-time profile. The correct F/M ratio for the batch test should give an OUR response that is well defined and allows: the initial OUR peak to be readily determined, the magnitude of the precipitous drop in OUR to be clear, and the area under the initial OUR peak to be accurately estimated in order to calculate S_S.

If F/M ratio is too low, the rate of utilisation of S_S will be high. S_S will be utilised rapidly resulting in a tall and narrow OUR response profile. On the other hand if F/M ratio is too high the response will be low, wide and flat, making it difficult to identify accurately the drop in OUR. In both cases correct estimation of Area 1 becomes difficult. Selection of the correct F/M ratio is important and it is not a simple task. Selection of the correct F/M ratio is influenced by several factors which include the following:

- the active biomass concentration in the mixed liquor used in the test is a function of sludge-age (and other factors) which vary from one situation to the next
- the maximum specific growth rate of the heterotrophic biomass which differs significantly between sludges

Hence there is no definitive guideline as to the correct F/M for all situations. The appropriate F/M ratio to be used in the test should be determined by trial. A recommended starting ratio is 0.6 mg COD/mg VSS (Melcer et al., 2003).

The aerobic batch test method has been used successfully to estimate the concentration of S_S in wastewater (Ekama et al.,1986; Henze et al., 1992; Kappelar and Gujer, 1992). However, the batch test requires sludge acclimatised to the wastewater to be used for reliable results. Acclimatised sludge can be generated in special laboratory-scale continuous flow through reactors (Ekama et al., 1986; Sollfrank and Gujer, 1991; Kappelar and Gujer, 1992) or obtained from a full scale plant (Nicholls et al., 1985).

Anoxic batch test methods

The basis for the anoxic batch test is the same as that of the aerobic batch test described above. In both batch tests, measured volumes of the wastewater and mixed liquor are mixed in a continuously stirred batch reactor. The difference in the anoxic batch test is that the test is done under anoxic conditions, instead of aerating the contents of the batch reactor and measuring the OUR, nitrate is added at the start of the test and the nitrate concentration is monitored for approximately 4 to 5 hours (Mbewe et al., 1995). In anoxic conditions, the nitrate serves as the electron acceptor like oxygen in the aerobic batch test. Figure 2.11 shows an example of a nitrate concentration time plot for an anoxic batch test.

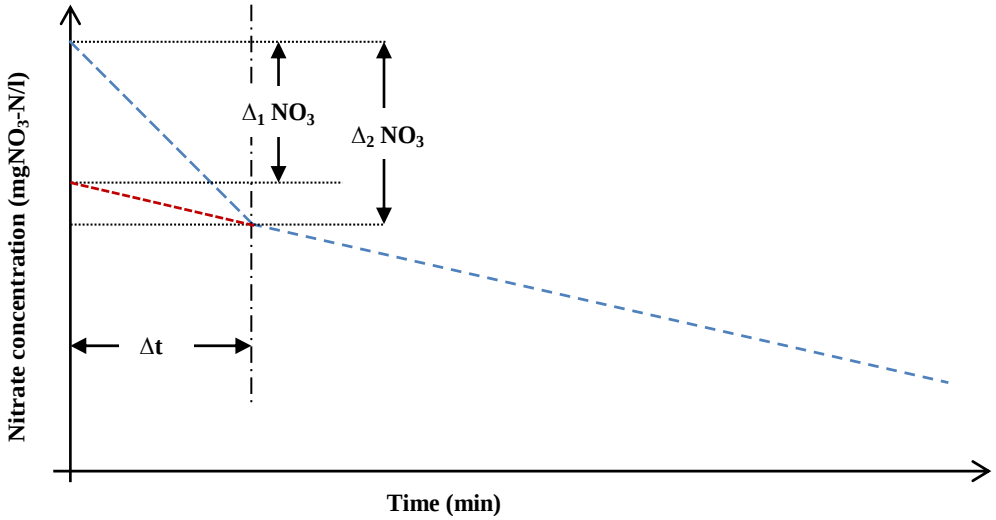

Figure 2.11 Nitrate concentration-time plot from an anoxic batch test for measuring wastewater readily biodegradable COD concentration (After Ekama et al., 1986) adapted from (Mbewe et al., 1995)

During the initial period of the batch test the concentration of the nitrate drops at a constant rapid rate. This is a reflection of the biomass utilising the S_S and X_S present in wastewater. The observed initial rate of de-nitrification is constant because the concentration of S_S is high enough for the growth rate of heterotrophic biomass to occur at maximum (Mbewe et al., 1995). This initial rapid rate is analogous to the initial high OUR observed in the aerobic batch test. When the S_S is exhausted, the de-nitrification rate reduces to a rate associated with the utilisation of X_S; this slower de-nitrification rate is analogous to the second plateau in the aerobic batch test (Mbewe et al., 1995).The amount of S_S present in the wastewater can be calculated

from the mass of nitrate utilised during the initial period of rapid de-nitrification rate. Details of thecalculations can be found in Ekama et al. (1986) and Henze (1991). The anoxic batch test suffers from the same restrictions and cautions identified for the aerobic batch test.

Aerobic batch method without activated sludge

Before Wentzel et al. (1995), conceptually, the bioassay tests already appeared to be the best method for measuring S_S in wastewater for modelling purposes. The bioassay tests provided a good estimate for S_S (Melcer et al., 2003). However a common short-coming in the bioassay methods was that the mixed liquor used in the tests must be acclimatised to the wastewater being tested (Mbewe et al., 1995). When the continuous-flow-through test is used, the acclimatised mixed liquor can be generated in the same reactor in which the test is done while in the batch test procedures it must be generated either in separate laboratory-scale reactors, or obtained from full-scale plants.

To address the above mentioned challenge associated with using pre-acclimatised mixed liquor in bioassay methods, Wentzel et al. (1995) developed a simple batch test method to quantify S_S and heterotrophic active biomass (X_{BH}). Unlike the aerobic and anoxic batch tests described earlier, the test by Wentzel et al. (1995) does not require any activated sludge seed. The unsettled influent wastewater is transferred into a continuously stirred reactor, aerated for about 12 h while the OUR is measured and recorded. The procedure is a modification of the work by Kappelar and Gujer (1992) which described a batch test to quantify X_{BH} in activated sludge. In the test by Kappelar and Gujer (1992), a small quantity of activated sludge was mixed with centrifuged wastewater supernatant and the OUR response monitored with time. Kappelar and Gujer (1992) noted that the test could be adapted to quantify the X_{BH} in the wastewater by excluding the activated sludge. In this light, Wentzel et al. (1995), modified and developed the bioassay test to quantify S_S and X_{BH}. Figure 2.12 shows an example of the OUR-time curve obtained from the simplified aerobic batch test by Wentzel et al. (1995).

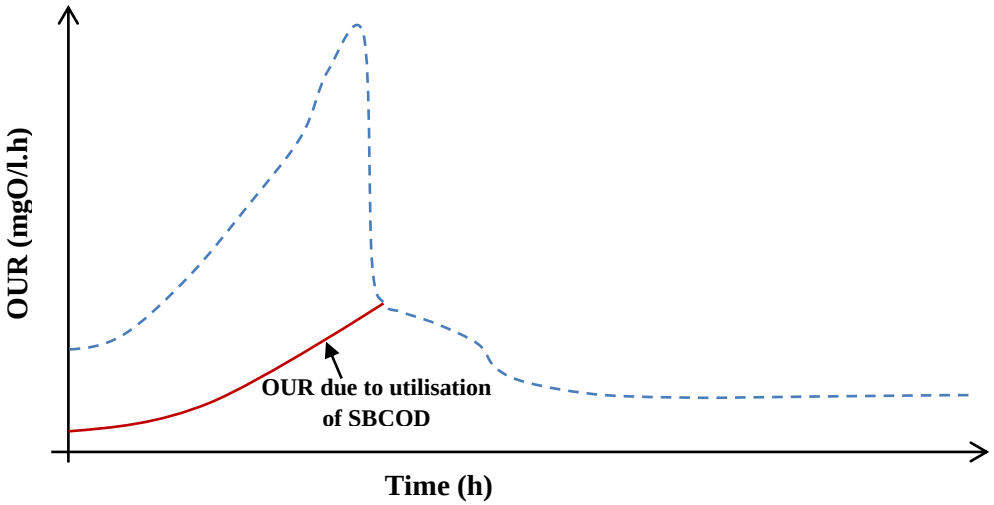

Figure 2.12 Oxygen utilisation rate (OUR) response with time for aerobic batch on test on raw municipal wastewater showing theoretical OUR for utilisation of the slowly biodegradable COD (Wentzel et al., 1995)

The observed OUR-time plot shows that during the initial period of the batch test the OUR exhibits an exponential increase due to the growth of X_{BH} on both S_S and X_S. This is followed by a precipitous drop of the OUR as soon as the S_S is depleted. Up to the precipitous drop, the OUR is the sum of both the OUR due to the utilisation of S_S and X_S. For the rest of the batch test the OUR exhibits an inverted 'S' pattern associated with saturation kinetics, due to the utilisation of X_S only (Wentzel et al., 1995). The OUR results can be interpreted in terms of the UCT (Dold et al., 1980; 1991) or IAWQ (Henze et al., 1987) models. In order to estimate the S_S the observed OUR before the precipitous drop must be separate into the S_S and X_S contributions. The OUR utilisation due to X_S can be predicted by equation (Wentzel et al., 1995) related to a mathematical model of the processes taking place inside the bioreactor. One such model is the UCT model (Dold et al., 1991). Figure 2.12 shows the predicted OUR curve due to the utilisation of X_S in the initial period of the batch test. X_{BH} is then calculated from the OUR response due to utilisation of S_S only. Detailed calculations are presented in Wenzel et al. (1995).

The batch test by Wentzel et al. (1995) provided a relatively simpler method for quantifying S_S and X_{BH}. No pre-acclimatised mixed liquor is required for this test. However the theoretical equation used to predict the OUR due to the utilisation of X_S in the initial period of the batch test requires the heterotrophic yield (Y_{ZH}) and specific death rate of biomass (b_H) to be determined independently. The other constants required for the calculations are obtained from the experimental data.

Wentzel et al. (1995) compared the estimates of S_S obtained from the batch test to the results from conventional flow through method. The estimates obtained from the batch test closely correlated (within 5%) to those from the conventional flow through method of Ekama and Marais (1979) (Mbewe et al. 1995).

2.5.2 Determining the heterotrophic active biomass (X_{HB})

In the past municipal influent wastewaters in South Africa have been considered to contain negligible concentrations of X_{BH} (Dold et al., 1980; Van Haandel et al., 1981) because the sewers in South Africa are generally considered to be short (retention in the sewer is less than 6 h) and anaerobic thus unlikely to support active biomass generation (Mbewe et al., 1995). However, reported values of influent X_{BH} in European wastewaters range from 7 to 25 per cent of the total influent COD (Kappelar and Gujer, 1992; Orhon and Cokgor, 1997). Confirmation of significant proportions of X_{BH} in wastewater highlighted the need for reliable and simple tests to measure this COD fraction.

Microbiological techniques such as colony counts (Gaudy and Gaudy, 1980) DNA analysis (Liebeskind and Dohmann, 1994; Blackall, 1994) have been proposed and are still being improved. A notable disadvantage of microbiological techniques is that the techniques require very sophisticated equipment that is not widely available.

Kappelar and Gujer (1992) proposed a batch test to quantify X_{BH} in an activated sludge sample. In the batch test, a measured sample of activated sludge is combined with centrifuged supernatant wastewater and the OUR response monitored with time. Kappelar and Gujer noted that the batch test could be adapted to quantify the X_{BH} in wastewater by excluding the activated sludge thus prompting Wentzel et al. (1995) to modify Kappelar and Gujer's method. In the batch test by Wentzel et al. (1995), a measured volume of influent wastewater of known COD concentration is placed in a continually stirred batch reactor and aerated while the OUR is measured for a period of 10 to 20 hours. At the beginning of the test, X_{BH} should be present together with an appreciable amount of S_S. The concentration of S_S at the beginning of the test should be well in excess of the half-saturation coefficient of biomass growth (Melcer, 2003). Consequently the first part of the test should show a logarithmic growth phase as show in Figure 2.12. The observed OUR response shows an exponential increase from an initial low value until the S_S is nearly consumed. This is followed by a precipitous drop in OUR when S_S is depleted. The amount of X_{BH} present in the influent wastewater can then be estimated from the OUR response using an appropriate activated sludge model. Wentzel et al. (1995) used the simplified UCT model (Dold et al., 1991) to estimate the quantity of X_{BH}. Details of the calculation can be found in Wentzel et al. (1995). In this test it is important to determine whether nitrification is contributing to the observed OUR response. Samples of the wastewater can be drawn at the beginning and at the end of the test and analysed for nitrate and nitrite. It is unlikely that significant nitration occurs due to the low concentration of nitrifiers relative to the heterotrophic biomass and the short duration of the test (Melcer, 2003). Nitrification can be inhibited by addition of an inhibitor such as allyl thiourea.

2.5.3 Determining the non-biodegradable soluble COD (S_I)

The non-biodegradable soluble COD (S_I) in influent wastewater is the soluble organic material which is not affected by the biological processes in the system. S_I makes up part of the treated effluent that leaves the system. Thus S_I in the influent is considered to be equal to the filtered treated effluent COD if it is assumed that the residual soluble biodegradable COD in the effluent is negligible compared to the non-biodegradable material and that there is no generation of soluble non-biodegradable COD within the system (Melcer, 2003).

During the treatment of wastewater using activated sludge in a biological reactor, all the S_S is considered to be consumed in a bioreactor operating at a sludge-age of greater than 3 days. The particulate slowly biodegradable COD, X_S and non-biodegradable COD, X_I are enmeshed in the activated sludge that is removed as settled solids in the secondary clarifiers (Mbewe et al., 1995). Hence the only soluble COD from the influent wastewater that will be in the treated effluent (secondary-clarifier-overflow) will be S_I.

If it is assumed that the generation of S_I by microbial action in the activated sludge system is negligible, (as discussed earlier) compared to that initially present in the influent thus S_I in the treated effluent from a long sludge-age activated sludge system will be equal to S_I in the influent.

Based on the above idea and assumptions, the experimental procedure recommended by Ekama et al. (1986) is to run a steady-state laboratory-scale activated sludge system at a sludge-age greater than 3 days and then determining the COD of the treated effluent filtered through 0.45 μm filter. At steady-state the COD of the filtered final effluent is considered equal to the S_I in the influent. Based on a similar principle and assumptions as Ekama et al. (1986), Lesouef et al. (1992) determined S_I in influent wastewater from an aerated batch test run for 10days before estimating S_I from the filtered treated effluent. The extended aeration time ensured total utilisation of the available soluble readily biodegradable COD meaning that only S_I remained in the final treated effluent. The accuracy of the result obtained from this approach is brought to question by the fact that several studies (Orhon et al., 1989; Boero et al., 1991; Germirli et al., 1991; Chudoba, 1985; Sollfrank et al., 1992, Pertesen et al., 2002) have confirmed the production of S_I in the activated sludge process. Germirli et al. (1991) gave evidence that the generation of S_I in the activated sludge process depends among other factors, on the wastewater type. Good estimates for S_I have been obtained in cases of low loaded activated sludge systems (Ekama et al., 1986). The drawback of the proposed methods is that the laboratory-scale activated sludge system (Ekama et al., 1986) is costly and time consuming, while the method proposed by Lesouef et al., 1992 requires a period of 10 days before an estimate of S_I can be obtained.

The review of methods available for quantifying S_S presented earlier, discussed the flocculation-filtration method of Mamais et al. (1993). The flocculation-filtration method of Mamais et al. (1993) introduced a step of flocculation of colloidal material in the influent wastewater before filtration through 0.45 µm filters. The filtrate collected in this method would contain both biodegradable and non-biodegradable soluble COD (S_S and S_I), thus making it necessary to determine the S_I independently in order to have an estimate for S_S. Mamais et al. (1993) used zinc sulphate as flocculant followed by pH adjustment to a pH of 10.5 by addition of sodium hydroxide since the optimum pH for flocculation using zinc sulphate is 10.5. Mbewe et al. (1995) considered this method of estimating S_S as one holding the most promise when compared to other methods presented that were being used at the time. Accordingly Mbewe et al. (1995) evaluated the methods proposed by Mamais et al. (1993) to measure S_S in influent wastewater by comparing the S_S concentration determined using the method by Mamais et al. (1993) with the S_S concentration determined from the batch test and flow-through square wave methods. Furthermore Mbewe et al. (1995) investigated extending the method by Mamais et al. (1993) to determine S_I.

Mbewe et al. (1995) replaced zinc sulphate with aluminium sulphate [$Al(SO_4)_3 \cdot 15H_2O$] for better flocculation and to avoid the need for pH adjustment. Addition of aluminium sulphate causes a drop in pH to between 6.0-6.3, a range suitable for aluminium flocculation; consequently the need for pH adjustment was eliminated. The procedure by Mbewe et al. (1995) began with dosing one litre of diluted wastewater with 10 ml of stock aluminium sulphate solution (50 g/l) followed by a rapid mixing phase achieved by stirring rapidly (~200 rpm) for two minutes. After mixing, the wastewater was transferred to a perspex cylinder (used as a settling column) equipped with a slow stirrer(~1 rpm) and flocculation was allowed to occur for 30 minutes. The flocs combine and settle out leaving a clear liquid zone at the top. 50 ml of the clear liquid was drawn, filtered through a glass fibre filter (Whatman's GF/C) and the filtrate COD determined. The filtrate collected through the glass fibre filter was further filtered through 0.45 µm filter (Millipore HVLP) paper and the filtrate COD determined. The filtrate collected will contain both S_S and S_I, thus making it necessary to determine S_I independently in order to have an estimate for S_S.

From the investigations carried out, Mbewe et al. (1995) concluded that the flocculant, zinc sulphate could be replaced by aluminium sulphate to eliminate the need for pH adjustment after flocculant addition. The flocculation-filtration method provided estimates of the RBCOD that correlated reasonably with those obtained from the batch test and conventional square wave methods. On comparing the use of glass fibre filters to 0.45 µm filter papers recommended by Mamais et al. (1993), Mbewe et al. (1995) concluded that the filters gave results that corresponded closely and further recommended the use of glass fibre filter paper to reduce the cost of the test.

Mbewe et al. (1993) followed the success of adapting the test procedure by Mamais et al. (1993), with applying the method to the aerobic batch test (Wentzel et al., 1995) used to determine S_S. The OUR profiles in the aerobic batch test indicated that the S_S is consumed after~10 h. After this time the remaining soluble COD is S_I. Mbewe et al. (1995) applied the adapted flocculation-filtration method to the wastewater that has been subjected to the batch test for more than 10 h. In the procedure of Mbewe et .,al, a litre of the contents of the batch test was drawn from the reactor after 1 or more days of running the batch test, and the flocculation-filtration method was applied using 0.45 µm filter papers. At this point of the test the filtrate COD should provide an estimate of the non-biodegradable soluble COD since the soluble biodegradable COD has been totally utilised. After evaluating the method, Mbewe et al. (1995) recommended that the batch test should be run for about 1 day before a sample is drawn for flocculation and filtration. Running the test for a period of more than 1 day, did not significantly affect the estimate of S_I.

Notably, advantages of the combination of the batch test and the flocculation-filtration procedure is that the method does not require effluent from an activated sludge system and this procedure allows the estimation of three COD fractions simultaneously, S_S, X_{BH} and S_I.

2.5.4 Determining the slowly biodegradable COD (X_S)

The slowly biodegradable COD (X_S) consists of complex organic material that requires extracellular enzymatic breakdown before utilisation by the micro-organisms. On a physical basis, X_S is considered to consist of fine particulate matter, colloidal matter and relatively large organic molecules that can be considered soluble (Melcer, 2003). However for modelling purposes, X_S is considered to be particulate (Henze et al., 2000).

It is a challenge to determine X_S and X_I in the influent wastewater. One of the reasons for this is that both the particulate COD fractions contribute to the mixed liquor solids in the bioreactor where it is not an easy task to separate the solids into different COD fractions. The mixed liquor solids also contain active biomass. As a result of this difficulty to quantify X_S, some researchers prefer to determine the X_S concentration by difference from the total COD of the wastewater and other previously estimated influent COD fractions (Melcer, 2003).

Procedures to quantify X_S have been proposed. Sollfrank and Gujer (1991) proposed a relatively quick method to estimate X_S in influent wastewater. In the proposed method, wastewater was centrifuged to separate the solids from the liquid. The resulting pellet from the centrifuge was then added to an activated

sludge system in which the feed had been stopped. The OUR response of the activated sludge system was monitored and then used to estimate the X_S. The drawback of this procedure is that the pellet does not contain all the X_S that was present in the influent wastewater, some of the X_S remains suspended in the supernatant after centrifuging, resulting in the underestimation of X_S if only the pellet is considered. For a more accurate estimate, the X_S in the supernatant should be determined independently. Sollfrank and Gujer (1991) recommended that the X_S in the supernatant be determined from a separate batch test in which the supernatant is added to mixed liquor and the OUR response monitored. However due to the low concentration of particulate matter in batch tests compared to the high concentrations of soluble biodegradable material it is implausible that accurate estimates for X_S can be obtained.

Another procedure for determining X_S was proposed by Kappelar and Gujer (1992). The proposed procedure was to use the aerobic batch test used for determining S_S for the estimation of X_S. In the aerobic batch test when the S_S has been consumed a precipitous drop in OUR occurs. After the precipitous drop in OUR, the observed OUR is due to utilisation of particulate organic material (X_S) and nitrification. Kappeler and Gujer (1992) added a nitrification inhibitor, allyl thiourea (ATU) to the contents of the bioreactor to eliminate the OUR due to nitrification. Once nitrification is inhibited, the observed OUR after the precipitous drop in OUR will be due to the utilisation of only X_S. However, the X_S being utilised is not only that which was present in the influent wastewater water but some of the X_S is generated from death or lysis of heterotrophic active biomass added to the batch test with mixed liquor. This introduces errors in the estimation of X_S since the OUR due to utilisation of X_S from the two sources cannot be separated.

2.5.5 Determining the non-biodegradable particulate COD (X_I)

In the activated sludge system, non-biodegradable particulate COD (X_I) from the influent wastewater is enmeshed in the activated sludge and with time accumulates in the system (Melcer, 2003). During modelling of the activated sludge process determining the quantity of X_I is crucial for predicting the production of the volatile solids in the activated sludge process. At steady-state the mass X_I entering the system is equal to the amount leaving the system through sludge wastage and the final effluent. Determining the quantity of X_I in the influent wastewater is a difficult task since the mixed liquor solids in the system are made up of other components besides X_I.

The solids in the mixed liquor include active biomass, endogenous mass and X_S. The procedures for determining the concentration of particulate X_I involve the analysis of the kinetics of a laboratory scale completely mixed activated sludge unit operated at steady-state with a sludge-age longer than 5 days (Orhon et al., 1996). Ekama et al. (1986) proposed a calculation of the concentration of X_I which involved

comparing the measured mixed liquor volatile suspended solids (MLVSS) concentration with the value calculated from the kinetics of the activated sludge system. The IAWPRC Task Group (Henze et al., 1987) recommends a similar approach based on the comparison of observed and calculated sludge production (Orhon et al., 1996). For these procedures, the heterotrophic yield, Y_{ZH} the endogenous decay rate, b_H and the inert fraction of biomass must be correctly determined by independent experiments.

X_I can be estimated from a simulation model of the activated sludge system by adjusting the magnitude of the fraction of influent non-biodegradable COD, f_{XI} until the observed and predicted mixed liquor volatile suspended solids (VSS) concentrations match (Melcer, 2003). In this procedure an initial value of f_{XI} is assumed and model predictions of VSS are compared to the measured VSS. The value of f_{XI}, is adjusted until good correspondence is obtained between the observed and predicted values. However, changing the value of f_{XI} does not only affect VSS. Predictions of oxygen utilisation rate (OUR) and other process variables such as nitrate concentration are also affected. Hence comparing observed and predicted values of the additional variables affected by the change in f_{XI} provides a useful cross-check on the value of f_{XI} (Melcer, 2003). An advantage of the model simulation approach is that the OUR and effluent nitrate concentration predictions can readily be compared to observed data together with the VSS prediction and model calibration can be done. It is important to use the same model in estimating the value of f_{XI} as the one that will be used for the further simulations of the activated sludge system. The steady-state Water Research Commission (1984) model is an example of a model that can be used to estimate value of f_{XI} (Melcer, 2003).

2.5.6 Discussion of methods and conclusion

A discussion of the methods used for the COD fractionation of influent wastewater is presented in the following sections. Guidelines of how to combine the individual methods of quantifying the COD fractions in order to obtain a complete set of wastewater COD fractions are discussed thereafter.

2.5.6.1 Overview of possible methods for COD fractionation

The development of activated sludge modelling has created a need for reliable methods of quantifying COD fractions in the influent wastewater. Over the years, several methods have been proposed and tried in an attempt to obtained full COD fractionation of different municipal influent wastewaters. The variation in the results obtained from different methods has highlighted the need for standardised guidelines on how the different methods presented in the above review can be used in order to obtain reliable complete COD fractionation.

The readily biodegradable COD, S_S can be estimated by bioassay or physical methods. Bioassay methods are based on the measurement of biomass response during substrate utilisation in wastewater or activated sludge while physical methods involve physical separation of COD fraction based on the difference in particle or molecular size. Filtration is the common physical separation process that is used.

When the filtration method is used to quantify S_S, both S_S and the non-biodegradable soluble COD, S_I go through the filter and S_I has to be determined independently and subtracted from the total COD of the filtrate to get S_S. The major setback in the filtration method is that the method does not clearly separate between the readily and slowly biodegradable COD due to the presence of colloidal matter that may contribute to both these COD fractions. Of the filtration methods presented above, the true readily biodegradable fraction appears to pass through the 0.1 µm filters according to Torrijos et al. (1994). By including a pre-flocculation step in the filtration method using 0.45µm filters as proposed by Mamais et al. (1993) better results were obtained compared to investigations carried out without pre-flocculation. As a precaution Mbewe et al. (1995) recommended that any filtration-based methods proposed for quantifying S_S have to be extensively evaluated by comparing the results obtained using the proposed method with results obtained from the conventional bioassay tests.

The bioassay methods used to determine S_S rely on measuring the utilisation rate of dissolved oxygen or nitrate followed by a model-based interpretation of the observations. One of the most reliable bioassay tests for quantifying S_S requires effluent from a flow-through activated sludge system (Dold et al., 1986; Bortone et al., 1994) or sequencing batch reactor (Mamais et al., 1993; Torrijos et al., 1993). The bioassay tests require more sophisticated equipment and expertise than physical methods (Melcer, 2003). Furthermore, model based interpretation of results can only be done by skilled laboratory staff with a modelling background and may be more suitable for research purposes.

Even though some guidelines (Roeleveld and van Loosdrecht, 2002) assume that the heterotrophic biomass, X_{BH} in influent wastewater characterisation must be considered as negligible, the importance of quantifying this COD has been highlighted and improved COD-fractionation-procedures such as Choubert et al. (2013) recommend quantifying X_{BH} in the influent wastewater. Quantifying the X_{BH} in the influent wastewater can be done in principle, by microbiological techniques such as colony counts, but these techniques are too sophisticated and not widely available. Bioassay tests such as the batch tests proposed by Wentzel et al. (1995) appear to be a better option.

The method used to quantify the non-biodegradable soluble COD, S_I in influent wastewater, is based on the assumption that the influent S_I is equal to the S_I present in the final treated effluent if the generation of S_I by microbial action in the activated sludge system is considered to be negligible. The contribution of the microbially generated COD is considered minimal in systems that have sludge-ages greater than 3 days (Wentzel et al., 1995) hence the extended batch test described in Mbewe et al. (1995) can be used to quantify S_I. Another proposed approach is the measurement of filtered COD over at least 10 days in a batch test (Lesouef et al., 1992) which is however, a time-consuming task.

The slowly biodegradable COD, X_S can be estimated by difference from the total COD of the wastewater and the sum of the other COD fractions (S_S, X_{BH}, S_I, and X_I) if they have already been quantified. The procedure proposed by Sollfrank and Gujer (1991) is also useful. Kappelar and Gujer (1992) proposed another procedure for estimating X_S in which the aerobic batch test used for determining S_S is used for the estimation of X_S as well by ensuring that nitrification is inhibited during the test and the measured OUR is interpreted accordingly.

The non-biodegradable particulate COD fraction, X_I in influent wastewater can be estimated using calculations based on the kinetics of the activated sludge process and modelling (Orhon et al., 1996). Ekama et al. (1986) proposed a calculation of the concentration of X_I which involved comparing the measured mixed liquor volatile suspended solids (MLVSS) concentration with the value calculated from the kinetics of the activated sludge system. The IAWPRC Task Group (Henze et al., 1987) recommends a similar approach based on the comparison of observed and calculated sludge production (Orhon et al., 1996). For these procedures, the heterotrophic yield, Y_{ZH} the endogenous decay rate, b_H and the inert fraction of biomass must be correctly determined by independent experiments.

2.5.6.2 Guidelines for complete COD fractionation

The review of different sources clearly presented possible methods for quantifying each COD fractionation in the influent wastewater, but in practice, workable guidelines for the complete COD fractionation of wastewater are not clearly provided in the limited publications that discuss the subject and there is lack of standardisation of the methods (Choubert et al., 2013).

The Dutch Foundation for Applied Water Research (Dutch acronym: STOWA) has attempted to address this need for guidelines. STOWA made an inventory of the various methods of COD fractionation, evaluated them based on reproducibility and ease of use in practice before formulating and publishing guidelines in 1996. The guidelines have since been applied and modified over the years (Roeleveld and Van Loosdrecht, 2002).

In the STOWA Guidelines discussed in Roeleveld and Van Loosdrecht (2002), it is assumed that the biomass fraction in influent wastewater is negligible hence only four COD fractions (S_S, S_I, X_I and X_S) need to be determined. The assumption to consider active biomass as negligible is backed by the theory that the bacterial diversity in activated sludge is a result of selection by the environment rather than inoculation by the wastewater (Curtis et al., 1998).

The sum of the soluble COD fractions (S_S and S_I) is determined by physical-chemical methods. S_S is determined using filtration through 0.1 µm filters or filtration after flocculation as discussed in (Torrijos et al., 1994; Mamais et al., 1993; STOWA, 1997). The STOWA guidelines considered biological methods for the estimation of S_S as more complex than the recommended physical-chemical methods. Since both S_S and S_I pass through the filter when filtration methods are used, S_I is determined independently from the inert soluble COD in the treated effluent and then subtracted from the soluble COD ($S_S + S_I$).

In the STOWA guidelines a BOD-analysis test is used to determine the biodegradable fraction (S_S+X_S) of the total influent COD. This BOD-analysis test involves measuring the BOD as a function of time on a non-filtered sample of the wastewater with ally thiourea to inhibit nitrification, over a period of up 25 days. Once all the other COD fractions (S_S, S_I and X_S) are determined X_I is found by difference, between the total COD and the sum of (S_S, S_I and X_S).The order of tests recommended by the STOWA guidelines for complete COD fraction of influent wastewater is to determine S_I from the treated effluent, and then determine S_S by subtracting S_I from the COD of the filtrate containing (S_S and S_I). X_S is determined by subtracting the fraction from the biodegradable COD (S_S and X_S) obtained from the BOD-analysis test.

Finally X_I can be determined by difference; Total COD minus the sum of S_I, S_S and X_S. Determining X_I by difference means that all the errors and inaccuracies in the other tests will be reflected in the COD fraction X_I, which is an important factor in the accurate prediction of sludge production in the activated sludge model (Choubert et al., 2013). The STOWA guidelines have been used in approximately 100 Dutch WWTPs and acceptable wastewater characterisation has been reported (Roeleveld and Van Loosdrecht, 2002).

Lu et al. (2010) recommended an integrated COD fractionation procedure after investigation several methods. Four physical-chemical methods were investigated (Lu, 2006), followed by an investigation of the feasibility of determination of S_S and X_S simultaneously from respirometric measurements on raw wastewater before comparing two methods of determining heterotrophic biomass in wastewater. From the results obtained Lu et al. (2010) recommended that S_S, X_S and X_{BH} be determined using respirometry, while S_I is measured by a combination of respirometry, flocculation and filtration through 0.45 µm membrane filters. Finally X_I would be determined by difference between the total wastewater COD and the sum of S_S, S_I, X_S and X_{BH}.

The need for standardisation of the methods and guidelines for COD fractionation of wastewater is apparent. Standardised guidelines would make COD fractionation results and the modelling based on these results comparable. The variation in results of COD fractions obtained from using different methods even on the same wastewater type further confirms the need for uniform methods of COD fractionation.

Efforts directed at addressing this challenge of standardising COD fractionation methods are met by complications such as the fact that wastewater characteristics vary from one catchment to the next. Variations in domestic wastewater characteristics across a given community tend to be relatively small, although variation between communities can be more readily detected. Hence COD fractionation of domestic wastewater is bound to be affected relatively less, by the aforementioned variation. COD fractionation studies carried out on domestic wastewaters give consistent results per region (Wun, 2006). However COD fractionation of industrial wastewater is more complex.

Industrial wastewater may vary significantly in composition depending on the type of industry and materials processed in that catchment area. In addition to the complex composition of industrial effluent, the flow pattern of industrial effluent streams can be very different from that of domestic effluent since the former would be influenced by the nature of the operations within a factory, such as shifts, whether a batch or continuous process is used, and other factors. Hence the COD fractionation of influent wastewater with industrial effluent for purposes of modelling WWTPs is a task associated with uncertainties and ever changing scenarios on the grounds which currently do not have a permanent and clearly defined standard protocol of handling COD fractionation of the wastewater.

The following chapter of presents COD fractionation of wastewater containing industrial effluent through a combination of existing methods of individual COD fraction followed by a proposed alternative which was motivated by challenges of the first attempt to fractionate the total COD at Verulam WWTP where problematic industrial wastewater is treated.

3 COD FRACTIONATION BASED ON RESPIROMETRY AND FLOCCULATION-FILTRATION

This chapter presents the methods and results of the attempt to fractionate the COD of influent wastewater received at Verulam WWTP. The objective of this step in the study was to obtain complete and reliable COD fractionation of the influent wastewater for ASM1 modelling purposes. The results that were obtained are presented and discussed. The difficulties and challenges that were encountered during the COD fractionation motivated the new approach to COD fractionation which is presented in the following chapter.

3.1 Introduction

From the literature review presented in Chapter 2 it was shown that different methods have been developed for the COD fractionation of wastewater for ASM1. Physical-chemical and biological methods are available for COD fractionation. To obtain complete COD fractionation of wastewater, a combination of different methods cannot be avoided in most cases. The different methods offer different types and amounts of information related to modelling and the methods also require different input to yield reliable COD fractionation results. Thus a comparison of these methods, guided by published guidelines of how the individual methods of quantifying the different COD fractions can be combined, is an important step in a study aimed at obtaining complete and reliable COD fractionation of wastewater. A summary of the different methods of determining COD fractions in wastewater and their key attributes are presented in Table 3.1 as the initial step of describing how the most appropriate method for the study was selected. The most appropriate method was selected after comparing the methods available in the reviewed literature. The available equipment for carrying out the tests was also a factor in the selection of the method to use for COD fractionation. The guidelines of how the individual methods of quantifying the different COD fractions can be combined in order to obtain complete COD fractionation were also considered.

Table 3.1 Summary of methods of determining COD fractions in wastewater

Symbol	Type of method	Method	Comment	Additional information required	Assumptions	References
S_S	Bioassay	Continuous flow-through method	Costly and difficult to operate.			Ekama and Marais (1979), Mbewe et al., 1995, Sollfrank and Gujer et al., 1991.
		Aerobic batch test	Requires sludge acclimatisation. Sludge is generated in a laboratory-scale continuous flow-through reactors or obtained from a full scale plant.			Ekama et al., 1986, Henze,1991;1992.
		Anoxic batch test	Requires sludge acclimatisation. Sludge is generated in an laboratory-scale continuous flow-through reactors or obtained from a full scale plant.			Mbewe et al., 1995, Ekama et al.,1986, Henze,1991.
		Aerobic batch test without activated sludge	No pre-acclimatised sludge is required. Test can be used to quantify another COD fraction, X_{BH}.	Heterotrophic yield (Y_{ZH}), specific death rate of biomass (b_H) to be determined independently.		Kappelar and Gujer 1992, Wentzel et al.,1995.
	Physical	Filtration	Dold et al., (1986) evaluated 0.45 µm filters and observed over estimation of S_S. Lesouef et al., (1992) evaluated 7-8 µm glass fibre filters and observed over estimation of S_S. Torrijos et al., (1994) evaluated 0.1µm observed a true indication of S_S.	Non-biodegradable soluble COD (S_I) needs to be determined independently.	Final treated effluent filtrate COD is equal to the influent S_I because there is no substantial generation of S_I in sample.	Dold et al., 1986, Lesouef et al.,1992, Torrijos et al.,1994, Mbewe et al., 1995.
		Flocculation + Filtration through membrane filters	Mamais et al., 1993 investigated flocculation + filtration using 0.45 µm filters and reported better estimates than those obtained in filtration without flocculation. Pre-Flocculation + filtration through 0.45 µm appears to be a reliable method.	Non-biodegradable soluble COD (S_I) needs to be determined independently.	Final treated effluent filtrate COD is equal to the influent S_I because there is no substantial generation of S_I in sample.	Mamais et al., 1993, Wentzel et al.,1999, Mbewe,1999.

Symbol	Type of method	Method	Comment	Additional information required	Assumptions	References
S_I	Bioassay + Physical	Aerobic batch test + Filtration	Aeration is used to deplete the biodegradable organic matter in the wastewater. Flocculation + filtration is used to separate the particulates from the wastewater, the remaining filtrate contains S_I.		Final treated effluent filtrate COD is equal to the influent S_I because there is no substantial generation of S_I in sample	Wentzel et al., 1995.
X_{BH}	Bioassay test	Aerobic batch test without activated sludge	No pre-acclimatised activated sludge seed is required. Can be used to quantify another COD fraction, S_S.	Heterotrophic yield (Y_{ZH}) specific death rate of biomass (b_H) to be determined independently.		Kappelar and Gujer 1992, Wentzel et al., 1995.
X_S	Physical + bioassay	Centrifugation followed by aerobic batch test	Particulate X_S and X_I are separated from wastewater by centrifuging the wastewater and the resulting pellet is added to activated sludge system in a bioassay test to estimate X_S. Method underestimates X_S since some of the X_S remains suspended in supernatant.	Suspended X_S in the supernatant must be determined in an independent experiment		Sollfrank and Gujer, 1991.
	Bioassay	Aerobic batch test	Requires wastewater and activated sludge. Over estimation of X_S since the test measures the OUR due to the utilisation of X_S in the wastewater and X_S generated from death or lysis of heterotrophic active biomass in the bioreactor.			Kappeler and Gujer 1992.

Symbol	Type of method	Method	Comment	Additional information required	Assumptions	References
X_I	Physical	Monitoring X_I in sludge wastage and final effluent from an activated sludge system.	Analysis of a lab scale completely mixed activated sludge unit operated at steady-state with sludge age of longer than 5 days.			Orhon et al., 1996.
	Modelling	Measuring and calculating parameters related to sludge production.	Comparing measured value of mixed liquor VSS concentration compared to the value calculated from the kinetics of the activated sludge system. Or comparing of observed and calculated sludge productions	Heterotrophic yield (Y_{ZH}) specific death rate of biomass (b_H) and the inert fraction of biomass must be correctly determined by independent experiments.		Ekama et al.,1996, Henze et al.,1987.
	Modelling	Simulation.	Fitting model predicted mixed liquor volatile suspended solids (VSS) concentrations to measured values by adjusted the value of X_I in the model.			Melcer, 2003.

The bioassay test presented in Wentzel et al. (1995) was selected and used to determine S_S and X_{BH} in the influent wastewater. The non-biodegradable soluble COD S_I was determined by a flocculation–filtration procedure recommended by Mbewe (1999) and outlined in Wentzel et al. (1999). To determine the inert particulate COD fraction X_I and the slowly biodegradable fraction X_S, it was proposed to model the experimental setup of the bioassay test used to determine S_S and X_{BH} using the modified UCT model (Dold et al., 1991) to model the biological process taking place inside the bioreactor used in the bioassay test. The model output (OUR) would then be compared to the measured OUR (respirogram) before tuning X_I and X_S to fit the model-predicted respirogram to the one obtained from experiment, thus estimating X_I and X_S simultaneously.

3.2 Use of respirometry for COD fractionation

Bioassay methods derive information from the observation of the biological system of concern, in this case a batch reactor containing wastewater or activated sludge. In bioassay methods of wastewater characterisation, respirometry has found wide application as evident in the work of several researchers (Ekama et al., 1987; Henze, 1992; Sollfrank and Gujer, 1991; Wentzel et al., 1995; Vanrolleghem et al., 1999; Sperandio and Paul, 2000).

To apply respirometry techniques, well defined experimental conditions are a prerequisite before measurement and interpretation of the biological oxygen utilisation rate (Copp, 2002). The appropriateness of respirometry in influent wastewater characterisation stems from the fact that oxygen consumption is directly associated with the utilisation of substrate by biomass. Respirometry can provide a direct indication of the specific activity of certain fractions of the biomass during processes such as utilisation of organic fractions present in wastewater. The COD fractions can then be estimated from the observed oxygen utilisation rates.

In respirometric experiments where the concentration of dissolved oxygen (DO) is measured in liquid phase, the respiration rate is calculated by making a general mass balance for oxygen in the liquid phase (Gernaey et al., 2001). The mass balance can be presented as equation 3.1

$$\frac{dS_O}{dt} = \frac{Q_{in}}{V} S_{O,in} - \frac{Q_{out}}{V} S_O + K_L a\left(S_O^0 - S_O\right) - r_O \qquad [3.1]$$

Where:

S_0 DO concentration in liquid phase

S_0^0 Saturation DO concentration in the liquid phase

$S_{O,in}$ DO concentration in the liquid phase entering the system

Q_{in} Flow rate of the liquid entering the system

Q_{out} Flow rate of the liquid leaving the system

$K_L a$ Oxygen mass transfer system based on liquid volume

r_O Respiration rate of the biomass in the liquid

V Volume of liquid phase

The first and the second terms in equation 3.1 represent advective flow of dissolved oxygen in the input and output streams of the bioreactor. The third term describes the transfer of oxygen from the gas phase to the liquid phase. The last term contains the respiration rate to be derived from the mass balance.

Depending on the design of the respirometer, the transport and aeration terms may not be required. For a static gas - static liquid respirometer the decline of the dissolved oxygen concentration with time in a closed vessel is monitored using a dissolved oxygen probe. In this sort of respirometer the mass balance equation becomes equation 3.2

$$\frac{dS_O}{dt} = -r_O \qquad [3.2]$$

In this case to obtain the respiration rate only the differential rate has to be determined. Measuring the decrease of DO due to respiration as a function of time will give an approximation of the respiration rate. If this principle is applied the DO may become exhausted after some time and re-aeration may be needed for continued measurement of r_O. For the above equation (equation 3.2) to apply, a completely closed vessel with no head space is required to ensure that aeration of the contents of the respirometer through surface aeration does not happen.

If an open vessel is used, surface aeration may influence the results of the experiment. In such a case equation 3.3 will apply for correct data interpretation.

$$\frac{dS_O}{dt} = K_L a\left(S_O^0 - S_O\right) - r_O \qquad [3.3]$$

The effects of surface aeration may be dealt with in the following ways, the choice depends on the required accuracy of the experimental results:

- the contribution of surface aeration can be neglected
- the liquid-air interface of the open vessel may be covered by small plastic balls which float on the liquid (Wentzel et al., 1995)
- use of a vessel with a narrow neck with the diameter equal to the diameter of the dissolved oxygen probe (Gernaey et al., 2001)

The respiration rate of biomass r_O can be determined by measuring the oxygen uptake rate (OUR) in a bioreactor. The OUR test essentially consists of adding a sample to a bioreactor placing the DO probe into the reactor and monitoring the decline in DO over time. The relationship between the decrease in oxygen concentration is normally found to be linear as shown in Figure 3.1. The slope of the linear portion of the DO profile with time is the OUR and has the units $mgO_2/L.h$.

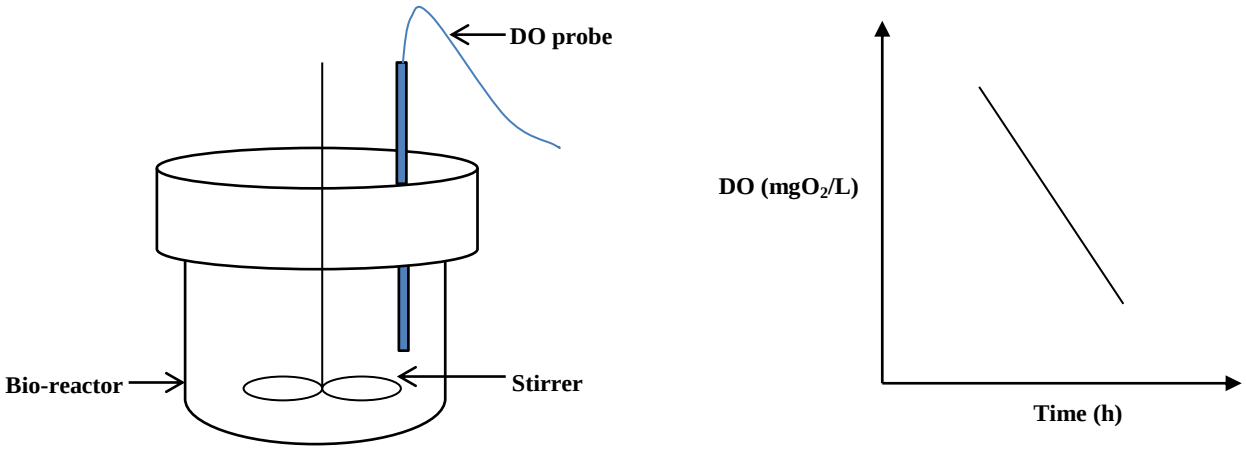

Figure 3.1 Illustration of the principle of OUR measurements

It is possible to have continuous measurements of the OUR in the bioreactor using a well-designed respirometer. The measured OUR data is then processed to produce a respirogram which has to be interpreted to determine the COD fractions present in the sample.

3.3 COD fractionation of influent wastewater at Verulam WWTP

Verulam WWTP is located in the Verulam Area which lies approximately 30 km north of the Durban Metropolitan City. The estimated population of Verulam is over 63 000 people (IYER, 2010). The town contains densely populated residential and industrial areas. Large farming areas, several built-up townships, and rural townships can be found in the outskirts of Verulam. Verulam WWTP has a hydraulic capacity of 12 ML/day. The WWTP is located approximately 10 km up the Mdloti River and serves all the households and factories in the Verulam Area. There are 6 major factories which discharge industrial wastewater into Verulam WWTP. The 6 factories operating within the Verulam WWTP catchment run different manufacturing processes resulting in a complex mixture of industrial effluent. The list of factories and their core business is presented in Table 3.2.

Table 3.2 List of factories and their core business in the Verulam WWTP Catchment area

Factory	Core business
JMV	Textiles: JMV are manufacturers, prints and dyes knitted fabrics.
Nampak	Manufactures paper, tissue paper and board packaging
Frimax Foods	Food: Produces chips, snacks and confectionary
Packo	Food: Produces pickles, sauces, spices, custard jellies and house hold chemicals (citric acid, borax, bicarbonate of soda, cream of tartar, tartaric acid, Epsom salts)
Colgate Palmolive	Manufactures detergents, tooth paste and soap
Budget soap	Manufactures soap and detergents

The list of major factories includes a textile factory, soap and tooth paste factory, soap and detergent factory, two food factories and a paper manufacturing factory. The factories listed above contribute industrial effluent of varying volumes and composition to the combined influent wastewater that flows into Verulam WWTP. The location of the factories relative to the WWTP is shown in Figure 3.2.

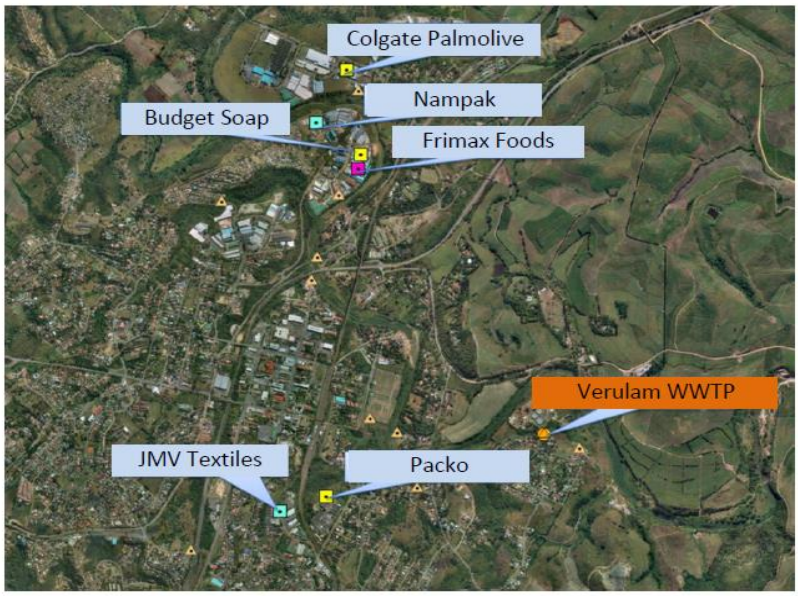

Figure 3.2 Location of factories relative to the WWTP in the Verulam WWTP catchment

The rest of the wastewater received at the head of works at the WWTP is domestic effluent from households in the catchment area and surface runoff during rainy days. The sewer reticulation relies on pipes whose diameters ranges from 150 to 450 mm. The sewage within the Verulam catchment area is pumped or gravitated to the 450 mm diameter trunk-line which flows to the Verulam WWTP (IYER, 2010).

The influent wastewater volume received at the Verulam WWTP consists of approximately 20 % industrial effluent and 80 % domestic effluent. The presence of industrial effluent in the catchment causes the wastewater received at the inlet of the WWTP to behave significantly different from purely domestic effluent during treatment. The flow patterns of the influent show diurnal and seasonal variations which can be explained by the daily behavioural pattern of the population living within the catchment and the rainfall pattern in the catchment. The main source of extraneous flow within the Verulam catchment is the stormwater flowing into the WWTP on rainy days.

3.3.1 Wastewater sampling

The aim of the wastewater sampling was to obtain a representative sample that would provide reliable information about the COD fractions present in the influent wastewater received at the WWTP. Collecting at the right point and preserving the integrity of the samples collected is crucial for reliable test results. Since the volume and strength characteristics of the wastewater vary throughout the day, 24 hour flow weighted samples were collected from the inlet of the WWTP. Hourly samples of influent were drawn from the inlet of the WWTP using a refrigerated ISCO 3700 auto-sampler for 24 hours to make up a flow-weighted composite sample. The samples were kept in ice and transported to the laboratory for analysis.

3.3.2 Equipment used

Several types of respirometers are available on the market and they offer different levels of sophistication. In this study the bioassay method that was adopted required OUR to be measured continuously in the liquid phase. The variation in oxygen concentration was followed by a dissolved oxygen sensor that consists of an electrode in an internal electrolyte solution (potassium iodide), separated from the wastewater by a semi permeable membrane. Dissolved oxygen molecules diffuse from the liquid (wastewater) through the membrane into the internal solution. The dissolved oxygen molecules are reduced on the cathode generating a current which is proportional to the diffusion rate of oxygen through the membrane, which in turn is proportional to the DO concentration in the solution. The relationship between electrical current and DO concentration is established by calibrating the DO sensor. A reliable respiration rate measurement is possible only if the DO sensor is correctly calibrated in the liquid and if a number of environmental variables, such as temperature and pressure, are accounted for. DO sensor also have a response time that must be accounted for in the respirometric setup (Vanrolleghem, 2002). The major components of the experimental setup the respirometric experiment include the biological reactor, air supply, OUR-meter and a computer. The layout of the experiment is shown in Figure 3.3.

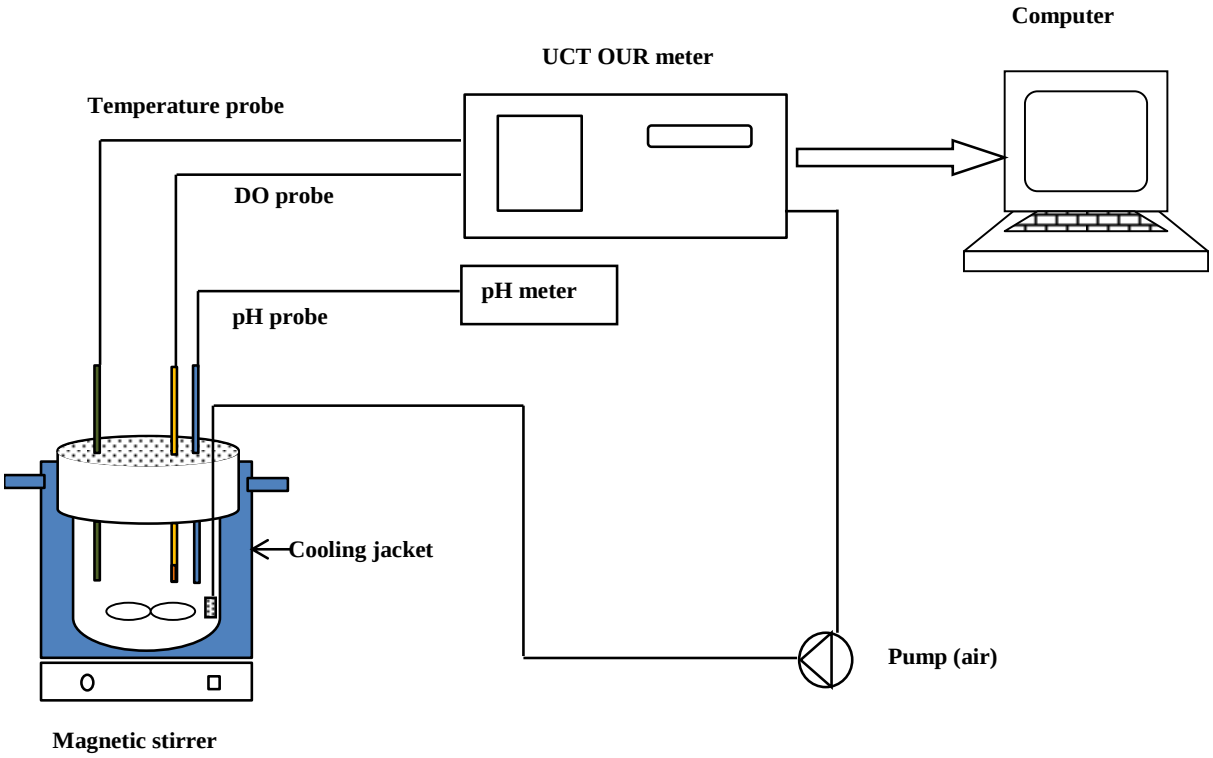

Figure 3.3 Schematic picture of OUR experimental set-up

3.3.3 Procedure

In order to determine the amount of readily biodegradable fraction S_S and heterotrophic active biomass X_{BH}, the batch test procedure outlined in Wentzel et al. (1995) was followed. 1.5 L of wastewater collected from WWTP was poured into a bioreactor. The stirrer was switched on before an aliquot of the uniformly mixed wastewater was drawn to determine the initial total COD. The total COD of wastewater was determined using the standard test presented in Standards Method (1995). A nitrification inhibitor, allyl thiourea (ATU) was added to the contents of the bioreactor. The bioreactor used had a cooling jacket which kept the contents of the reactor at 20 ± 1°C during the course of the experiment. Agitation was provided by a magnetic stirrer and the contents of the beaker were assumed to be completely mixed. The sample was aerated intermittently using an air pump and an aeration stone. The pH in the respirometer was maintained at 7.0 ± 0.2 by addition of hydrochloric acid and sodium hydroxide. The dissolved oxygen concentration (DO) was measured with an oxygen sensor (YSI DO probe) connected to the UCT OUR meter. The oxygen uptake rate (OUR) was calculated and stored inside the UCT OUR meter which also controlled the aeration in the bioreactor. The aeration intervals were set at 4.5 to 6 mgO_2/L. Surface aeration of the contents of the bioreactor was prevented by introducing a predetermined nitrogen and air mixture on the surface of the contents of the bioreactor. A simplified version of the UCT Model (Dold et al., 1991) was used to interpret the respirogram.

The inert soluble substrate, S_I was determined by a flocculation-filtration procedure on the wastewater collected at the end of the batch respirometric test (Wentzel et al., 1999). After running the batch test

for 24 h or more, the only soluble COD remaining should be non-biodegradable soluble COD (Wentzel et al., 1999). Therefore, at the end of the batch test, 1 L of the bio reactor contents was drawn as sample, flocculated and filtered using a 0.45 μm filter. The COD of the filtrate gives the inert soluble fraction of the total COD of the wastewater.

To determine the inert particulate COD fraction X_I and slowly biodegradable fraction X_S a model of the biological processes taking place in the bioreactor was proposed. The modified UCT model (Dold et al., 1991) was used to model the biological processes taking place inside the bioreactor during the experiment. The model output (OUR) was then compared to the measured OUR (respirogram) before X_I and X_S were tuned to fit the model predicted respirogram to the one obtained from experiment. This procedure is based on the following calculation: For a set of parameters and initial conditions (θ), the mathematical model is solved numerically using the most appropriate method such as a fourth-order Runge-Kutta routine. The error or objective function (E) defined and calculated by a least squares method, comparing the model-simulated (OUR_{mod}) and experimental OUR (OUR_{exp}) respirogram:

$$E(\theta) = \sum_{i=1}^{N} (OUR_{\text{mod}}(\theta, t_i) - OUR_{\text{exp}}(t_i))^2$$

An optimisation procedure is then used to minimize the above function and X_I and X_S are then identified simultaneously. In such a procedure the reliability of the results are related to the identifiability of model parameters. Hence it is important to study the identifiability of the model parameters before using the model for parameters estimation, in this case, the estimation of X_I and X_S.

In an identification study the aim is to establish whether a unique combination of parameters can be obtained when the model predicted data are fitted to experimental data assuming that a certain number of state variables are available for measurements. Identifiability can be structural or practical. Structural identifiability addresses the question of whether it is possible to obtain unique parameter values assuming perfect noise free data while practical identifiability takes into account the noise corrupted data. Consequently parameters may be practically unidentifiable although they are structurally identifiable (Petersen et al., 2003).

Testing for structural identifiability in linear systems is well understood and methods are available and documented while the structural identifiability of non-linear models such as Monod models is more complex to assess and fewer methods are available (Petersen et al., 2003). Hence the commonly used approach to testing for structural identifiability in non-linear models is to work out and establish conditions that may allow conclusions on structural identifiability to be drawn. This approach includes, transformation of the non-linear model into a linear model (Walter, 1982); Ljung et al., 1994), using the series expansion method (Walter, 1982; Phjanpalo et al., 1978; Walter et al., 1995; Petersen, 2000),

using the similarity transformation approach or local state isomorphism (Chappell et al., 1990; Walter et al., 1995; Vajda et al 1989; Chappell et al., 1992) and study of the observability properties of the nonlinear systems (Casti, 1985).

3.3.4 Interpretation of the aerobic batch test results for X_{BH} and S_S

The respirograms obtained from the aerobic batch test can be interpreted in terms of the simplified UCT model (Dold et al., 1980; 1991 or the IAWQ model (Henze et al., 1987). In this study the simplified UCT model was used to interpret the OUR results obtained from the aerobic batch test. The simplification of the UCT model for use in the interpretation of results obtained in the aerobic batch test is based on the specific conditions that prevail in the bioreactor (Wentzel et al., 1995). The conditions in the bioreactor can be summarised as follows;

- The environment is aerobic, de-nitrification processes need not be included in the model
- No nitrification processes need to be included in the model since there is no nitrification
- There is excess ammonia present hence nitrate as a N-source for growth need not be considered and the transformation from organic to ammonia nitrogen need not be included

Applying the following conditions simplifies the original UCT model to that presented in Table 3.4 in a format known as the Petersen matrix. The Petersen matrix presents processes taking place in the bioreactor, the corresponding process rates and the components (or the compounds) that are participating in the processes. The components present in the simplified UCT model are presented and described in Table 3.3.

Table 3.3 Model components of the Simplified UCT model

Symbol	Component
Z_{BH}	Heterotrophic active biomass
Z_E	Endogenous mass
Z_I	Inert mass
S_{ads}	Adsorbed slowly biodegradable substrate
S_{enm}	Enmeshed slowly biodegradable substrate
S_{bs}	Readily biodegradable soluble substrate
S_{us}	Unbiodegradable soluble COD
O	Oxygen

Four processes are responsible for the transformation of the identified components. The processes are listed in the first column of the Petersen matrix presented in Table 3.4. The corresponding process rates appear on the last column of the Petersen matrix. The elements within the matrix consist of the stoichiometric coefficients that set out the mass-relationships between the components in the individual

processes. For example the aerobic growth of heterotrophic biomass Z_{BH} on readily biodegradable soluble substrate S_{bs} produces more biomass (+1) but it occurs at the expense of S_{bs} ($-1/Y_{ZH}$); oxygen is also utilised in this metabolic process [$-(1-Y_{ZH})/Y_{ZH}$]. The negative and positive signs are used to highlight consumption and production of components respectively. Consistent units are used across the matrix. All organic constituents are expressed as equivalent amounts of chemical oxygen demand COD, likewise oxygen demand. The stoichiometry constants are defined in the lower left corner of the matrix while the kinetic constants are defined on the lower right hand corner.

Table 3.4 Simplified UCT model (Dold et al., 1991) for the conditions present in the aerobic batch test

i COMPOUND → / **↓ j PROCESS**	**Z_{BH}** Active heterotrophic biomass (M COD. L^{-3})	**Z_E** Endogenous mass (M COD. L^{-3})	**Z_I** Inert mass (M COD. L^{-3})	**S_{ads}** Adsorbed slowly biodegradable substrate (M COD. L^{-3})	**S_{enm}** Enmeshed slowly biodegradable substrate (M COD. L^{-3})	**S_{bs}** Readily biodegradable soluble substrate (M COD. L^{-3})	**S_{us}** Un-biodegradable soluble substrate (M COD. L^{-3})	**O** Oxygen (M COD. L^{-3})	**PROCESS RATE, ρ_j**
Aerobic growth of Z_{BH} on S_{bs}	1					$\frac{-1}{Y_{ZH}}$		$-\frac{(1-Y_{ZH})}{Y_{ZH}}$	$\mu_H \cdot \frac{S_{bS}}{K_{SH}+Sb_S} \cdot Z_{BH}$
Aerobic growth of Z_{BH} on S_{ads}	1			$\frac{-1}{Y_{ZH}}$				$-\frac{(1-Y_{ZH})}{Y_{ZH}}$	$K_{MP} \cdot \frac{S_{ads}/Z_{BH}}{K_{SP}+S_{ads}/Z_{BH}} \cdot Z_{BH}$
Death of Z_{BH}	-1	f_E			1- f_E				$b_H \cdot Z_{BH}$
Adsorption of S_{enm}									$K_A S_{enm}\ Z_{BH}(f_{MA}- S_{ads}/ Z_{BH})$
Stoichiometric constants Y_{ZH} – Heterotrophic yield f_E –Endogenous residue f_{MA}- Max. ratio S_{ads}/ Z_{BH}									Kinetic constants μ_H -heterotrophic max. specific growth rate on S_{bs} K_{SH} –heterotrophic half saturation on S_{bs} K_{SP} -heterotrophic half saturation on S_{ads} b_H -heterotrophic specific death rate K_A -S_{enm} specific adsorption rate

The matrix allows quick and easy assessment of the fate of each component in the model and makes it easy to prepare mass balance equations and perform a continuity check. The basic equation for a mass balance within a defined system boundary may be expressed as follows:

Input – Output + Reaction = Accumulation

The input and output terms are transport terms and depend upon the physical characteristics of the system being modelled. The reaction term r_i for each component can be obtained from the matrix by moving down the column of the particular component and summing up the product of the stoichiometric coefficients and the process rate expressions for the component being considered. For example if Z_{BH} is considered;

$$r_{Z_{BH}} = \hat{\mu}_H \cdot \frac{S_{bs}}{K_{SH} + S_{bs}} \cdot Z_{BH} + K_{MP} \cdot \frac{S_{ads}/Z_{BH}}{K_{SP} + S_{ads}/Z_{BH}} \cdot Z_{BH} - b_H \cdot Z_{BH}$$

Continuity can be checked by moving across the matrix provided consistent units are used. The sum of the stoichiometric coefficients must be zero. Using the process; Aerobic growth of Z_{BH} on S_{ads} as an example the matrix shows that biomass Z_{BH} is generated (+1) at the expense of S_{ads} ($-1/Y_{ZH}$) and oxygen [$(1-Y_{ZH})/Y_{ZH}$]. The sum of these three stoichiometric coefficients is equal to zero because the substrate COD lost due to the growth of biomass into new cells must be equal to the oxygen utilised during the synthesis of the cells.

The typical OUR profile that is obtained from the aerobic batch test is shown in Figure 3.4. An increase in the OUR is observed from the start of the test, when the amount of readily biodegradable COD S_S present is not limiting the growth of biomass. This is followed by a sharp decrease in OUR, when the readily biodegradable COD is depleted. After this period the readily biodegradable COD being utilised is only available due to the hydrolysis of slowly biodegradable COD X_S. The OUR measured during the period of non-limited growth is due to the utilisation of both S_S and X_S.

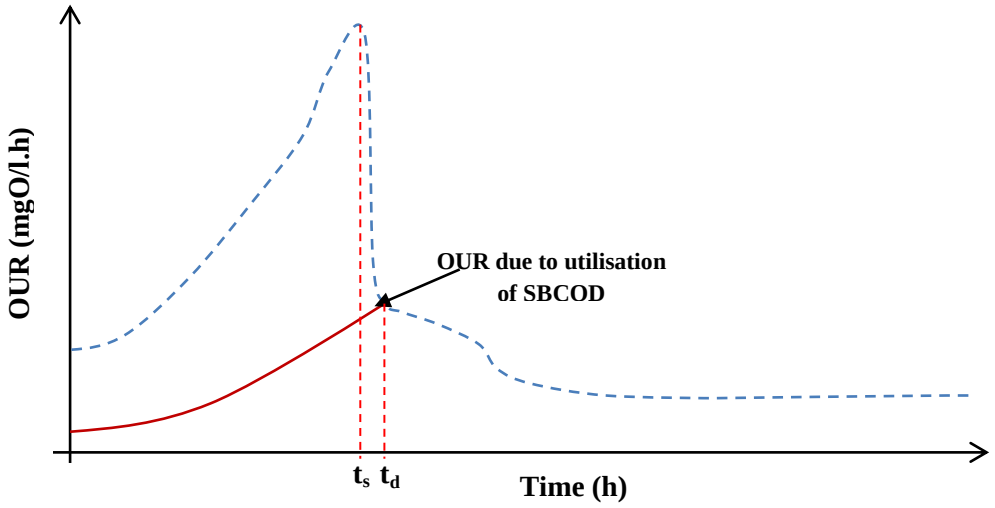

Figure 3.4 Typical OUR profile obtained from the aerobic batch test and the theoretical OUR for utilisation of slowly biodegradable COD

From this respirogram and the simplified UCT model the following information can be obtained

- The heterotrophic active biomass Z_{BH} present in the water
- The readily biodegradable COD S_S
- The wastewater heterotrophic maximum specific growth rate on RBCOD $\hat{\mu}_H$
- The wastewater heterotrophic maximum specific growth rate on SBCOD K_{MP}
- COD recovery

The heterotrophic biomass specific death rate, b_H and the heterotroph yield, Y_{ZH} need to be determined from separate experiments or values may be assumed from literature sources of similar experimental

work. In this study the value of b_H and Y_{ZH} were taken as 0.62/d and 0.66 mgCOD/mgCOD. The source of these values was Wentzel et al. (1995). The theory for obtaining Z_{BH}, S_S, $\hat{\mu}_H$ and K_{MP} is presented in Appendix B.

The acceptability of the results obtained from the batch test is evaluated by checking the COD balance in the test. To perform this evaluation the COD of the wastewater in the bioreactor is measured before and after the experiment and the area under the OUR curve is determined. The COD balance is then calculated as shown in equation 3.4.

$$\%\ COD\,recovery \frac{COD_{t=T} + \int_{t=0}^{t=T} OUR \cdot dt}{COD_{t=0}} \cdot 100 \qquad [3.4]$$

Where: t = Time (h)

T = Time used at the end of the experiment (h)

$COD_{t=T}$ = Total COD concentration at the end of experiment (mg COD/L)

$COD_{t=0}$ = Total COD concentration at the beginning of experiment (mg COD/L)

A COD recovery in the range of 95 to 105 % indicates that the OUR measurements are reliable (Wentzel et al., 1995).

3.4 Results of the aerobic batch test on wastewater from Verulam WWTP

Some of the OUR profiles obtained from the aerobic batch test on composite samples of wastewater from Verulam WWTP are presented in this section. An OUR profile from an aerobic batch test done on raw domestic effluent with no industrial effluent from Shallcross WWTP is shown on Figure 3.5 for comparison with OUR profiles obtained from the aerobic batch test on composite samples of wastewater from Verulam WWTP (Figure 3.6 to Figure 3.10). The OUR profile for domestic effluent shows an increase of the OUR at the start of the test when the amount of readily biodegradable substrate present is not limiting the biomass-growth. This is followed by a sharp decrease in OUR, when the readily biodegradable substrate is depleted. After this period the readily biodegradable substrate is only available due to the hydrolysis of slowly biodegradable substrate. This behaviour similar to OUR profiles discussed in Wentzel et al. (1995) and to results obtained from the batch test on wastewater samples from Borcherds Quarry and Mitchells Plain WWTPs in Cape Town, South Africa tested by Wentzel et al. (1999). However the OUR results obtained from the composite samples collected from Verulam WWTP exhibited different profiles from Figure 3.5.

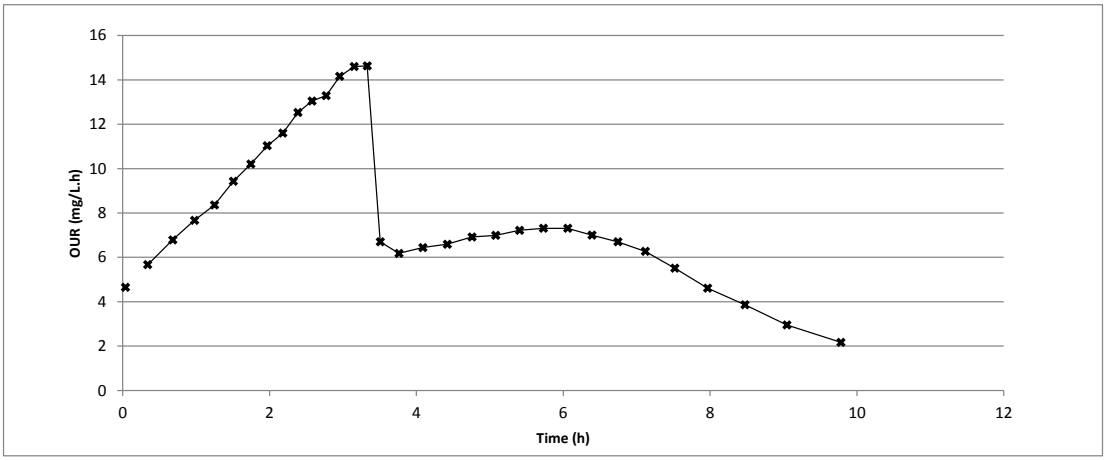

Figure 3.5 OUR response with time from the batch test on raw domestic effluent from Shallcross WWTP (24 July 2012)

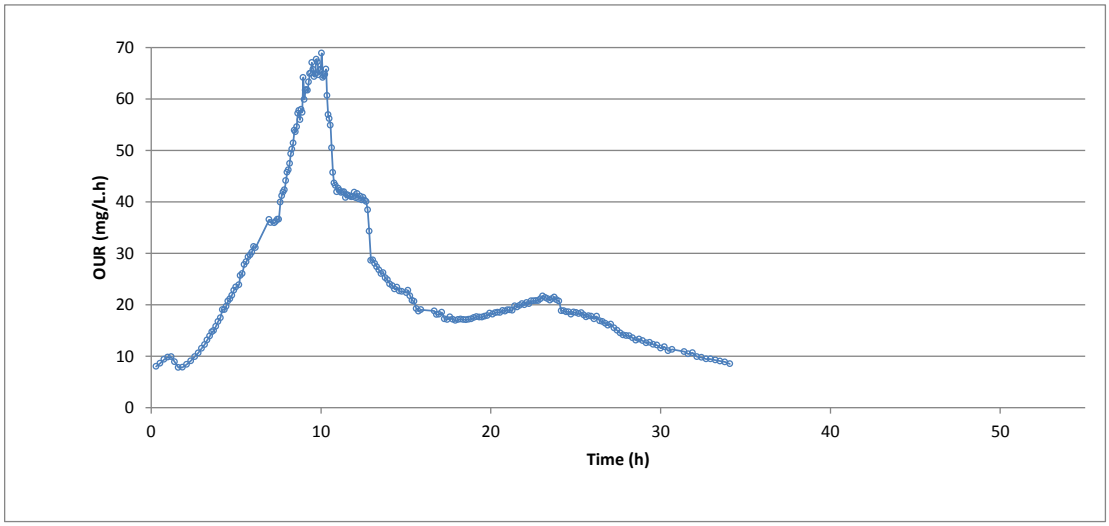

Figure 3.6 OUR response with time from the batch test on industrial effluent from Verulam WWTP (19 June 2012)

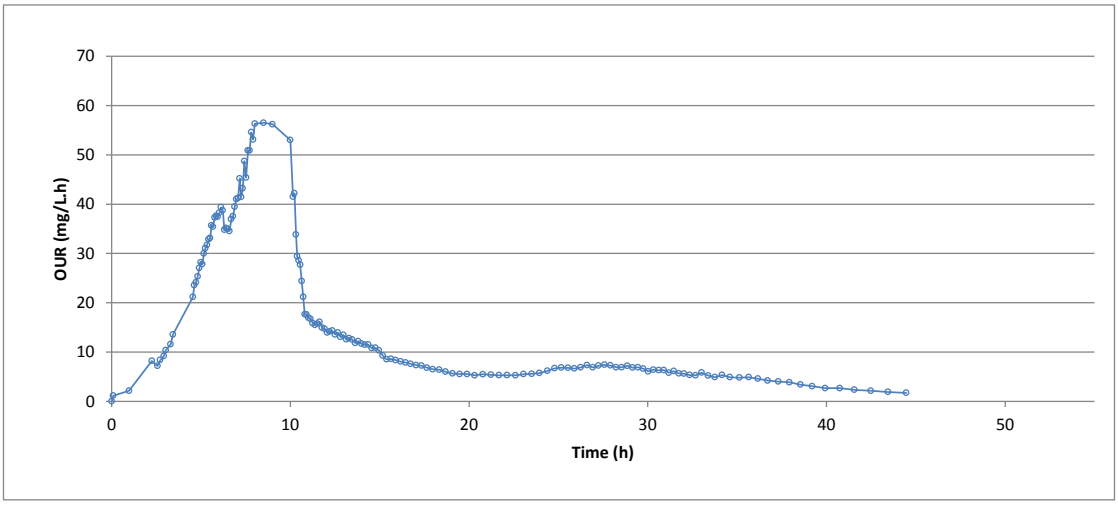

Figure 3.7 OUR response with time from the batch test on industrial effluent from Verulam WWTP (28 June 2012)

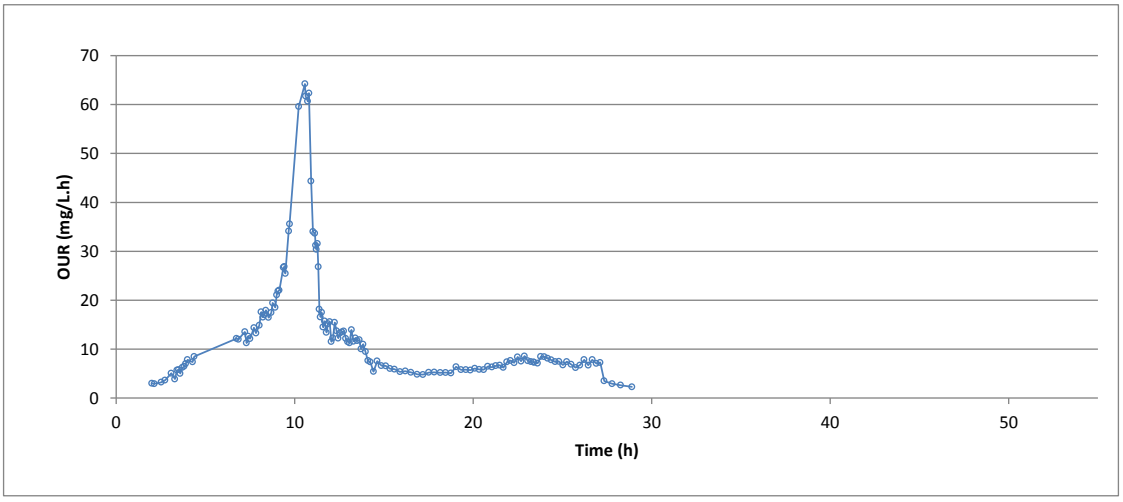

Figure 3.8 OUR response with time from the batch test on industrial effluent from Verulam WWTP (20 July 2012)

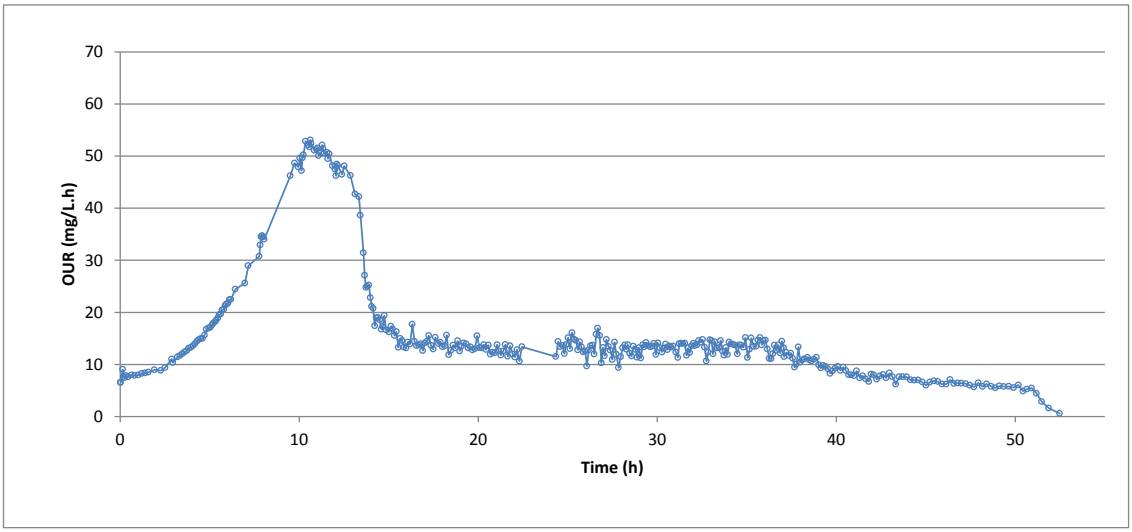

Figure 3.9 OUR response with time from the batch test on industrial effluent from Verulam WWTP (26 July 2012)

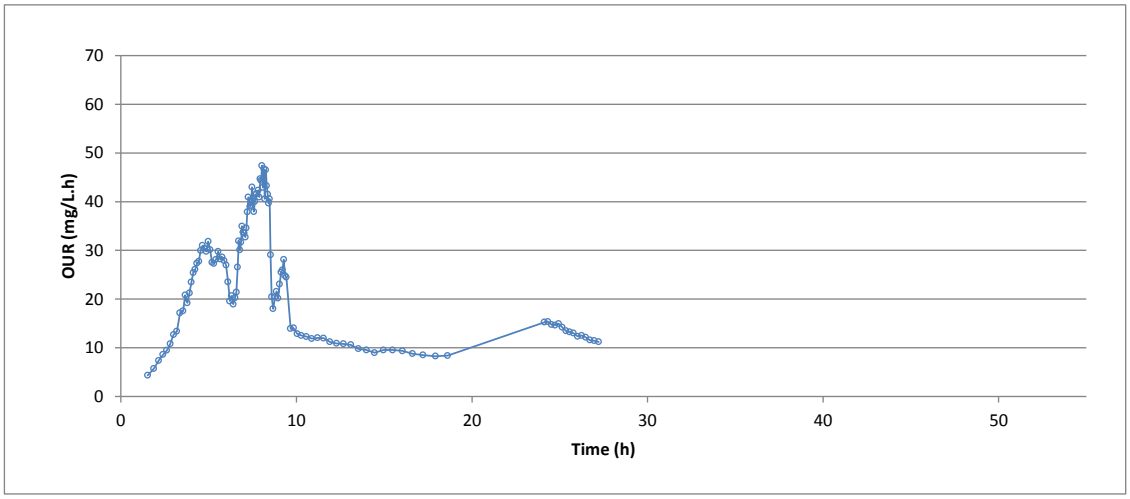

Figure 3.10 OUR response with time from the batch test on industrial effluent from Verulam WWTP (27 July 2012)

The significant variations observed in the OUR profiles for the combined wastewater collected from Verulam WWTP when compared with OUR profiles from purely domestic effluent from Shallcross WWTP were as follows:

- While Figure 3.6 to Figure 3.10 show the expected increase in OUR at the beginning of the test until the OUR reaches a maximum value when the readily biodegradable substrate runs out, it takes a longer time to utilise the readily biodegradable substrate in wastewater from Verulam WWTP (up to 10 h) as compared to domestic effluent from Shallcross WWTP, which takes about 4 h. This might be due to the higher average total COD of the industrial effluent (1 600 mg/L) than domestic effluent (715 mg/L), and a slower rate of utilising the readily biodegradable substrate and other components present in wastewater from Verulam WWTP.
- After the readily biodegradable substrate runs out in in the wastewater from Verulam WWTP, the expected precipitous drop seen in Figure 3.5 (domestic effluent) does not occur. Instead a slower decline of the OUR is observed. The profile of the decline in OUR has a 'shoulder' before the OUR gets to the endogenous phase as seen in Figure 3.7. The cause for this 'shoulder' cannot be explained with certainty at this point. A possible explanation can be the presence of a slowly biodegradable substrate that undergoes hydrolysis before it is utilised. The delay, from the start of the test, in utilising this suspected substrate might be the time it takes the biomass to acclimatise and be able to utilise this suspected substrate. Further exploration of this idea is being considered.
- The area under the OUR profile between the start of the test and the beginning of the endogenous phase for the wastewater from Verulam WWTP is much larger than that for the domestic effluent. This corresponds to the average initial total COD concentrations of the two different wastewaters. The average total COD of the domestic effluent was lower (715 mg/L), while it was higher (1 600 mg/L) for the wastewater from Verulam WWTP.

The absence of a clearly defined precipitous drop of the OUR after utilising the available readily biodegradable substrate for wastewater collected from Verulam WWTP makes it difficult to interpret the OUR results using the modified UCT model. The modified UCT model does not take into account the degradation of substrate during the time period between just after the precipitous drop and before the start of the endogenous phase, hence reliable COD fractionation for the industrial effluent from Verulam WWTP cannot be obtained using the current modified UCT model at this point. Even though the above mentioned challenge was observed an attempt to interpret the OUR results from Verulam WWTP was done and the results obtained are summarised Table 3.5.

Table 3.5 COD fractionation obtained from interpreting OUR results using the modified UCT model

Exp	*C_T	X_{BH}		S_S		S_I		COD Recovery
	(mg/L)	(mg/L)	% of C_T	(mg/L)	% of C_T	(mg/L)	% of C_T	(%)
1	1 954	25	1.3	569	29.1	422	21.6	64.3
2	2 511	43	1.7	215	8.6	1 722	68.6	108.4
3	1 204	52	4.3	1 087	90.3	842	69.9	137.5
4	804	12	1.5	163	20.3	52	6.5	107.7
5	1 581	22	1.4	301	19.0	389	24.6	88.7
6	1 748	46	2.6	187	10.7	101	5.8	71.6
7	1 333	43	3.2	194	14.5	105	7.8	70.9
8	2 128	43	2.0	531	25.0	101	4.8	41.7
9	1 089	67	6.1	437	40.2	53	4.8	49.7

*C_T is the Total COD of the composite sample, Exp means Experiment

The estimation of heterotrophic biomass, X_{BH} from the OUR results appears to be reasonable and almost consistent when the results from different experiments are compared. The estimated fraction of X_{BH} is obtained by interpreting the first part of the respirogram which displays exponential increase of the OUR. Since the respirograms obtained for Verulam WWTP are similar to the expected profile the results obtained for X_{BH} might be reflecting the true composition of heterotrophic biomass in the composite sample. However, the results for S_S and S_I show significant variation and poor overall COD recovery is obtained at the end of the test.

A similar batch test carried out by Wentzel et al. (1999) on municipal wastewater samples collected from Borcherds Quarry and Mitchells Plain WWTPs in Cape Town, South Africa was used to estimate COD fractions present in the wastewater. The mean percentage recoveries obtained from the batch tests for samples from Borcherds Quarry and Mitchells Plain WWTPs were 96 % and 99 % with standard errors of 0.76 % and 0.82 % respectively, confirming the reliability of the results obtained. The ranges of the average percentages of X_{BH} was 7 - 16 %, S_S was 11 – 23 % and S_I was 8 – 11 % for Borcherds Quarry WWTP, while for Mitchells Plain WWTP, the ranges of the average percentage of X_{BH} was 3-12 %, S_S was 17 – 26 % and S_I was 7 - 9% .

The ranges of the estimates obtained for the wastewater samples collected at Verulam WWTP were 1.3-6.1% for X_{BH}, 8.6 - 90.3 % for S_S and 4.8 - 69.9%. With percentage COD recoveries for the test falling out of the required range for the tests carried out in this study, it has little value to compare the results for Verulam WWTP with other studies such as Wentzel et al. (1999). However the comparison done here shows the significant difference between the results, further highlighting that the batch test did not work well on the Verulam wastewater samples.

The poor COD recovery was investigated during the aerobic batch test. Aliquots of wastewater were drawn from the bioreactor during the test and analysed for total COD. The area under the observed OUR profile was then used to estimate the COD at the times when the samples were drawn. The estimated COD values were then compared with those obtained from the test. The cumulative area under the OUR profile that were used to determine the COD of the samples collected (Sample 1, 2 and 3) are shown in Figure 3.11 and Figure 3.12. The results are compared in Table 3.6.

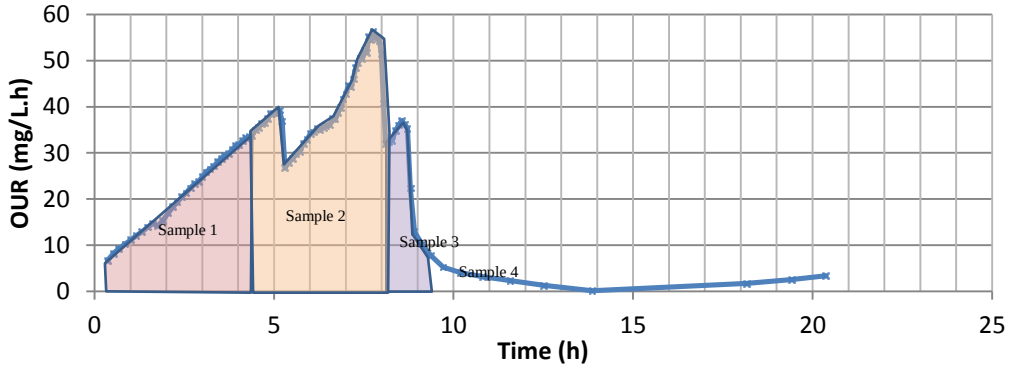

Figure 3.11 Respirogram for wastewater collected on 13 August 2012 (Exp. 1)

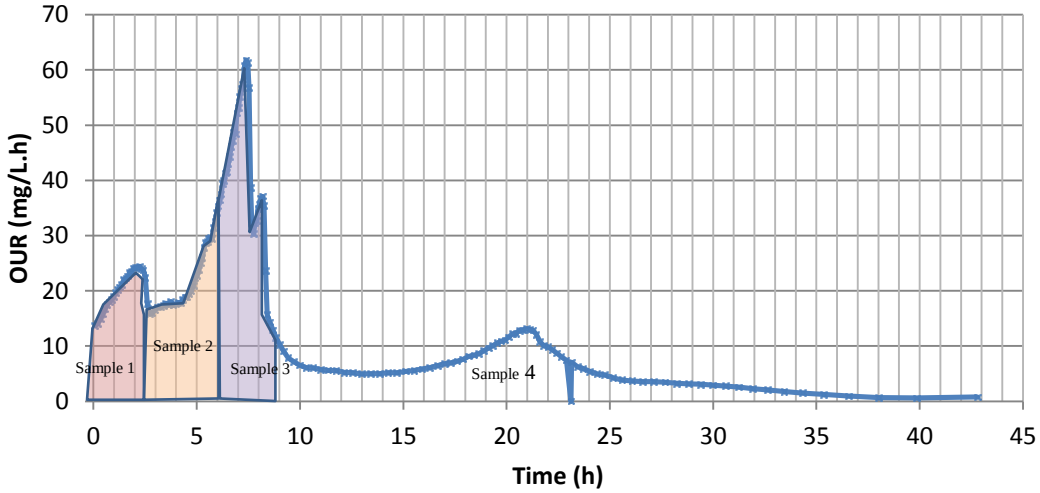

Figure 3.12 Respirogram for wastewater collected on 14 August 2012 (Exp. 2)

Table 3.6 Comparison of estimated COD and Experimental COD values Experiment (Exp) 1 and 2

	Sample 1 COD (mg/L)		Sample 2 COD (mg/L)		Sample 3 COD (mg/L)		Sample 4 COD (mg/L)	
Exp	**Estimated**	**Tested**	**Estimated**	**Tested**	**Estimated**	**Tested**	**Estimated**	**Tested**
1	245	1 024	666	659	717	772	768	834
2	165	717	590	581	701	528	1 149	158

The overall % COD recovery for Experiment 1 and 2 were 48.7% and 49.2% respectively. These values are much lower than the range of 95-105 % provided by Wentzel et al. (1995) which is required in order to consider the COD fractions as acceptable. The estimated and tested COD results obtained from the samples drawn from the bioreactor during the aerobic batch test show significant variation for Sample 1 in both experiments. At the beginning of the test the COD of the sample is high while the calculated area under the curve is smaller than the area calculated later in the experiment hence the higher tested COD values than the estimated values. Almost matching values were obtained for Samples 2, 3 and 4 in Experiment 1 and Samples 2 and 3 in Experiment 2. The estimated and tested COD values for Sample 4 in Experiment 2 show a significant difference. The estimated COD (1149 mg/L) is far much higher that the tested COD of 158 mg/L. Experiment 2 ran for over 40 h and this might explain the low final COD of 158 mg/L. However this does not explain the discrepancies in COD values.

The inaccurate values for S_S are probably due to the absence of a clearly defined precipitous drop of the OUR after utilising the available readily biodegradable as mentioned earlier. This makes it difficult to interpret the OUR results accurately using the modified UCT model. The values for S_I appear to be higher than expected, when compared with the S_I values measured in the WWTP final effluent.

3.5 Conclusion

The COD fraction results obtained from interpreting the respirograms for industrial effluent from Verulam WWTP could not be accurately interpreted using the modified UCT model, thus a complete COD fractionation could not be obtained. It appears that the substrate in the wastewater sample is being utilised in a different mechanism from that proposed by the UCT model. Another possibility is that components present in the wastewater interfere with the DO probe and result in atypical DO profiles of the respirograms obtained. Comparison of the results of COD fractions obtained from Verulam WWTP samples and results obtained by Wentzel et al. (1999) further indicated that the batch test was not successful with this particular wastewater from Verulam WWTP. The COD recoveries obtained from the experiments were either too low or too high when compared to the acceptable range of 95- 105%, indicating that the results obtained from the test could not be accepted.

At this point in the study a solution to make the experimental approach to COD fractionation work could not be found. An alternative approach was proposed by the candidate. The following chapters (4 and 5) present the proposed catchment-balance-approach that was used to estimate the COD fractions present in the influent wastewater received at Verulam WWTP.

4 VOLUMES OF WASTEWATER STREAMS IN VERULAM WWTP

4.1 Introduction

In order to run dynamic simulations using the ASM1, complete influent wastewater characterisation is essential. Complete influent wastewater characterisation requires the volumetric flow rates of the influent wastewater and the concentrations of the relevant components present in the influent wastewater, to be quantified.

The influent characteristics (composition) in ASM1 are represented by a total of 13 components. These 13 components include COD fractions of the total influent COD and other components representing the nitrogenous matter present in the wastewater, alkalinity and dissolved oxygen concentrations of the influent wastewater. All the 13 components need to be determined in order to have complete influent wastewater characterisation for modelling purposes. Out of the 13 components, the COD fractions were the most difficult to estimate since the respirometric experiments were not successful. This chapter presents the different steps taken to estimate the COD fractions in influent wastewater and the rest of the ASM1 components representing nitrogenous matter, alkalinity and dissolved oxygen.

The approach used to estimate the COD fractions in influent wastewater at Verulam WWTP involved a wastewater flow balance of the WWTP catchment. The two obvious wastewater contributors in the Verulam WWTP catchment were identified as domestic wastewater from households and industrial wastewater from factories. The sewer network connected to Verulam WWTP is not a combined sewer network. The sewer network was designed to collect and transport domestic and industrial wastewater. However during rain events significant volumes of stormwater find their way into the WWTP. Thus, stormwater infiltration was identified as the additional source of wastewater received at Verulam WWTP. Figure 4.1 illustrates the sources of wastewater in the Verulam WWTP catchment area.

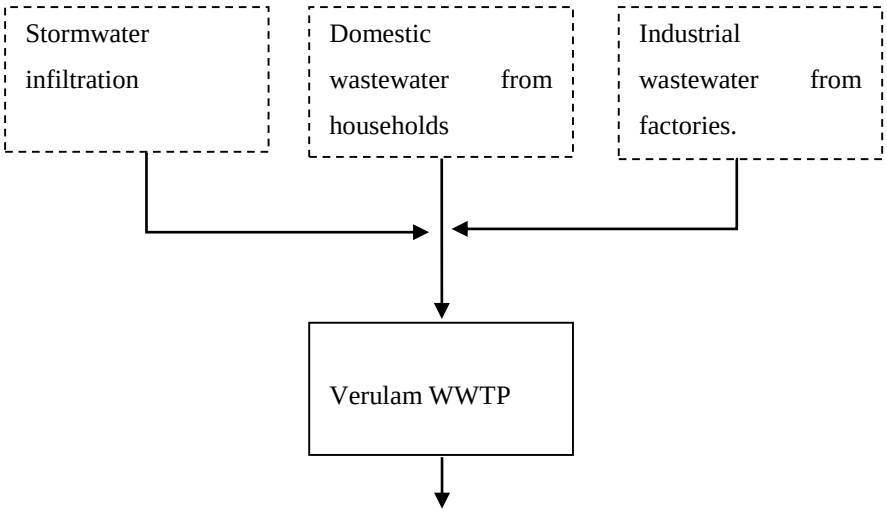

Figure 4.1 Sources of wastewater within the Verulam WWTP catchment area

While the combined total influent wastewater flow is measured at the inlet of the WWTP, the contributions of stormwater infiltration and domestic wastewater are not recorded. The industrial wastewater flows from factories were available on monthly basis. Before the input file representing the dynamic variation of influent wastewater flow at the WWTP could be created, different methods were used on the historical data and various information streams that were available, to bring them to a common daily basis for modelling purposes.

Knowledge of the characteristics of the different wastewater streams in the catchment was required for the purpose of performing a catchment flow and component balance. While the COD is the main variable of interest in demonstrating COD fractionation, other characteristics of the wastewater are presented and discussed in the following sections for the purpose of describing the overall characteristics of the wastewater streams. The data for the wastewater characteristics were obtained from different sources for each major contributor of wastewater in the catchment area. Wastewater flows are discussed first (Chapter 4) followed by the composition of the wastewater streams (Chapter 5).

4.2 Urban wastewater catchments

The major components that make up an urban wastewater system are the catchment, sewer system, wastewater treatment and the receiving water body (Saagi, 2014). The wastewater flow from a community to a WWTP depends on the type of collection system used. The collection system usually includes 4 sources; domestic wastewater, industrial wastewater, infiltration and stormwater (Metcalf and Eddy, 2003). Domestic wastewater is discharged from residential and commercial institutions and similar facilities while industrial wastewater is discharged from the factories located in the community. Infiltration is water that enters the catchment through leaking joints, cracks or porous walls of the sewer system. Stormwater is runoff resulting from rainfall or melting snow. Three wastewater collection systems are used to collect wastewater in communities; sanitary sewer, stormwater sewer and combined sewer systems. Sanitary sewer systems are designed to transport domestic wastewater or industrial wastewater, while stormwater collecting systems collect and transport stormwater. Combined sewer networks transport wastewater from domestic or, and industrial sources together with stormwater. The transported wastewater is treated in WWTPs before being discharged to the receiving water body such as a river or lake.

Separate and different models exist for the elements that make up the urban wastewater system and they have been applied in various studies that include Henze et al., 2000, Rossmann, 2009 and Shanahan et al., 2001. Combining the individual sub-models representing different elements in the urban wastewater system, results in a more complex integrated model of the urban wastewater system that can be used for management of wastewater systems. However it can be a challenge to integrate the sub-models of an

urban wastewater system due to various reasons which include interface problems between sub-models, sub-models developed using different approaches for different purposes (Schmitt et al., 2006) and running on different time scales are difficult to interface (Rauch et al., 2002). A simpler approach to analyse the flows and composition of wastewater generated in the Verulam WWTP catchment was adopted in this study.

4.3 Methods of determining wastewater flows in the Verulam WWTP catchment

Most of the historical data recorded at Verulam WWTP were available as daily totals or averages and the factories located in the catchment were operating on daily cycles. Thus, it was decided to carry out the modelling of the WWTP based on the volumetric flow rates of the influent wastewater expressed as daily totals and the concentrations of the wastewater components as daily averages. Hence the different types of data that were available for each source of wastewater were handled using different methods to come up with the required frequency and structure of data for modelling purposes.

4.3.1 Stormwater infiltration

Stormwater runoff is water that flows over the ground during precipitation events. Stormwater runoff either flows directly into surface waterways or is channelled into storm sewers, which eventually discharge to surface waters. In the Verulam WWTP catchment, some of the stormwater finds its way to the WWTP as infiltration. No measurements were available for the infiltration in the Verulam WWTP catchment. The only available data that could be linked to infiltration was daily rainfall data recorded at the WWTP. In an ideal situation, rainfall data and other streams of information such as land use and the nature of the ground surfaces of the catchment can be used in complex mathematical models to predict the volumes of stormwater that ends up at the WWTP. In this study the measured data that were available only allowed a very simplified modelling approach of estimating stormwater infiltration in the Verulam WWTP catchment.

Rainfall data was used to predict stormwater infiltration in the Verulam WWTP catchment. Several types of models relating rainfall and runoff flow have been developed and applied in many catchments. Empirical relationships for rainfall and runoff flow have been used in some studies (Walker, 2003). Examples include rainfall-excess models such as the Soil Conservation Services curve number method (USDA-SCS, 1985) and linear regression analysis of rainfall data and runoff data as in Hensley et al. (2000). For more realistic and dynamic models of the runoff process, deterministic models are considered more appropriate (Walker, 2003). In all these models detailed rainfall intensity data is required for successful estimation of the runoff (Connolly et al., 1998), unlike in the past where daily rainfall data was adequate as input in stochastic runoff-models (Walker, 2003).

A model that can be used for estimating stormwater infiltration in the South African catchments is the ACRU (Agricultural Catchments Research Unit) model. The ACRU model is a multi-purpose model integrating various water budgeting and runoff production components of the terrestrial hydrological system. The model has been structured such that it is highly sensitive to climate and land cover, land use and management changes on the soil water and runoff regimes (Schulze, 2004). ACRU is a physical-conceptual model based on variables estimated from physically based characteristics of the catchment, rather than optimised parameter values. The model is not made up of parameters that are calibrated to produce a good fit (Schulze, 2004). Thus in order to assess the performance of the model in simulating data, a confirmation study is required. This model was not used in this study due to lack of data that are required to adequately represent the different parts of the ACRU model for successful simulations.

In the Verulam WWTP catchment the rainfall data were collected from measurements carried out by a simple rain gauge fixed on the open grounds at the WWTP. The daily amount of rainfall was measured and recorded in millimetres. The data were not time weighted and the rainfall intensity was not measured. The original purpose for collected data was not for modelling runoff. Since data requirements for modelling rainfall runoff using already developed models could not be met, it was impossible to use the available models for estimating the runoff in the Verulam WWTP catchment. Faced with this challenge, an attempt to estimate runoff flow from the available rainfall data was the only option left to fill this information gap in the study.

The first step in the simplified modelling approach to predict the stormwater flow in the WWTP catchment was to investigate the correlation between rainfall and the total influent wastewater received at the WWTP. Visual inspection of a plot of influent wastewater volumes at the WWTP and rainfall shown in Figure 4.20 suggested possible correlation between the two variables. The measure of this correlation was investigated by analysing the daily wastewater flow data measured at WWTP and daily rainfall data collected in all the months of the years 2009, 2010 and 2011.

The Pearson product –moment correlation coefficient was used to measure the extent to which the two random variables were correlated. The sample correlation coefficient was computed as the quotient of the covariance of the two variables ($\mathrm{cov}(X,Y)$) and the product of the standard deviations ($\sigma_X \sigma_Y$) as shown in Equation 4.1.

$$r_{XY} = \frac{\mathrm{cov}(X,Y)}{\sigma_X \sigma_Y} \qquad [4.1]$$

The Pearson correlation coefficient of +1 indicates perfect positive linear relationship while a coefficient of -1 indicates perfect negative linear relationship (anti-correlation). Values of the coefficient between -1 and +1 indicate the degree of linear dependence between the variables of concern. Values closer to -1 or +1 indicate strong correlation between variables while values approaching zero indicate moving towards uncorrelated variables.

After investigating the correlation between rainfall and stormwater flow a simple model was put together using the available rainfall data. The hypothesis behind the modelling attempt was that multiple linear regression can be applied to a range of independent variables in order to predict the stormwater infiltration into the sewer due to rainfall. The strategy employed was to separate the rainy days from the dry days based on the recorded rainfall data. The influent wastewater volumes recorded on rainy days were considered to include runoff contribution and the days with no rain were considered not to have runoff contribution. However after analysing the influent wastewater volume and rainfall data it became evident that the effect of the rainfall (contribution of wastewater by runoff) extended beyond the actual day when it rained. The contribution by runoff to the influent wastewater received at the WWTP appeared to last for up to 3 to 5 days in some cases after the rain had stopped. Hence the selected dry days were considered as those where there had been no rain for the previous 5 days.

To estimate the amount of runoff the influent wastewater flow measured during the days that were identified and classified as having no runoff contribution were separated from the rainy days and then this series of values was subjected to a 15 day smoothing moving average. The resulting series of value was termed the 'base-flow". The difference between the smoothed values (base-flow) and the measured daily totals of influent wastewater was considered as the infiltration due to runoff.

To define a relationship between infiltration and runoff, the calculated infiltration due to runoff and measured rainfall was then fitted to a linear function using multiple linear regression. Since it was observed that the effect of rainfall on the amount of infiltration extended beyond the specific day of the rain, multiple linear regression analysis was selected to define a simple model relating infiltration to the day when rainfall was recorded and for the previous 2 days. The multiple linear regression analysis was used to estimate regression coefficients for each of the rainfall values recorded for the day and for the previous 2 days from the infiltration and rainfall data. The infiltration predicted by the linear function was then taken as the contribution by rain to the influent wastewater stream. The goodness of fit of the regression analysis was measured by the coefficient of determination, R^2 and the significance of the regression was assessed by the P-value.

To define the prediction equation for infiltration, 3 regressors were used against the infiltration values obtained as the difference of (base-flow) and the measured daily totals of influent wastewater. The three regressors were the rainfall measured: on a specific day and the previous 2 days. It was opted to consider the day of the measured rainfall and the previous 2 days because extending the regressors to beyond 2 days showed weak correlation between the rainfall and infiltration on these extra days. The weak correlation was observed after assessing the corresponding regression coefficients. Thus the regression model used was in the form of Equation 4.2.

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \varepsilon \quad [4.2]$$

The prediction equations resulting from the regression analysis of data from the years 2009, 2010 and 2011 are presented as Equation 4.3, 4.4 and 4.5 respectively.

$$Y = 24.11X_1 + 8.77X_2 + 3.65X_3 \quad [4.3]$$

$$Y = 83.26X_1 + 38.59X_2 + 8.28X_3 \quad [4.4]$$

$$Y = 59.59X_1 + 38.71X_2 + 28.47X_3 \quad [4.5]$$

4.3.2 Domestic wastewater flow

No measurements were available for the volumetric flow rates of domestic wastewater from households in the Verulam WWTP catchment. Hence the wastewater contribution of households was calculated from the overall flow balance of the catchment.

4.3.3 Industrial wastewater flow

The volumes of effluent generated by the factories in the Verulam WWTP catchment are recorded monthly by the municipality for purposes of billing the factories for wastewater disposal into the municipal sewer. The industrial effluent from factories is referred to as 'trade effluent'. Combined flows in Verulam WWTP.The monthly trade effluent volumes from the factories were used to generate estimates for daily flows for each day of the month by applying distribution fitting and Monte Carlo simulations on the available data.

Several assumptions are central to statistical theory relating to probability distribution fitting. Statistical theory relating to probability distribution fitting assumes that the sample data represents random occurrences of the variable of interest and therefore depends upon the data being independent and the data must be from the same statistical population. Before fitting data to probability distributions, one has to establish that the data is independent, stationary (show no trends) and homogeneous. There must be no outliers in the sample data. Thus, the monthly total volumes of wastewater from each factory were inspected for statistical independence, stationary, trends, homogeneity and outliers before distribution

fitting. The data sets were inspected as sets of monthly total volumes recorded annually for each factory and then the 3 data sets for each year (2009, 2010 and 2011) for each factory were combined into one data set and inspected as one data set. The larger data set comprising of data from each year would eventually be used for distribution fitting if it met the statistical requirements for distribution fitting.

Statistical independence of two random variables means that knowing the value of one of them does not yield any information of the other. The degree of independence for stationary data can be characterised by determining the autocorrelation function of the observed data or by constructing an auto-correlogram from the data (Zaidman, 2002). Stochastically independent variables must show no correlation. Several methods exist for testing auto-correlation. These methods include the Wald-Wolfowitz Test, Durbin-Watson statistic and the Anderson's Test. These tests are not expected to work well if there is limited data such as was the case in this study. Thus the validity of the assumption of statistical independence was established by assessing the nature of the variable against the qualitative definition of statistical independence. The total monthly trade effluent volumes from each factory were considered to be statistically independent since the recorded monthly effluent volumes for one month does not affect or depend on the value of another month. Furthermore the data did not exhibit significant trends.

After establishing the applicability of the key assumptions for fitting probability distributions, the monthly trade effluent volumes from the factories was used to generate estimates for daily flows for each day of the month by taking the following steps:

- The measured monthly trade effluent volumes were divided by the number of days of the month to get a daily average wastewater flow rate for each month.
- The resulting vales of the daily average wastewater flow rate were fitted to different distributions in an attempt to find the type of distribution and the values of the parameters (mean and variance) of the distribution that would give the highest probability of producing the daily average wastewater flow data. The Chi-Square test was used to evaluate the goodness-of-fit of the fitted distributions. The best distribution was selected based on the chi-squared statistic. The mean and variance of the selected distribution was recorded.
- It was assumed that the distribution of the daily average wastewater flow rate would be the same as that of the random daily flows, except that the variances of the distribution would be different. This was based on statistical theory that relates the variance of the sampling distribution of the sample mean and the population variance. The variance of the sampling distribution of the mean is the population variance divided by the sample size.

$$\sigma_M^2 = \frac{\sigma^2}{N}$$

where σ_M^2 is the variance of the sampling distribution of the sample mean,

σ^2 is the population variance and N is the sample size.

- Thus, a new variance for the population was calculated as described above and then daily flow data was generated using the selected distribution and the calculated variance, by running Monte Carlo simulations which generated random daily flows that fit the specified probability distribution.
- To evaluate the goodness of the daily flow volumes generated by the Monte Carlo simulations, the generated daily flows were summed up for each month to get a value of the monthly trade effluent volume. Since the daily flow volumes were generated by a Monte Carlo simulations the chance of the simulated monthly totals matching the measure monthly totals are low. Therefore to compare the measured monthly trade effluent volumes to the simulated monthly trade effluent volumes, the respective sets of data were split into bins defined by specified ranges of flow volumes and then the frequencies of monthly trade effluent volumes falling into each bin were plotted in order to compare the measured and simulated distribution of monthly flow totals.
- Reliable simulated data were expected to have similar frequencies in each bin as the measured data. Where there was room for improvement, the variance of the distribution used to generate the daily flow volumes was further adjusted to improve the match between simulated and measured monthly trade effluent volumes.

The software package used for distribution fitting was @RISK version 5.5 (May 2009) obtained from the Palisade Corporation in New York, USA. In this software program, for sample data, distribution parameters are estimated using Maximum Likelihood Estimators (MLEs). For density and cumulative data (collectively known as curve data), the method of least squares is used to minimize the root-mean square error between the curve points and the theoretical function.

The MLEs of a distribution are the parameters of that function that maximize the probability of obtaining the given data set. For any density distribution *f(x)* with one parameter α, and a corresponding set of *n* sampled values X_i, an expression called the likelihood may be defined:

$$L = \prod_{i=1}^{n} f(X_i, \alpha)$$

To find the MLE, simply maximize *L* with respect to α:

$$\frac{dL}{d\alpha} = 0$$

and then solve for α. The method described above can be easily generalized to distributions with more than one parameter. However for some distributions the MLE method does not work therefore @RISK will resort to a hybrid algorithm which combines the standard MLE approach with a moment matching procedure.

4.3.4 Combined influent wastewater flows

The wastewater streams from different sources meet in the sewer system and arrive at the inlet of the WWTP as a combined wastewater stream. Dynamic variation of the combined influent wastewater flow rate was obtained from the on-line measurements done at the inlet of the WWTP. The daily total influent wastewater volumes were available from 2009 for all the days that the WWTP was operational.

4.3.5 The flow balance of the Verulam WWTP catchment

The main contributors of wastewater in the Verulam WWTP catchment were identified as stormwater infiltration, industrial wastewater from factories and domestic wastewater from households. The industrial effluent is discharged by six factories located in the catchment. The percentage contributions by volume of the identified contributors were determined from the factory trade effluent data, stormwater infiltration was predicted from simplified modelling and the daily wastewater volumes measured at the WWTP for the specified years. The contribution of domestic wastewater from households was determined by difference between the total volume of wastewater measured at the WWTP and the sum of the industrial wastewater and the stormwater from the rain.

4.4 Results

The results obtained from analysing and transforming the available data to daily flow averages for the different wastewater sources in the Verulam WWTP catchment are presented and discussed in the following sections. The results of the catchment flow balance are also presented.

4.4.1 Storm water infiltration flow

The correlation coefficients obtained from analysing the monthly data for the years 2009, 2010 and 2011 for each month suggested varying measures of correlation between rainfall and influent wastewater flow received at the WWTP. Table 4.1 shows the correlation coefficients for influent wastewater flow and rainfall. The measure of correlation between rainfall and influent wastewater flow rate did not exhibit strong correlation across all months in the year. The correlation coefficients showed that there was strong correlation in some months and less to no correlation in other months.

Table 4.1: Correlation coefficients for influent wastewater flows and rainfall

Month	Correlation coefficient		
	2009	2010	2011
Jan	0.80	0.18	0.57
Feb	0.004	0.50	-0.02
Mar	0.67	0.65	0.45
Apr	-0.31	0.04	0.69
May	-0.02	-	0.36
Jun	-	0.14	0.51
Jul	0.28	0.18	0.62
Aug	-0.06	0.04	0.32
Sep	0.49	0.06	0.30
Oct	0.09	0.14	0.71
Nov	0.53	0.70	0.29
Dec	0.30	0.71	0.14

- Incorrectly recorded data

The reason for this variation in correlation is thought to be due to several issues. Firstly the monthly influent wastewater totals include stormwater, industrial wastewater and domestic wastewater. The strong correlation between rainfall and stormwater which might exist could be obscured by the fact that industrial and domestic wastewaters are part of the total monthly influent wastewater volume. Secondly the variation of the correlation might be due to the fact that the volume of stormwater that ends up at the WWTP depends on several factors whose relationship is complex and in this case was unknown. When it rains, not all the rainfall contributes to stormwater that ends up at the WWTP. Some of the rain is lost through interception by vegetation and depression storage on the ground and wetting of the ground. Another portion, classified as continuous losses, includes losses due to wind drift, evapotranspiration and infiltration (Butler, 2004).

The long term balance between the amount of water gained by a catchment area due to rainfall and the amount of water losses from that catchment area in the form of evapotranspiration form a crucial and complex relationship that is used to determine the amount of runoff flow (Walker, 2003). This relationship between annual totals of rainfall and evapotranspiration is modified by rainfall distribution and vegetation cover. Thus, a model taking into account the above mentioned factors is usually used to generate stormwater volumes (De Toffol 2006). Considering the aforementioned factors the relationship between rainfall and influent wastewater received at the WWTP is a complex one. With this knowledge a more informed modelling attempt to predict the stormwater infiltration flows in the Verulam WWTP catchment was initiated.

The results of the regression indicated that for the year 2009 the three regressors explained 22 % of the variation in infiltration (R^2 =0.22, F (3,358) =33.75, p<0.1). It was found that the day when the rainfall was measured significantly predicted the infiltration (β_1 = 24.11, p<0.01), while the two previous days showed reduced positive beta coefficients (β_2 = 8.78, p<0.01 and β_3= 3.64, p<0.01) which were also significant since was p<0.01. The regression analysis correctly confirms that the correlation between rainfall and filtration is highest on the day when it rains and becomes weaker on the days that follow or the days prior to the measured rainfall.

For the year 2010 the three regressors explained 37 % of the variation in infiltration (R^2 =0.37, F (3,358) =69.53, p<0.1). The regression analysis showed that the first two regression coefficients significantly predicted the infiltration significantly (β_1 = 83.26, p<0.01 and β_2 = 38.59, p<0.01), while the third coefficient showed had a reduced positive value with lesser significance than the other coefficients (β_3= 8.28, p<0.5). The year 2011 showed a similar trend in regression coefficients. The regression coefficients reduced from the day rainfall was measured through the days previous to the day of the rain (β_1 = 59.59, p<0.01; β_2= 38.71, p<0.5 and β_3 = 28.47, p<0.01). All regression coefficients were significant since p<0.01. The regressors explained 36 % of the variation in infiltration (R^2 =0.36, F (3,358) =66.91, p<0.1).

The prediction equations, Equation 4.3, 4.4 and 4.5 were used to generate infiltration data for the years 2009, 2010 and 2011. The predicted infiltration was compared to the rainfall, base-flow, and daily influent totals. Figure 4.2 to Figure 4.4 show the comparison.

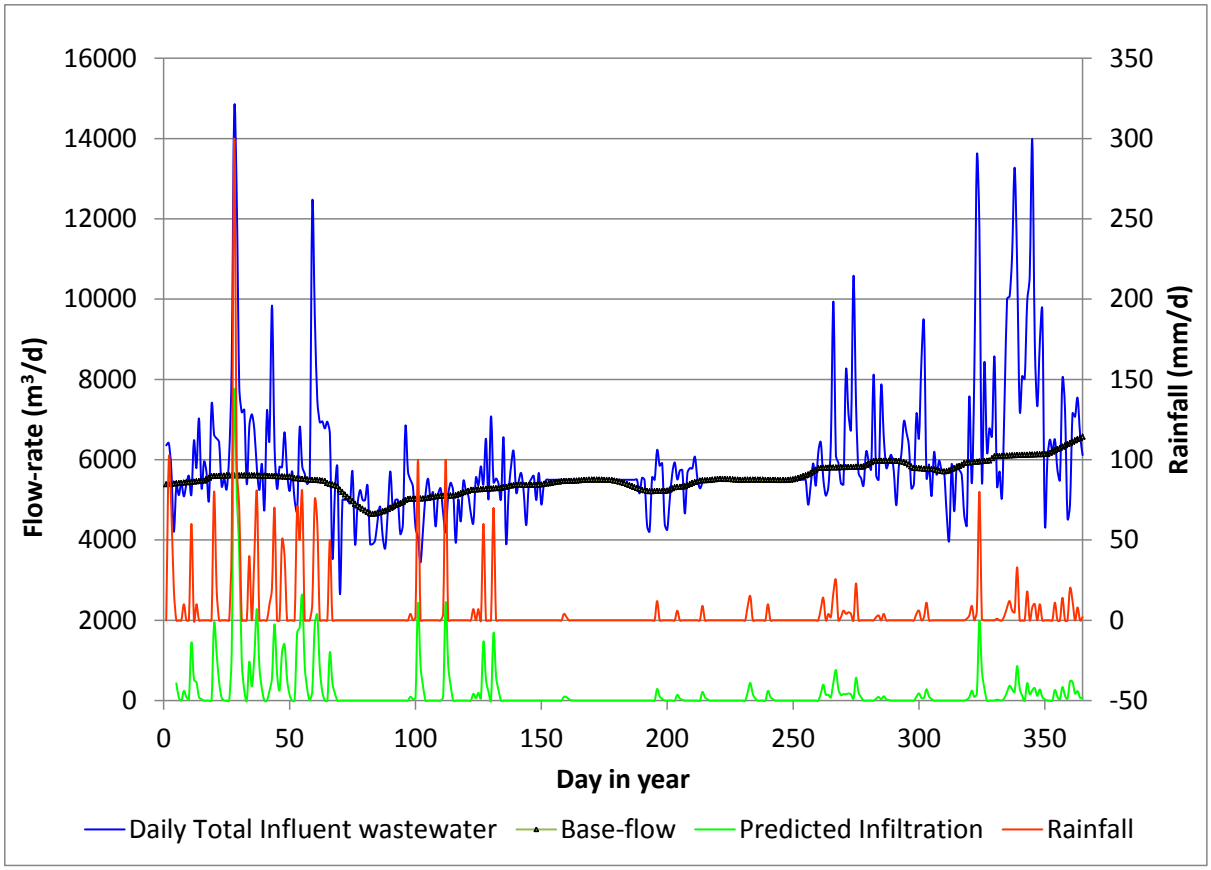

Figure 4.2 Rainfall, infiltration, base-flow and total influent wastewater for 2009

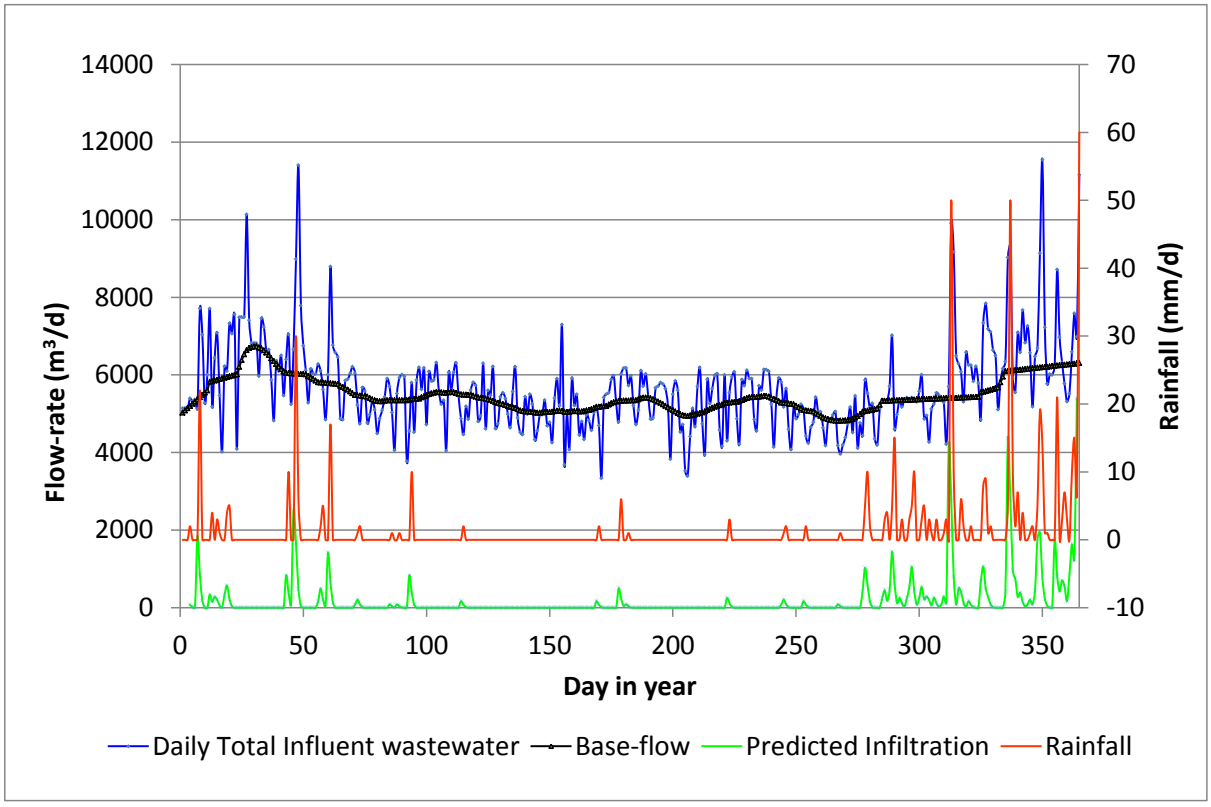

Figure 4.3 Rainfall, infiltration, base-flow and total influent wastewater for 2010

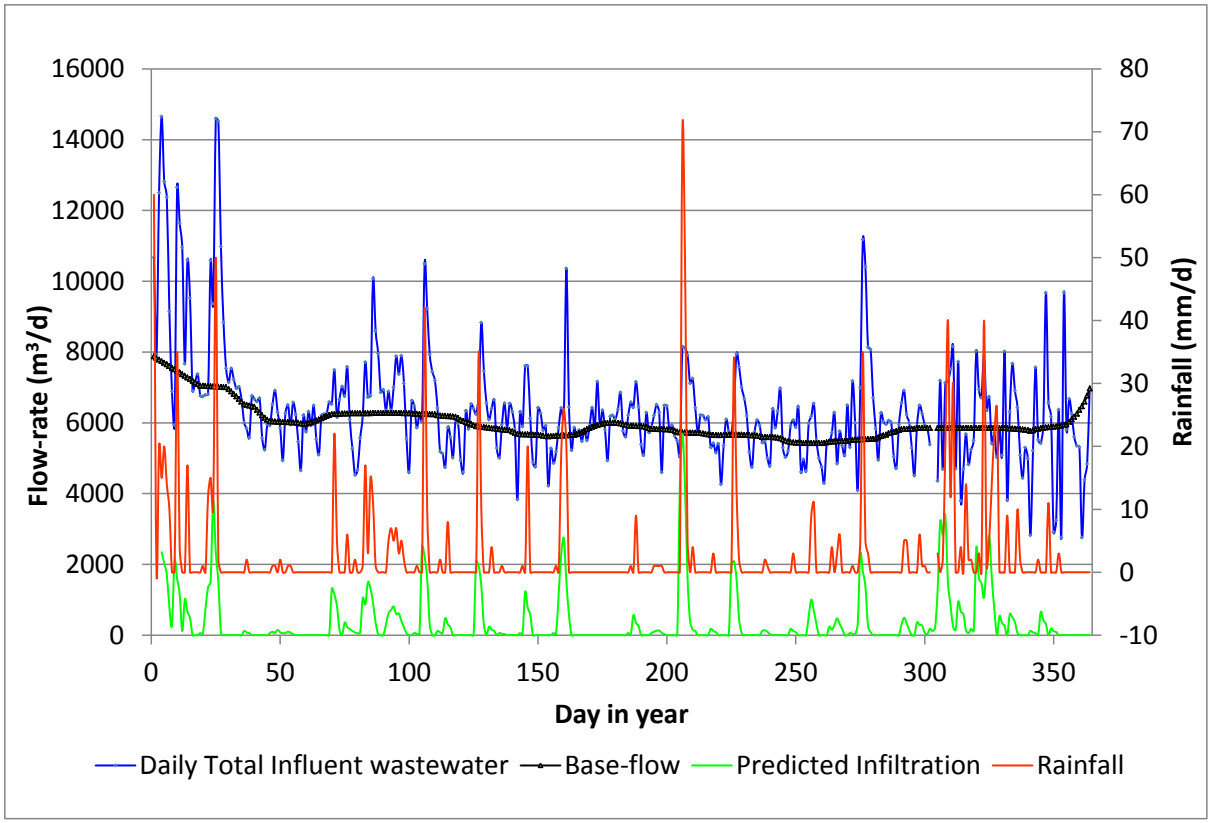

Figure 4.4 Rainfall, infiltration, base-flow and total influent wastewater for 2011

While the results of the predicted infiltration were accepted for this case study, it is acknowledged that the relationship between rainfall and the stormwater that ends up in the WWTP is more complicated than what the adopted approach suggests. Many factors that affect the complex relationship of rainfall and stormwater received at the WWTP have been left out due to lack of data and the necessary information to include them in the model used to predict infiltration flows in the catchment. Furthermore several assumptions were made in order to use multiple linear regression to predict the contribution of stormwater infiltration to the total influent wastewater at the WWTP. The predictions made using the above simplified approach were used in the catchment flow balance.

The base-flow represents an estimate of the variation of influent wastewater with time in the absence of infiltration. For all the years assessed, the predicted volumes of infiltration are relatively higher on days with more rainfall as compared to days with less or no rainfall. The influence of the infiltration on the total influent wastewater volumes received at the WWTP can be seen on Figure 4.2, Figure 4.3 and Figure 4.4. High volumes of influent wastewater are recorded during days when the predicted infiltration is also high.

4.4.2 Domestic wastewater flow

The volume of wastewater discharged by households in the Verulam WWTP catchment was estimated from a wastewater flow balance carried out in the catchment. The wastewater flow balance is presented in the Annexure on the CD accompanying the thesis. The wastewater flow balance showed that approximately 80% of the total volume received at the WWTP comes from households.

4.4.3 Industrial wastewater

The monthly trade effluent volumes of the major factories in the Verulam catchment indicate that JMV Textiles discharges the highest volume of trade effluent as shown in Figure 4.5 to Figure 4.7. Trade effluent volumes of up to 18 000 m^3/month have been recorded for JMV Textiles.

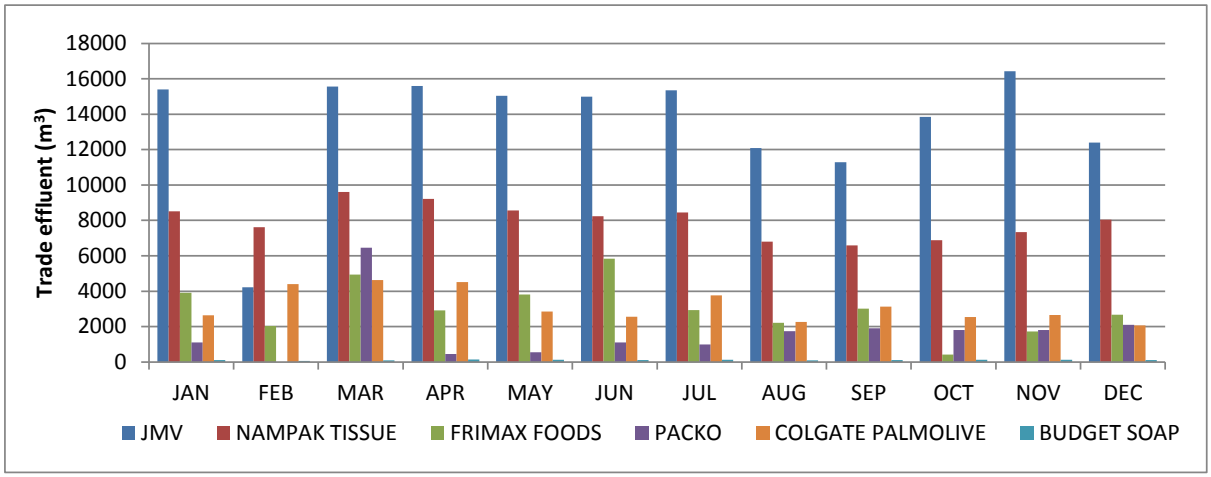

Figure 4.5 Monthly trade effluent volumes from Verulam WWTP catchment for 2009

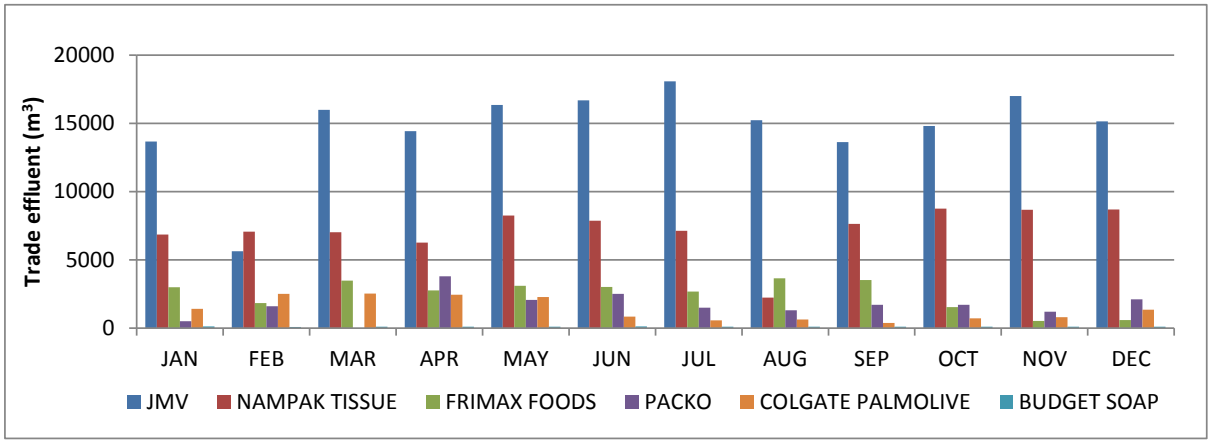

Figure 4.6 Monthly trade effluent volumes from Verulam WWTP catchment for 2010

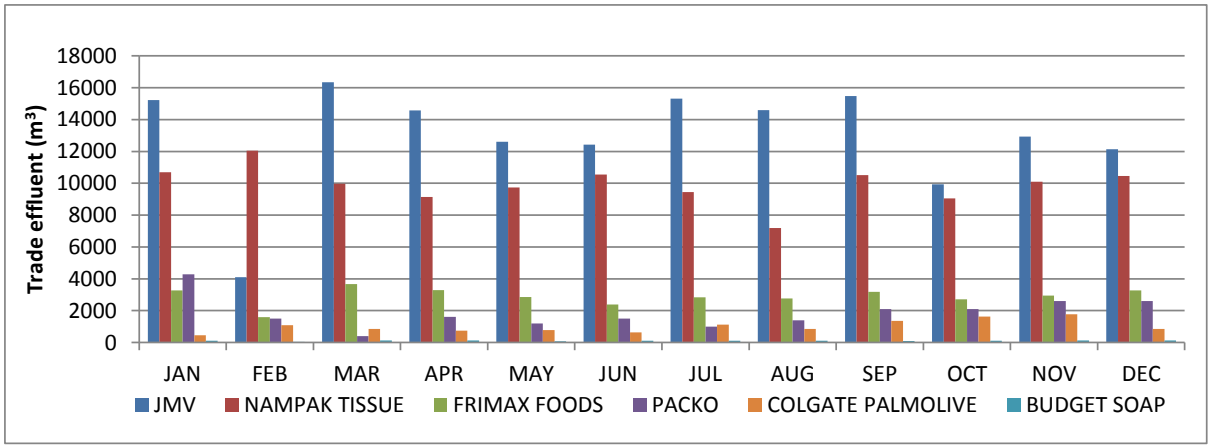

Figure 4.7 Monthly trade effluent volumes from Verulam WWTP catchment for 2011

The order of the major factories in the Verulam WWTP catchment when ranked according to the monthly trade effluent volumes starting with the highest is as follows: JMV Textiles followed by Nampak Tissue, Frimax Foods, Packo, Colgate Palmolive and Budget Soap. The trade effluent volumes from each factory were available as monthly totals for the years 2009, 2010 and 2011. The descriptive statistics of the available monthly wastewater volumes from the factories in the Verulam WWTP catchment are presented in Table 4.2.

Table 4.2 Descriptive statistics of monthly trade effluent volumes 2009 to 2011

	JMV	**Nampak Tissue**	**Frimax Foods**	**Packo**	**Colgate Palmolive**	**Budget Soap**
2009						
No. of Samples	12	12	12	11	12	12
Mean (m^3/month)	13 517	7 988	3 034	1 818	3 167	110
Standard deviation (m^3/month)	3 346	965	1 456	1 635	919	18
2010						
No. of Samples	12	12	12	11	12	12
Mean (m^3/month)	14 719	7 199	2 466	1 814	1 364	100
Standard deviation (m^3/month)	3 163	1 766	1 094	842	847	13
2011						
No. of Samples	12	12	12	12	12	12
Mean (m^3/month)	12 972	9 906	2 898	1 857	1 010	106
Standard deviation (m^3/month)	3 337	1 181	533	997	399	25

The monthly wastewater flows were considered stationary after investigation the plots, the mean and variance of the data. The flow data was inspected for outliers. Figure 4.8 to Figure 4.10 shows the monthly total volumes for the 2009, 2010 and 2011.

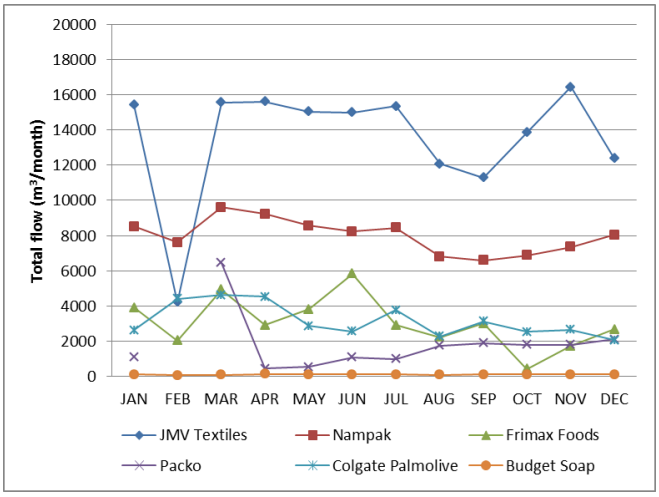

Figure 4.8 Monthly trade effluent volumes 2009

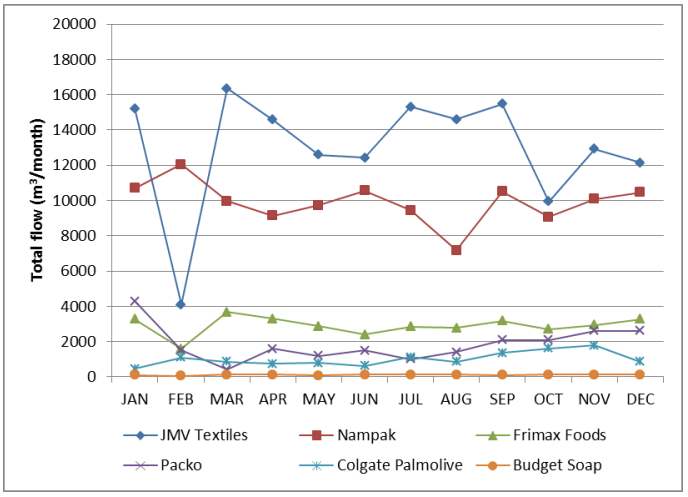

Figure 4.9 Monthly trade effluent volumes 2010

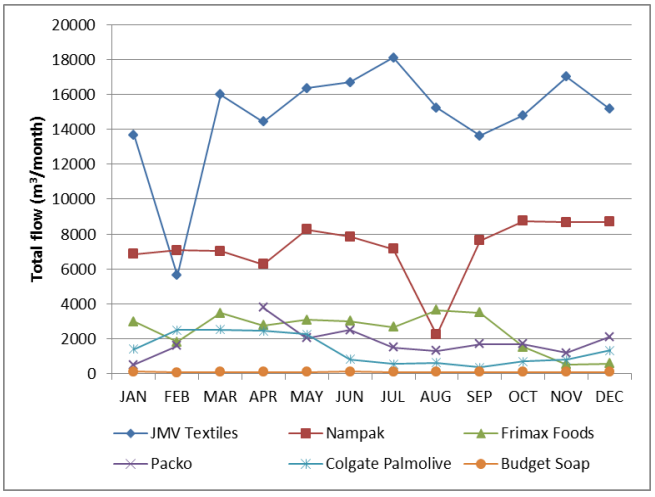

Figure 4.10 Monthly trade effluent volumes 2011

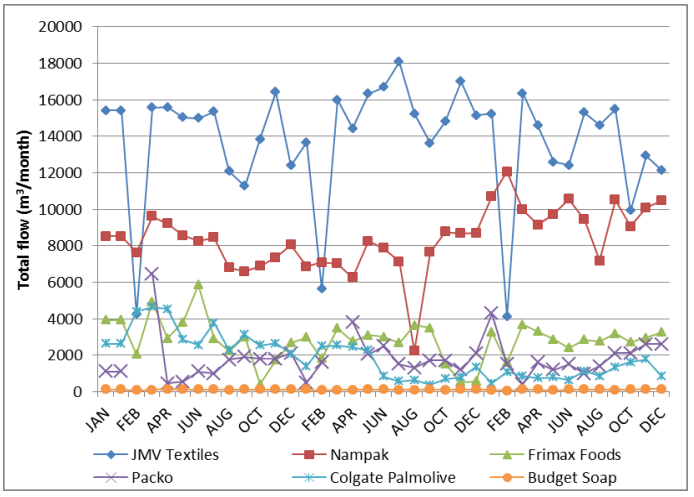

Figure 4.11 Monthly trade effluent volumes 2009-2011

No significant outliers were identified in the historical flow data except for one measurement for Nampak recorded in August 2010 and all measurements for the month of February for JMV Textile for all years. A relatively low value of wastewater was discharged from the Nampak factory in August 2010. The cause of this low discharge of wastewater from Nampak could not be established. For JMV Textiles, the wastewater monthly total volumes for the month of February for each year were not reflective of the factory's normal operation since the factory is on shut down every February. These data points were excluded from the data used in probability distribution fitting. The time series plots of the measured monthly totals for the years 2009, 2010 and 2011were inspected for cyclicality in the data and no significant patterns were observed.

The results of fitting probability distributions to the daily average wastewater flow data for each factory are presented in this section, followed by the daily wastewater flows generated from the Monte Carlo simulations. Firstly the top five probability distribution functions (PDFs), for each set of data from each factory are presented in tables. The probability distribution functions were ranked by their goodness-of-fit. The cumulative distribution function (CDF) and as probability density function are plotted and presented followed by quantile-quantile (Q-Q) and probability-probability (P-P) plots for the best fitting distribution. Lastly, a comparison of the simulated and measured monthly trade effluent volumes is presented in the form of frequency histograms.

Figure 4.12 to Figure 4.17 show the results for the case of JMV Textiles. The top five distributions that best fit the wastewater flow data from JMV Textiles, ranked by their chi-squared statistic values, were the Weibull, Beta General, Gamma, Inverse Gaussian and the Log normal distributions. The chi-squared statistics for each distribution are presents in Table 4.3.

Table 4.3 Ranking of probability distributions fitted to daily average trade effluent volumes for JMV Textiles

Rank	Distribution	Chi-squared statistic
1	Weibull	3.2727
2	Beta general	4.9697
3	Gamma	9.2121
4	Inverse Gaussian	9.2121
5	Log normal	9.2121

It is worth noting that, while the chi-squared statistic is a formal goodness of fit test among other tests such as the Kolmogorov-Smirnov and Anderson-Darling test, in practice the chi-squared statistic test cannot always have the highest discriminatory power when selecting the best distributions. Such a goodness of fit test is generally best for rejecting poor distribution fits than for identifying good fits (EPA, 1997). The sample size of the measured data (which is relatively small) is also a reason why numerical goodness-of-fit tests are not powerful enough to be the only discriminating factor in selecting the best distribution fit. Thus graphical methods (visual inspection of PDF, CDF, P-P and Q-Q plots) were also used to assess the distribution fits, in order to overcome the weakness in the numerical goodness-of-fit such as the chi-square statistic.

Visual comparison is often the most straight forward way of determining whether the fitted distribution is a good representation of the observed data. Figure 4.12 and Figure 4.13 illustrate the CDF for the top five probability distribution functions and the best distribution fit (Weibull PDF) respectively. The

figures indicate that, whilst the distributions have different chi-square statistics there is little to no difference between the CDF plots which all describe the main body of the data very well. Figure 4.14 and Figure 4.15 illustrate the corresponding PDF plots which also exhibit distribution shapes similar to each other and limited variation. With all five distributions fitting the data to almost the same goodness of fit the top distribution was selected based on the chi-squared value.

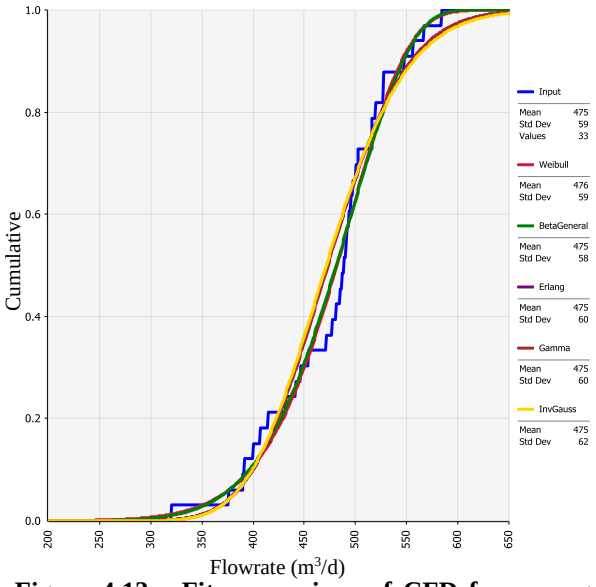

Figure 4.12 Fit comparison of CFD for average daily flows for JMV Textiles, for top 5 distributions

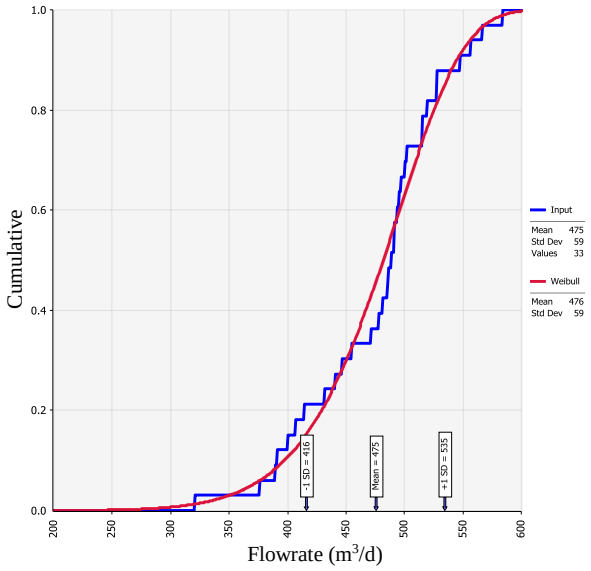

Figure 4.13 CFD for average daily flows for JMV Textiles, for top ranking distribution (Weibull)

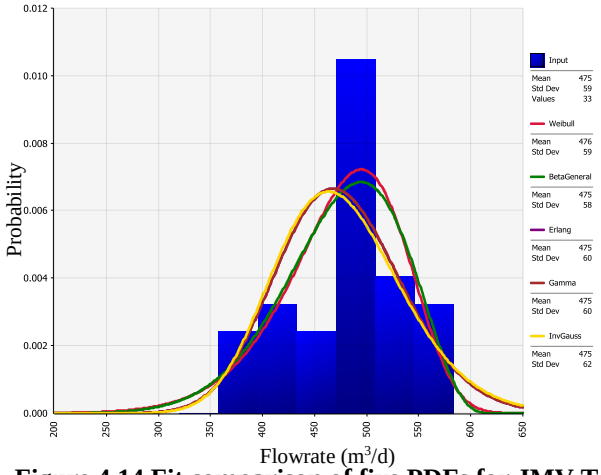

Figure 4.14 Fit comparison of five PDFs for JMV Textiles daily average flows, for top 5 distributions

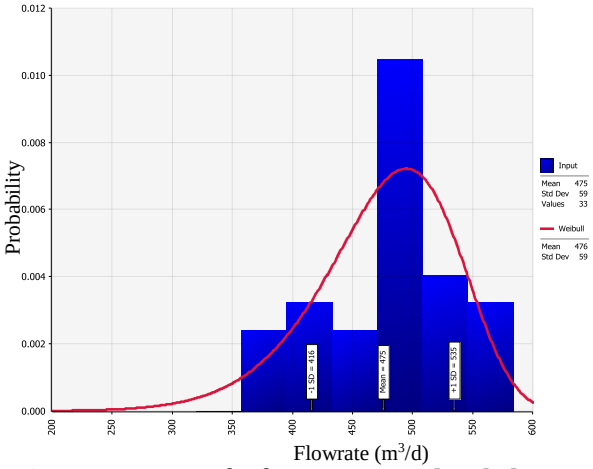

Figure 4.15 PDF fit for JMV Textiles daily average flows , for top ranking distribution (Weibull)

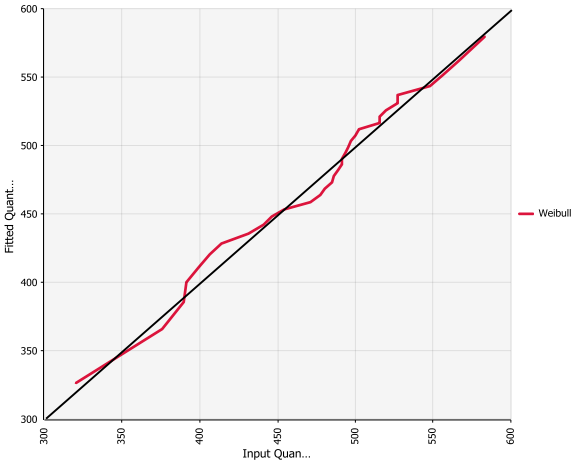

Figure 4.16 Quantile-Quantile plot for JMV Textiles daily average flows for top raking distribution (Weibull)

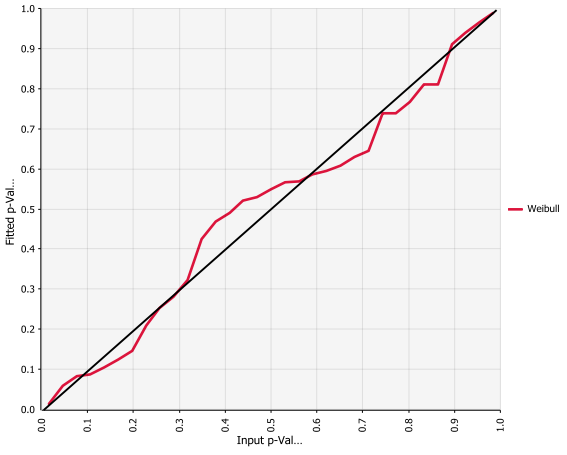

Figure 4.17 Probability-Probability plot JMV Textiles daily average flows for top raking distribution

Figure 4.16 and Figure 4.17 show Q-Q and P-P plots for the best distribution fit for the daily average flows from JMV Textiles, respectively. Q-Q plots compare two probability distributions by plotting their quantiles against each other. If the two distributions being compared are similar the points in the Q-Q will lie on the $y=x$ line. The P-P plot is used to assess how closely two data sets agree by plotting the cumulative distribution functions against each other. If the two distributions match the points of the plot will lie on the $y=x$ line. The Q-Q and P-P shown in Figure 4.16 and Figure 4.17 both display plots that are almost linear and close to the $y=x$ line, thus indicating that the fitted distribution is acceptable.

The daily wastewater flow volumes generated using the Monte Carlo were summed up to determine the simulated monthly trade effluent volumes. These simulated monthly trade effluent volumes were then compared to the measured monthly trade effluent volumes. Figure 4.18 shows frequency histograms of the simulated and measured monthly trade effluent volumes for different Monte Carlo simulations based on the best distribution fit (Weibull with an adjusted variance).

The histograms show the random nature of the Monte Carlo simulations. Each simulation presented (represented by each graph in Figure 4.18) shows different frequencies of monthly trade effluent volume values that fall into the specified bin-ranges. Each simulation is obtained after 10 000 iterations. In some simulations the simulated monthly trade effluent volume frequencies match the measured data better than in other simulations. It was considered imprudent to manually run countless simulations in pursuit of a perfect match between simulated and measured monthly trade effluent volumes due to the random nature of the results and the limited value the exercise would add to the results. The limited sample size of the measured flow data was another reason why there was so much variation in the simulated monthly trade effluent volumes. Thus any set of daily flows generated by the Monte Carlo simulations based on the selected best distribution fit, was considered good enough at this point of the study.

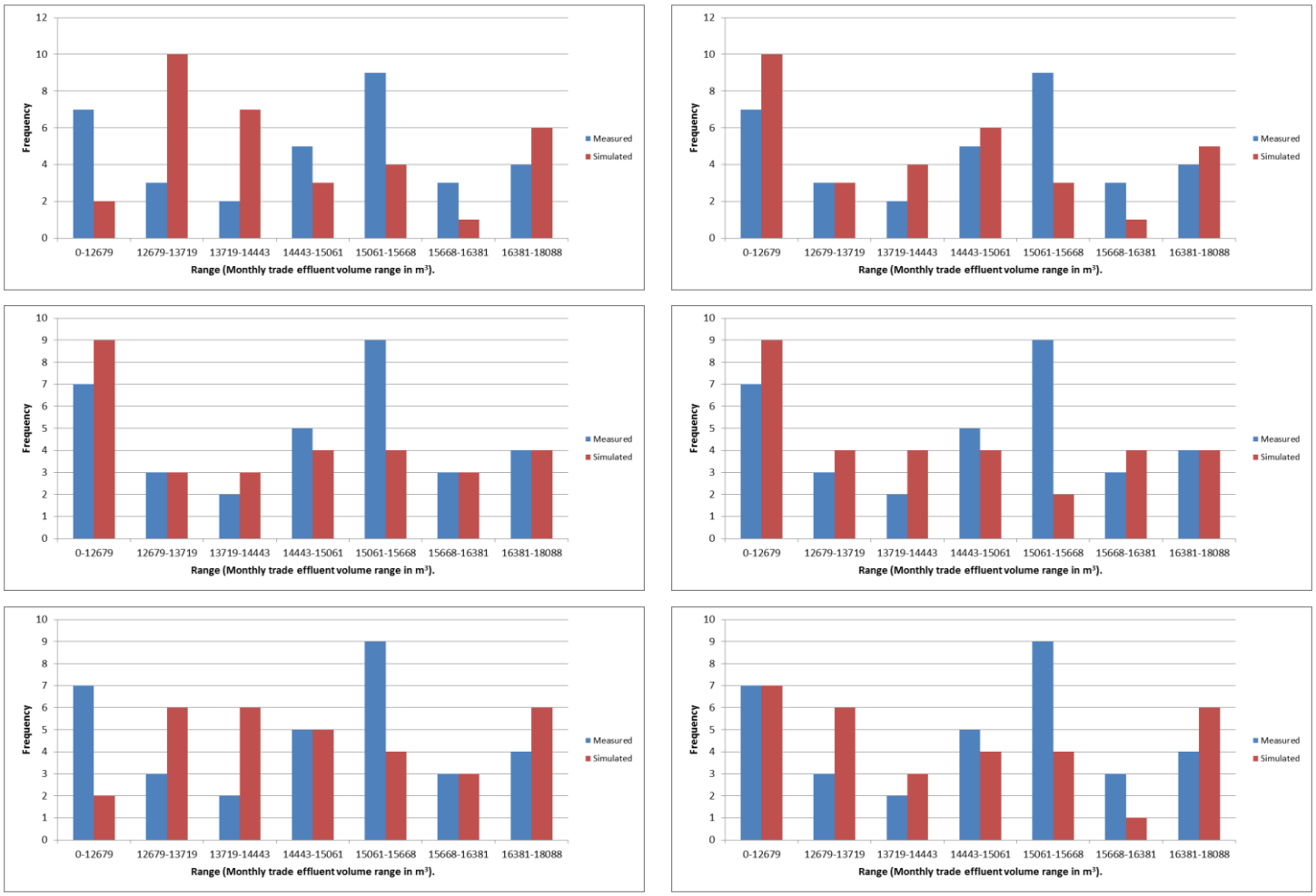

Figure 4.18 Distribution of measured and simulated monthly trade effluent volumes-JMV Textiles

The daily average flow data from the rest of the factories in the Verulam WWTP catchment were handled in a similar way to the data from JMV Textiles. Categorically, the results obtained for each factory were almost similar. The top five probability distributions fitting the data described the measured data very well. The best distribution was selected from the rest based on the Chi-squared statistic. The selected distribution was then used to generate daily flows using the Monte Carlo, which gave different sets of simulated monthly trade effluent volumes. When the simulated monthly trade effluent volumes were compared to the measured monthly trade effluent volumes the matches between the two sets of data varied randomly from poor to good matches. The results obtained for the rest of the factories in the WWTP catchment are described in the following sections and summarised in the tables and figures in Appendix C1.

For the case of the Nampak factory, the best distribution that fit data from Nampak was the Weibull distribution. The probability distribution functions were ranked by their chi squared statistic values. The best distribution being the one with the lowest chi squared statistic value. The Weibull distribution was used in the Monte Carlo simulation to generate daily trade effluent volumes.

For the case of Frimax Foods, according to the chi squared test, the triangular distribution was ranked the best distribution to fit the data from Frimax Foods. However, the Weibull distribution which was ranked second, gave better simulation results of the month trade effluent volumes. For this reason the Weibull distribution was adopted for the case of Frimax Foods.

For the case of Packo, the best distribution that fit data from Packo was the Rayleigh distribution based on the chi squared test. However the Weibull distribution gave the best simulation of the total monthly trade effluent volumes hence its adoption instead of the Rayleigh distribution, for the Monte Carlo simulations. The Weibull distribution was used in the Monte Carlo simulation to generate daily trade effluent volumes.

For the case of Colgate Palmolive, based on the chi-squared statistic, the best distribution that fit data from Colgate Palmolive was the triangular distribution. However the Weibull distribution gave the best simulation of the total monthly trade effluent volumes hence its adoption instead of the triangular distribution, for the Monte Carlo simulations.

For the case of Budget Soap, the best distribution that fit data from Budget Soap was the Weibull distribution. The Weibull distribution was used in the Monte Carlo simulation to generate daily trade effluent volumes.

4.4.4 Combined flows at Verulam WWTP

The short term variations of influent-wastewater flow rates observed at Verulam WWTP follow a diurnal pattern. Figure 4.19 shows the influent-wastewater flow rate variations for 1 week in the month of September of 2011.

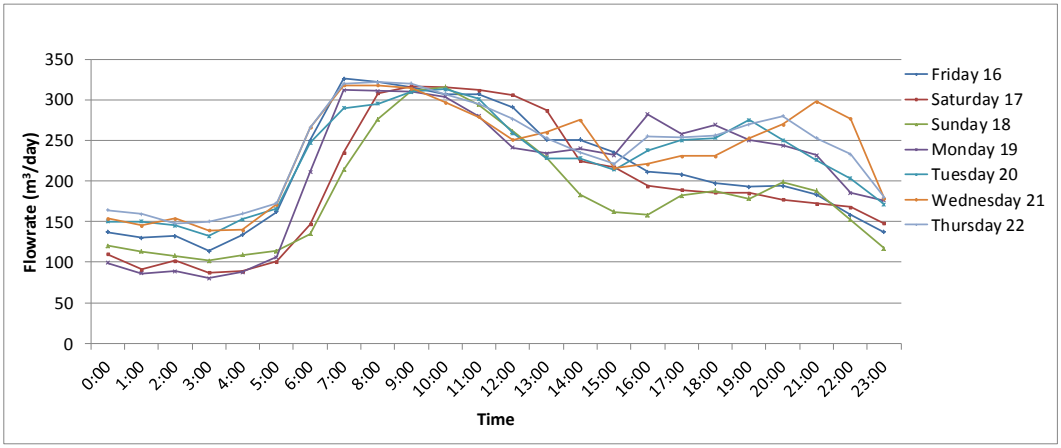

Figure 4.19 Diurnal variation of wastewater influent flow rate at Verulam WWTP head of Works

The time of occurrence and amplitude of the peak flow rates measured in a wastewater treatment plant vary with the size of the community being served and the distance between the source of the wastewater and the wastewater treatment plant (Metcalf and Eddy, 2003). At the Verulam WWTP minimum flows are experienced during the early hours of the morning when water consumption is lowest. The base flow consists of infiltration and small quantities of sanitary wastewater. The first peak occurs in the late morning between 7 and 11 a.m. when wastewater from the peak morning water use reaches the wastewater treatment plant. A second peak flow is observed in the early evening between 7 and 10 p.m. before the flow drops to the early morning minimum flow.

Total monthly influent flow volumes at Verulam WWTP vary across the year. The effect of rainfall on the total influent monthly flow volumes at the head of works can be seen in Figure 4.20 and Figure 4.21.

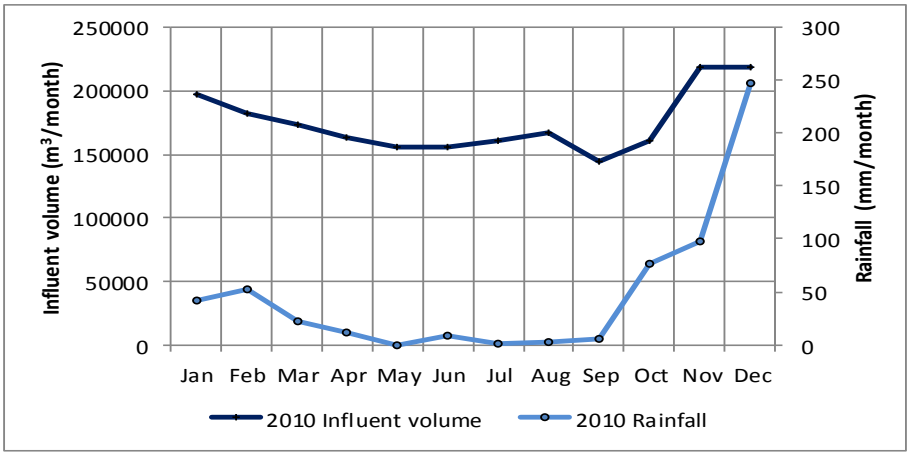

Figure 4.20 Rainfall and total monthly influent volumes for the year 2010

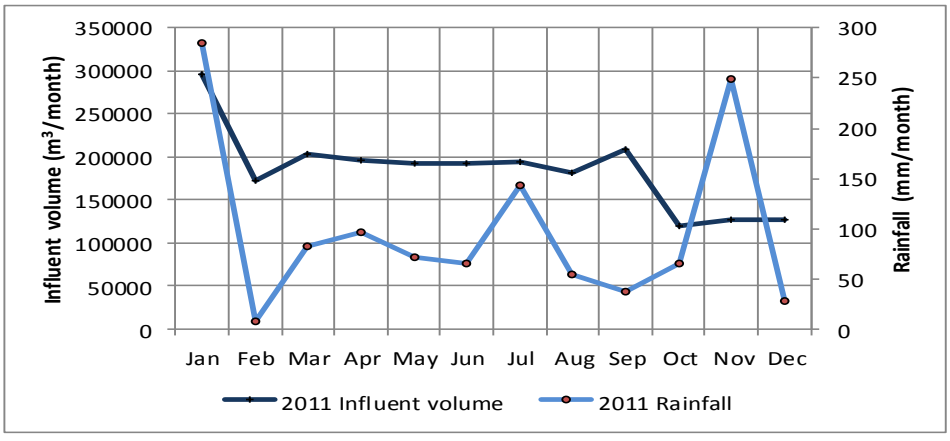

Figure 4.21 Rainfall and total monthly influent volumes for the year 2011

The historical data confirm that Verulam WWTP receives significant infiltration during rainy months. The Verulam area is predominantly a summer rainfall region with high intensity rainfall occurring over a short time period which begins in November and ends in April, hence the observed increase in influent volumes at the WWTP due to infiltration during the summer rainfall period.

4.4.5 Results of catchment flow balance

Figure 4.22 shows a summary of the contributions by volume of the identified contributors of wastewater received at the WWTP for the years 2009, 2010 and 2011.

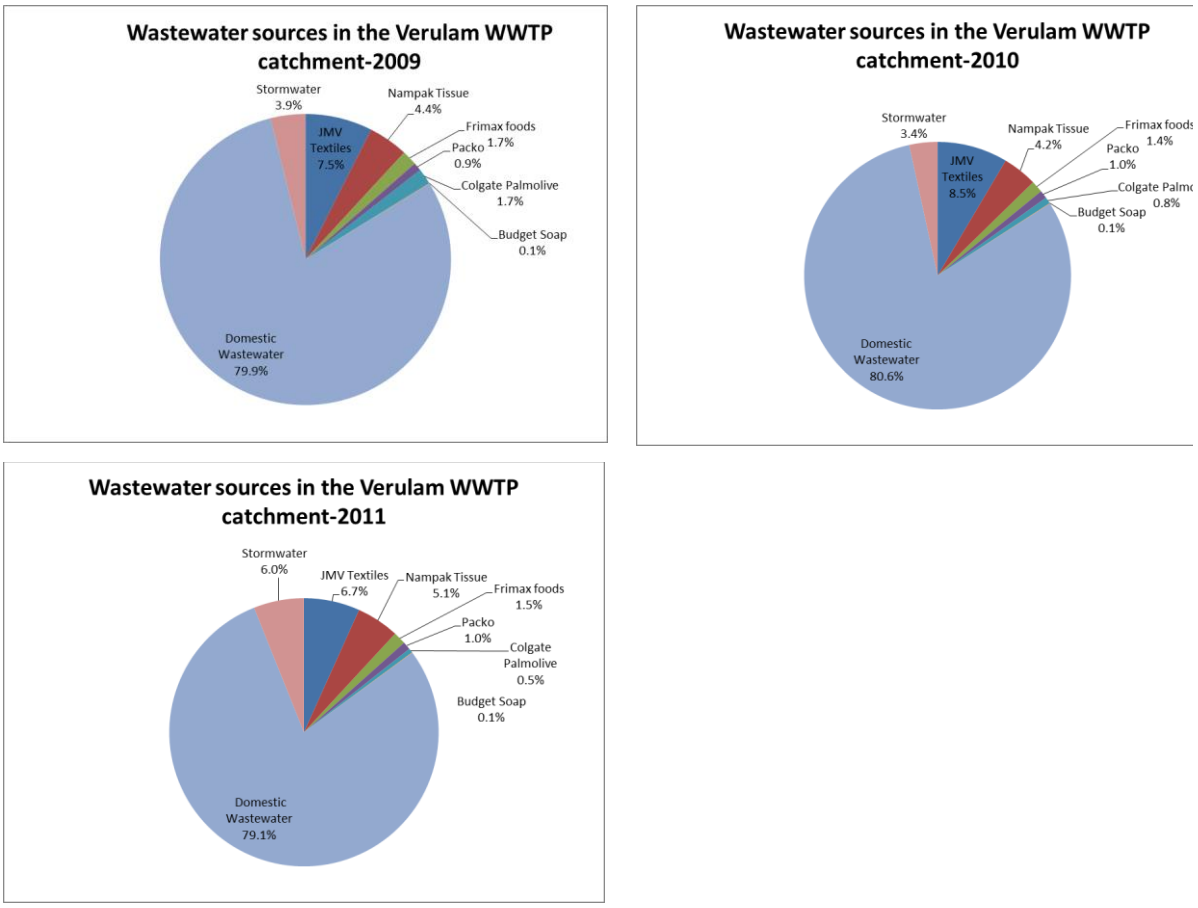

Figure 4.22: % Contribution by volume of major sources of wastewater Verulam WWTP catchment

The proportion of industrial effluent and domestic effluent appear to be consistent over the 3 years. The percentage contributions of domestic wastewater were 79.9, 80.6 and 79.1 % for 2009, 2010 and 2011 respectively. The corresponding industrial proportions were 16.3, 15.9 and 14.9 %. The actual volumes contributed appear in Table 4.4. JMV Textiles contributes approximately 50% of the industrial effluent, followed by Nampak which contributes almost 30%. The rest of the industrial effluent comes from the four remaining factories.

Table 4.4 Trade effluent volumes from major factories in the catchment for Verulam WWTP

	2009		2010		2011	
Source	**Volume (m^3/y)**	**Contribution to total (%)**	**Volume (m^3/y)**	**Contribution to total (%)**	**Volume (m^3/y)**	**Contribution to total (%)**
Industrial effluent						
JMV	162 200	7.5	176 630	8.5	155 664	6.7
Nampak	95 859	4.4	86 391	4.2	118 874	5.1
Frimax Foods	36 407	1.7	29 594	1.4	34 775	1.5
Packo	20 001	0.9	19 949	1.0	22 283	1.0
Colgate Palmolive	38 012	1.7	16 362	0.8	12 108	0.5
Budget Soap	1 325	0.1	1 201	0.1	1 276	0.1
Total	353 804	16.3	330 127	15.9	344 980	14.9
Domestic effluent	1 737 853	79.9	1 669 696	80.6	1 831 566	79.1
Storm water	84 185	3.9	70 748	3.4	140 138	6.0
Combined	**2 175 842**	**100**	**2 400 698**	**100**	**2 661 664**	**100**

The descriptive statistics of the annual trade effluent volumes from the factories in the catchment are presented in Table 4.5. The monthly volume of trade effluent that is discharged by each factory was

recorded and used to determine the mean and the rest of the statistics presented in Table 4.5.

Table 4.5 Descriptive Statistics of monthly Trade effluent volumes

		JMV	Nampak Tissue	Frimax Foods	Packo	Colgate Palmolive	Budget Soap
2009							
No. of Samples	(-)	12	12	12	11	12	12
Mean	(m^3)	13 517	7 988	3 034	1 818	3 167	110
Standard deviation	(m^3)	3 346	965	1 456	1 635	919	18
2010							
No. of Samples	(-)	12	12	12	11	12	12
Mean (m^3)	(m^3)	14 719	7 199	2 466	1 814	1 364	100
Standard deviation	(m^3)	3 163	1 766	1 094	842	847	13
2011							
No. of Samples	(-)	12	12	12	12	12	12
Mean	(m^3)	12 972	9 906	2 898	1 857	1 010	106
Standard deviation	(m^3)	3 337	1 181	533	997	399	25

4.5 Conclusion

The concept of fitting distributions to daily average trade effluent volume data and using the best distribution fit in Monte Carlo simulations to generate daily flows can be a useful method of generating the required flow data for modelling. However, in the current case study several issues seem to affect the quality of results at different stages of the methodology. These issues are discussed below:

- The sample size of the measured data was small: as a result the reliability of the distribution results was affected. In general, the larger the sample size, the greater the confidence in the selected probability distribution. Levels of uncertainty associated with parameters such as means, modes and predicted probabilities of occurrence, decrease with increasing sample size (Crawley, 2002). Furthermore, for small sample sizes goodness-of-fit tests will often fail to reject some probability distribution functions during the selection of the best distribution and when sample sizes are small, outliers carry more weight in analyses than if more data were available to buffer the effect. In this study the effect of the relatively small sample size of the measured data could be seen in the distribution fitting exercise. For data sets which had several values that could have been classified as outliers but had been allowed to be part of the limited sample data, the effect of these potential outliers made the choice of the best distribution difficult.

- Since the sample size was considered as small, both the numerical goodness of fit test (chi-squared test) and qualitative evaluation of the PDF plots were used to select the best distribution fit. It was evident in some cases that the chi-squared statistic obtained from limited sample data was not the best criteria to select or reject distributions. Some distributions that were ranked high by the chi-squared test did not give good simulations and lower ranked distributions modelled the measured data better and gave better simulation results. In general, there is no rule of thumb for the minimum sample size needed to specify a distribution for variability or uncertainty, however in most cases, to get reliable distribution fitting results one must have a sample size of at least 75 to 100 data points.
- The assumption from statistical theory, that the distribution of the daily flow averages would be the same as that of the random daily flows, except that the variances of the distribution would be different, was applied in the distribution fitting procedure. However, averages and variances of the distribution used to generated daily flows were adjusted in some cases to improve the match of measured and simulated monthly trade effluent volumes.

In conclusion, with a larger sample size and more measurements taken more frequently, distribution fitting and use of Monte Carlo simulations would yield better results. However the constraint would be the cost of carrying out intensive sampling and analysis of factory effluents. If the predictions made by WWTP model developed using the available data turn out to be acceptable, then no additional data will be required.

5 COMPOSITION OF WASTEWATER STREAMS IN THE VERULAM WWTP CATCHMENT

5.1 Introduction

The identified contributors of wastewater in the Verulam WWTP catchment were industrial wastewater from factories, stormwater infiltration, and domestic wastewater from households. Knowledge of the characteristics of the different wastewater streams in the catchment was required for the purpose of performing a catchment flow and component balance with special focus on the COD. While the COD is the main variable of interest in demonstrating COD fractionation, other characteristics of the wastewater are presented and discussed in the following sections for the purpose of describing the overall characteristics of the wastewater streams. The following sections present the source of wastewater composition data for the identified sources of wastewater in the Verulam WWTP catchment, which are presented under the heading 'Methods'. This is followed by the discussion of results obtained. The COD fractions in the combined influent wastewater entering Verulam WWTP were estimated. A summary of how the rest of the ASM1 components that are considered to be present in influent wastewater, were determined is also presented.

After estimating the average COD concentration of each contributing stream, effort was made to break down the total COD concentrations of each stream into fractions required for modelling. Successful fractionation of the contributing streams would then enable the estimation of the COD fractions in the combined influent wastewater received at the WWTP, using a COD fraction balance. It is a fact that wastewater quality is site-specific and the most accurate characterisation of a particular wastewater stream can be obtained by sampling and analysing the samples for that particular case. In the case of Verulam WWTP, determination of the COD fractions of individual wastewater streams experimentally was not possible, hence the adoption of the aforementioned approach. The search in literature, for COD fractions of wastewaters similar to the wastewater streams in the Verulam catchment was already a compromise in accuracy of the COD fractionation since the COD fractions from a different wastewater were going to be considered as applicable to another case. To reduce the inaccuracy, where information was available, effort was made to identify a wastewater type with the most similar characteristics to the wastewater stream in the Verulam catchment.

5.2 Methods of determining composition of wastewater streams in Verulam WWTP catchment

The methods used to determine the composition of wastewater from the factories, rainfall runoff, domestic wastewater from households and the combined wastewater received at Verulam WWTP, are present in the following sections.

5.2.1 Composition of industrial wastewater

The data for the characteristics of industrial wastewater were obtained from measurements made during the time to time monitoring of individual factory trade-effluent-quality done by municipal inspectors from the Pollution and Environmental Department of eThekwini Water and Sanitation (EWS) at eThekwini Municipality.

Monte Carlo simulations were used to generate daily average COD concentrations for each trade effluent stream, from the available measurements. The immediate challenge that presented itself from the beginning of the exercise was the limited number of measurements resulting in limited data for probability distribution fitting, a key step in generating data using Monte Carlo simulations. A limited number of measurements poses a serious challenge to obtaining the best probability distribution fits for the measured data. Faced with this challenge, probability distribution fitting and Monte Carlo simulations were carried out for the purpose of evaluating how well or bad the distribution obtained by fitting this data would be for the purpose of influent characterization. It was clear from the beginning of the exercise that the results of the distribution fitting would severely be affected by the lack of enough measurements. The procedure of generating the daily COD values for each stream of trade effluent wastewater was as follows:

- Various probability distributions were fitted to the available measured COD data. The best fitting distribution was selected by comparing the theoretical goodness-of-fit test. The Kolmogorov-Smirnov (K-S) method was used to evaluate the goodness-of-fit of the fitted distributions.
- It was assumed that the daily average COD values would follow the same distribution as that obtained from the measured COD values.
- Random values of daily average COD, fitting the selected distributions were then generated and used as the daily average COD concentrations for each wastewater stream from each factory.

5.2.1.1 Determining COD fractionation of industrial wastewater

Six major factories discharge industrial wastewater into the sewer system that transports wastewater to Verulam WWTP. The factories and their core business are summarised in Table 5.1

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Table 5.1 Factories operating within the Verulam WWTP catchment

Factory	Core business
JMV	Textiles: JMV are manufacturers, prints and dyes knitted fabrics.
Nampak	Manufactures paper, tissue paper and board packaging
Frimax Foods	Food: Produces chips, snacks and confectionary
Packo	Food: Produces pickles, sauces, spices, custard jellies and house hold chemicals (citric acid, borax, bicarbonate of soda, cream of tartar, tartaric acid, Epsom salts)
Colgate Palmolive	Manufactures detergents, tooth paste and soap
Budget soap	Manufactures soap and detergents

JMV Textiles manufacturers, prints and dyes knitted fabric. Processing of textiles involves a complex sequence of different process-stages from which wastewater is generated. The volumes and composition of the wastewater generated depends on the type of process and the materials involved in the process (Bisschops and Spanjers, 2003).The wastewater from the textile industry usually contains high and variable concentrations of BOD and COD together with a variety of priority pollutants.

Two food factories were identified in the Verulam catchment; Frimax Foods and Packo. Frimax Foods produces a range of food products which can be broadly classified as confectionary products. Packo produces pickles, sources, spices, custard jellies and household chemicals (citric acid, borax, bicarbonate of soda, cream of tartar, tartaric acid, Epsom salts). Industrial wastewater from food factories is generally characterised by high BOD and COD along with fats, oil, grease and many other recoverable nutrients like nitrogen, phosphorous and Potassium (Qasim et al., 2013).

Nampak manufactures tissue paper, packaging material, fluff, baby nappies and other household products such as aluminium foil. While Nampak is not a heavy industrial pulp and paper mill, the composition of its wastewater was assumed to have similarities to the wastewater from a pulp and paper mill. Wastewater from pulp and paper mills is usually alkaline in nature, has high suspended solids, high total solids, high COD and relatively low BOD. According to Patwardhan (2009), the approximate analysis of wastewater from a typical pulp and paper mill is as follows: pH value: 8.0-9.0; Total solids: 1500-2500 mg/L; Suspended solids: 600-1500 mg/L; COD: 300-2500 mg/L; BOD_5: 150- 1000 mg/L.

Colgate Palmolive manufactures soap, detergents and tooth paste, while Budget Soap manufactures soap and detergents. The soap and detergent industry can be classified as a chemical manufacturing industry in which mixing and chemical reaction of raw materials are involved in the production process (Wang, 2005). The soap and detergent industry produces liquid and solid cleaning agents. The industry

can be broadly split into soap manufacturing based on processing of natural fat and detergent manufacturing. The typical components present in wastewater from the detergent manufacturing industry are ionic and non-ionic surfactants, builders, perfumes enzymes and bleachers (Kowalska et al., 2005). The main source of pollutants in the wastewater from detergent manufacturing is the residual products in the reactor, which have to be washed away when the production line is being cleaned for the manufacture of other products (Kowalska et al., 2005).

The COD fractionation of the industrial wastewater streams were obtained from different literature sources. Results from (Ubay Cokgor, 1997) on COD fractionation of a wide range of domestic and industrial wastewaters were used to estimate the COD fractions in the wastewater streams from JMV Textiles, Packo and Frimax. Where there was more than one set of COD fractions to choose from, the one set whose total COD matched or was close to the measured average COD of the industrial wastewater stream was chosen. The total COD of wastewater was split into five fractions in Ubay Cokgor (1997). The biodegradable fraction of the total COD was split into readily biodegradable COD, slowly biodegradable COD and readily hydrolysable COD. In ASM1 the biodegradable fraction of the total COD of wastewater is only split into readily biodegradable COD and slowly biodegradable COD. The readily hydrolysable COD fraction is not used. Hence in order to use the COD fractionation results presented in Ubay Cokgor (1997) for ASM1 modelling, the readily hydrolysable COD fraction was combined with the readily biodegradable fraction. The non-biodegradable fraction of the total COD was split into soluble inert COD and particulate inert COD.

Reported data on the COD fractions for the pulp and paper mill wastewater are scarce. A study by El-Fadel (2012) evaluated the treatability of wastewater from a paper mill using laboratory scale sequencing batch reactor and the ASM1 modelling was used to estimate COD fractions of the wastewater from the paper mill. The estimated COD fractions were 33% inert soluble COD (S_I), 28% readily biodegradable soluble (S_S), 5% inert particulate COD X_I and 34% slowly biodegradable (X_S). Keskitalo et al., 2010 modified the standard ASM1 to model a full scale WWTP treating pulp mill wastewater. Wastewater characterisation was based on respirometric batch experiments on wastewater sampled from the WWTP. The estimated mean of COD fractions were 26.1% inert soluble COD (S_I), 44.9% readily biodegradable soluble (S_S), 7.8% inert particulate COD (X_I) and 21.2% slowly biodegradable COD (X_S). COD fractions obtained from El-Fadel (2012) were adopted as an estimate for the COD fractionation of wastewater from Nampak.

The COD fractions of wastewater from the soap and detergent factories such as Budget Soap and Colgate Palmolive appear to have not been researched as shown by the lack of literature on this subject. The flow weighted COD contributions by Budget Soap and Colgate Palmolive to the total COD load received by the WWTP were determined to be 0.02% and 4.2% respectively for the year 2010, and

0.02% and 2.8% respectively for the year 2011. After considering that the flow weighted contribution of all the factories combined for the years 2010 and 2011 were 27.2% and 26.6% of the total flow weighted COD load at the WWTP inlet, respectively, it was concluded that errors introduced by assuming COD fractions for the smaller contributors such as Budget soap and Colgate Palmolive would have less adverse effects on the overall COD fractionation. However it was a challenge to assign values to COD fractions making up the total COD of the wastewater from the two factories. The grab samples of wastewater from Budget Soap and Colgate Palmolive are analysed for COD, conductivity, setteable solids, pH, sugars and vegetable oils by municipal inspectors. These parameters cannot be used to directly estimate COD fractions; hence a more qualitative assumption was adopted.

It was initially assumed that more than 60% of the COD in the wastewater from factories was biodegradable after consulting Wang, (2005) who describe a case study of the treatment of wastewater from a Colgate Palmolive plant in Jeffersonville in Indiana (USA) by Brownell et al., (1975). After making the mentioned assumption percentages were assigned to the various COD fractions to fit the assumption of 60% biodegradable COD. It was assumed that the COD fractions of wastewater from Budget Soap and Colgate Palmolive were the same since they both produce similar products. It acknowledged that in reality this would not be the case. The reason why the assumption was accepted is that, during running of simulations, the COD fractionations of the wastewater stream from the two factories were changed while all parameters in the model were kept constant in order to investigate how sensitive the overall results were to the values assigned to the COD fractions of these two wastewater streams from the smaller factories.

5.2.2 Determining composition of surface runoff

Several studies on urban runoff generation and quality have been reported in literature, mainly in North America and Europe (Simpson, 1988).Lesser research has been done in South Africa. Studies focused on monitoring runoff at a variety of sites in South Africa turned out to be of limited use in this study. Out of the more than fifty case studies conducted in South Africa that were reviewed by Schoeman (1995) very few could present runoff composition together with the corresponding runoff flow volume measurements related to the rainfall in the site and the nature of the land usage .

For the ideal case where both flow volumes and quality are obtained within the same study, modelling and simulations can be done with less difficulty and more information can be extracted from the particular study. In the runoff studies reviewed, detailed physical, geographical and demographic information was often not recorded hence it was impossible to find a catchment similar to the Verulam catchment in terms of physical, geographical and demographic information.

In an effort to relate the runoff quality and general sewage effluent quality in South Africa, the work of Dallas and Day (1992) was reviewed. In this work Dallas and Day (1992) compared general urban runoff water quality with treated sewage effluent in South Africa and presented the following findings

- the concentration of non-filterable residues was twenty times higher for urban runoff than for treated sewage effluent,
- biochemical oxygen demand of urban runoff was twice that of treated sewage effluent,
- the phosphate and total nitrogen concentrations were fifteen times higher for urban runoff than for treated sewage effluent, and
- urban runoff contained higher concentrations of suspended solids than treated sewage effluent

Besides the reviewed work of other researchers there were no measurements available for the composition of surface runoff in the Verulam WWTP. It was not necessary to have estimates of other constituents of the surface runoff besides the COD concentration and fractions. Thus effort was made to obtain estimates of COD fractions in surface runoff in order to carry out the COD balance in the catchment.

5.2.2.1 Determining COD fractions of surface runoff

The nature of pollutants and the resulting pollutant load in stormwater infiltration depends mainly on the prevailing degree of air and surface pollution. Thus COD fractionation of stormwater infiltration will be site specific. However an assumption was made in this study concerning the transferability of COD fractions from one case study to another since there was no direct way of estimating the COD fractions for stormwater in the Verulam WWTP catchment. The results from a study carried out by Zawilski et al. (2009) were used as estimates for the COD fractions for the stormwater flowing into Verulam WWTP. In the study by Zawilski et al. (2009) the variability of the dry and wet weather wastewater composition for a particular wastewater treatment plant receiving combined sewage was investigated and the percentage contribution of particular fractions in the total COD of wet weather wastewater was determined. During the rainy season a significant increase in the inert and particulate COD fractions was observed in the wastewater and this increase can be attributed to stormwater bringing in more particulates and inert material as it runs off different surfaces of the catchment. Since there was no other source of estimates for COD fractions of stormwater in South Africa and beyond, the study by Zawilski et al. (2009) provided the closest estimate of COD fractions.

5.2.3 Determining composition of domestic wastewater from households

No measurements were available for the composition of domestic wastewater from households in the WWTP catchment since it was not feasible to locate a sampling point where all the domestic effluent from the catchment passes through before combining with the industrial effluent from the factories.

5.2.3.1 Determining COD fractions of domestic wastewater

COD fractions of different domestic wastewaters from different countries have been investigated in a number of studies (Hydromantis, 2007; Ekama et al., 1986; Kappeler and Gujer, 1992; Henze, 1992; Wichern et al., 2003; Melcer et al., 2003 and others). The estimate of the COD fractions of the domestic wastewater stream in the Verulam WWTP catchment was obtained from Ekama et al. (1986) where the average COD fractionation of South African wastewater is given.

5.2.4 Determining composition of the combined wastewater

Historical data of the composition of the combined influent wastewater were available from the WWTP database. Influent wastewater composite samples are collected at the head of works (WWTP inlet) for the purpose of assessing the wastewater characteristics before treatment. An average of eight composite samples per month are collected and analysed for colour, free and saline ammonia, COD, pH , permanganate value (PV4), settleable solids and suspended solids.

5.2.4.1 Determining COD fractions of the combined wastewater

After identifying the major contributors of wastewater in the Verulam catchment, estimating the average COD concentration of each contributing stream and COD fractions, a combined flow and component (COD) balance was carried out in order to come up with the COD fractionations of the combined wastewater stream received at the WWTP.

5.2.5 Determining the COD load distribution at Verulam WWTP catchment

The COD load distribution within the Verulam WWTP catchment was determined from the wastewater-flow data and wastewater COD for each identified major contributor. The annual flow weighted COD contributions in the Verulam WWTP catchment were obtained as the product of annual wastewater volume and the average COD of the particular wastewater stream. The average COD values for the industrial effluent streams were obtained from one data set comprising of samples collected in 2010 and 2011 since the COD data was limited to a few samples (less than 12 samples) during the period of 2010-2011. The obtained COD average values were then used for the calculation of the flow weighted contributions for both years (2010 and 2011). Attempting to determine an average value for each separate year would have meant that only two COD values would be used to calculate the average COD for each stream for the year 2010 since the information available was limited to two results

5.3 Determining other ASM1 influent wastewater components

No historical measurements were available for inert particulate organic matter produced from biomass decay X_P, autotrophic active biomass X_{BA}, slowly biodegradable organic nitrogen X_{ND}, alkalinity $S_{ALK,}$ readily biodegradable organic nitrogen S_{ND}, nitrate + nitrite nitrogen S_{NO} and dissolved oxygen S_O.

Particulate products of biomass decay (X_P) and autotrophic biomass (X_{BA}) are considered to be of negligible concentration in the influent wastewater (Henze et al., 2000). The values for S_{NO}, S_{ND} and X_{ND} in the influent wastewater were estimated by assuming that the influent wastewater at Verulam WWTP can be classified as medium strength raw municipal wastewater based on the average measured values of free ammonia and total suspended solids. The typical concentrations of S_{NO}, and combined (S_{ND}+X_{ND}) in medium strength raw municipal wastewater were obtained from Henze, (2008). S_{NO} is given explicitly given as 0.2 mg/L, while S_{ND} and X_{ND} were obtained from the typical concentration of organic nitrogen (S_{ND} + X_{ND}) in medium strength raw municipal wastewater in Henze, (2008). The organic nitrogen is the sum of S_{ND} and X_{ND}. Henze, (2008) reports a value of 10 mg/L for the organic nitrogen in medium strength raw municipal wastewater receiving minor contributions of industrial wastewater. Assuming that the readily and slowly biodegradable organic fraction in the influent wastewater is proportioned in the same way as the readily and slowly biodegradable COD in the influent then the following equation can be used to estimate S_{ND} (Henze et al., 1987).

$$\frac{S_{ND}}{X_{ND} + S_{ND}} = \frac{S_S}{X_S + S_S}$$

Knowing the total organic nitrogen (S_{ND} + X_{ND}) and the COD fractions (X_S+S_S) S_{ND} and X_{ND} can be estimated. Table 5.2 identifies the additional components in the influent wastewater and gives information on how each component was estimated to represent the influent characteristics of the influent at Verulam WWTP.

Table 5.2 Influent wastewater components in ASM1 excluding COD fractions quantified by experiment

Symbol	Component	Source of values
X_P	Inert particulate organic matter produced from biomass decay	Assume that concentration is negligible (Henze et al., 2000)
X_{BA}	Autotrophic active biomass	Assume that concentration is negligible (Henze et al., 2000)
X_{ND}	Slowly biodegradable organic nitrogen	Estimated using (Henze, 2008;Henze et al., 1987)
S_{ALK}	Alkalinity	Estimated from typical values measured at other similar WWTPs, since no measurements were available
S_{ND}	Readily biodegradable organic nitrogen	Estimated using (Henze, 2008; Henze et al., 1987)
S_{NO}	Nitrate + nitrite nitrogen	Assumed the concentration of medium strength raw municipal wastewater with minor contributions of industrial wastewater (Henze,2008)
S_{NH}	Ammonia nitrogen	Obtained from historical data measured at the WWTP
S_O	Dissolved oxygen	Estimated from typical values measured at other similar WWTPs, since no measurements were available

5.4 Results

The results of the above mentioned steps of wastewater charaterisation are presented in the following sections.

5.4.1 Characteristics of industrial wastewater in Verulam WWTP catchment

Table 5.3 presents the characteristics of industrial wastewater streams discharged by factories located in the catchment of Verulam WWTP. The complete data set is presented in in the Annexure on the CD accompanying the thesis.

Table 5.3 Mean wastewater-characteristics of streams in Verulam WWTP catchment for 2010 and 2011

	JMV Textiles	Nampak	Frimax Foods	Packo	Colgate Palmolive	Budget Soap
No of samples	9	9	11	7	10	11
Physical properties						
Settleable Solids (mL/L)	<1	2	30	1	2	<1
Suspended solids (mg/L)	-	223	-	-	-	-
Vegetable oils (mg/L)	-	-	110	163	65	7
Conductivity (mS/m)	458	122	98	251	781	449
pH	8.6	8.0	9.1	7.8	8.00	8.3
Chemical properties						
COD (mg/L)	885	2 333	1 993	1 203	4 910	344
Sugar (mg/L)	-	-	56	36	-	-
Sulphate (mg/L)	1 799	44	60	15	-	-
Sulphide mg/L)	187	130	-	7	-	-

- No measurements available

The composition data available for the contributing streams in the Verulam catchment were limited to results obtained from analysing a few samples per year (<15 samples) which were collected by municipal inspectors monitoring the trade-effluent-quality of the trade effluent discharged by the factories into the municipal sewer network. The available data was from the years 2010 and 2011. No data were available for the year 2009. Grab samples are collected by municipal inspectors from the factories and tested for nine parameters. Not all nine parameters are tested for in each sample that is collected. Each sample is tested for those parameters that are considered to be present in high concentrations and of importance for that particular factory trade effluent.

COD concentration is measured in all the wastewater streams from all the factories. However the frequency of sampling and testing of samples is very low (between 9 and 11 samples for the 2010-2011 period). Daily average COD concentrations from each factory trade effluent stream were required to complete the catchment COD balance.

5.4.1.1 COD concentrations of industrial wastewater streams

The values of average COD of each trade effluent stream are presented in the Table 5.3. The descriptive statistics of the available measurements is presented in Table 5.4 and the raw data is presented in Appendix E. The standard deviations presented in Table 5.4 show that the COD measurements exhibit significant deviation from the calculated means. The most likely reason for this significant deviation is the limited number of samples and also the fact that samples that were tested were grab samples collected at different times of the day. The grab samples are not the best representative of the daily average COD concentration of the wastewater streams.

5.4.2 Concentrations of other components in industrial wastewater streams

The wastewater samples from the factories are also tested for other components which are expected to be significant or problematic during wastewater treatment. A summary of the measurements is presented in Table 5.3. The descriptive statistics of the available measurements for the wastewater components is presented in Table 5.4 and the raw data is presented in Appendix E.

The measurements presented in

Table 5.3 show that Frimax Foods has the highest concentration of settleable solids (30 mL/L). Effluent from Nampak is the only factory effluent whose suspended solids are measured. The average suspended solids concentration is 223 mg/L. The food factories, Frimax Foods and Packo discharge trade effluent with the highest concentration of vegetable oil since they use vegetable oil to prepare food products. Conductivity is highest in the effluent from Colgate Palmolive followed by Budget Soap. Both these factories manufacture soaps and detergents hence the relative high
concentrations of conductivity. The concentration of sugars in industrial effluent is only monitored in the effluent from the food industries, Frimax Foods and Packo. The highest concentration of sulphates and sulphides are found in the textile effluent from JMV Textiles.

The descriptive statistics of the pollutants measured in the different streams of industrial wastewater from factories show the mean and standard deviations of the data. The number of samples for the measurements is indicated. The limited number of measurements calls for caution in interpretation of the mean and could be the reason for high standard deviations observed in some on the measurements.

Table 5.4 Descriptive statistics of components present in factory grab samples (2010 and 2011)

	JMV	Nampak	Frimax Foods	Packo	Colgate Palmolive	Budget Soap
COD						
No. of Samples (-)	9	9	11	9	10	11
Mean (mg/L)	885	2 333	1 993	885	4 910	344
Standard deviation (mg/L)	707	1 172	2 087	707	4 767	260
Conductivity						
No. of Samples (-)	9	9	11	5	10	11
Mean (mg/L)	458	122	98	251	781	449
Standard deviation (mg/L)	599	14	44	91	338	405
Settleable Solids						
No. of Samples (-)	9	9	11	7	10	11
Mean (mg/L)	0.3	1.6	29.5	1.2	1.8	0.3
Standard deviation (mg/L)	1.0	3.2	21.5	2.2	2.9	0.7
Suspended solids						
No. of Samples (-)		9				
Mean (mg/L)		223				
Standard deviation (mg/L)		151				
Sugar						
No. of Samples (-)			11	5		
Mean (mg/L)			56	36		
Standard deviation (mg/L)			57	39		
pH						
No. of Samples (-)	9	9	11	5	10	11
Median	9	8	10	8	8	9
Sulphate						
No. of Samples (-)	9	9	11	5		
Mean (mg/L)	1799	40	60	15		
Standard deviation (mg/L)	2952	34	102	7		
Sulphide						
No. of Samples (-)	9	9		5		
Mean (mg/L)	187	130		7		
Standard deviation (mg/L)	217	121		4		
Vegetable oils						
No. of Samples (-)			8	9	7	8
Mean (mg/L)			110	3288	65	7
Standard deviation (mg/L)			269	5648	35	7
Colour						
No. of Samples (-)	9					
Mean (mg/L)	3288					
Standard deviation (mg/L)	151					

5.4.3 Results of Monte Carlo simulations-daily COD values of industrial effluent

A summary of results from fitting distributions to the measured COD data for each factory is presented in this section. The results from the distribution fitting exercise are presented in the form of graphs and statistics measuring the goodness-of-fit of the fitted probability distributions. Since the structure of the results obtained for the different factories is similar, only the results obtained for JMV Textiles are presented in this chapter. The results obtained from other factories are presented in detail in Appendix C 2. A summary is provided in this chapter. Table 5.5 shows the top five distributions fitted to measured COD data from the JMV Textiles.

Table 5.5 Ranking of probability distributions fitted to daily average trade effluent volumes for JMV Textiles

Rank	Distribution	Kolmogorov-Smirnov statistic
1	Weibull	0.1435
2	LogLogistic	0.1548
3	Gamma	0.1623
4	Triangular	0.1983
5	Rayleigh	0.2118

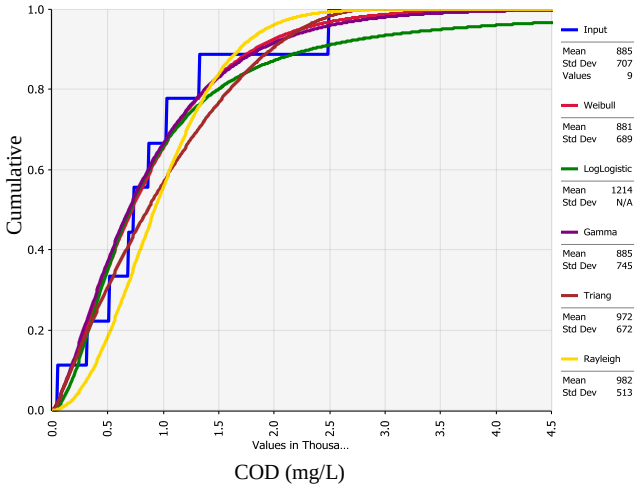
Based on the K-S statistic, the best distribution fits for the measured COD of trade effluent from each factory were the Weibull for JMV Textiles, Triangular for Nampak, Pearson6 for Frimax Foods, Rayleigh for Packo, Betageneral for Colgate Palmolive and Gamma distribution for Budget Soap. The selection of the best distribution in this exercise does not imply that these are the absolute best fits since the conditions of the whole distribution fitting exercise were far from ideal. The above presented results were accepted for the purpose of continuity in the investigation to determine how well or how bad it is to use the Monte Carlo simulations based on distributions obtained from limited measured data.

Figure 5.1 to Figure 5.6 show different plots (cumulative distribution functions (CDFs), probability distribution functions (PDFs), Q-Q plots, and P-P plots) of results obtained from the distribution fitting exercise for the case of JMV Textiles. The plots corresponding to the cases of the rest of the factories are presented in Appendix C2 where the cumulative distribution functions and the probability distribution functions of the top five distributions (based on the K-S statistic) that fit the data from each factory are presented. The Q-Q and P-P plots of the best fitting distribution are also presented.

The CFDs and PDFs of the top five fitted distributions for each factory appear to fit the data to almost the same goodness of fit. The best fitted distribution in each case is set apart from the other distributions

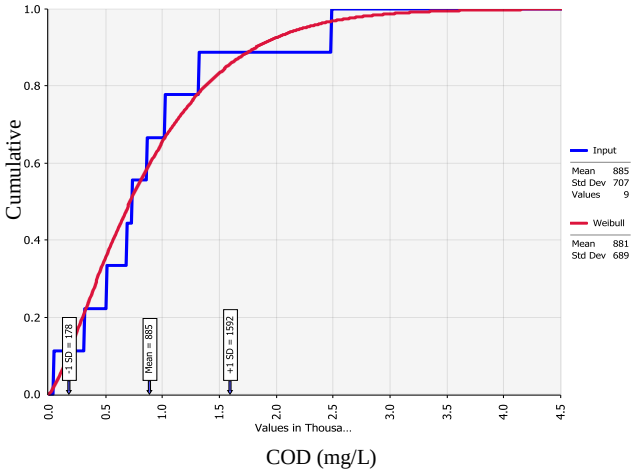
by its K-S statistic more than its ability to fit the data better than other distributions. The basic idea behind the Q-Q plot is to compare statistically expected value for each data point based on the distribution and the measured data. The observed P-P plots exhibit similar patterns and variations as the Q-Q plots.

Distribution fitting results for daily COD from JMV Textiles



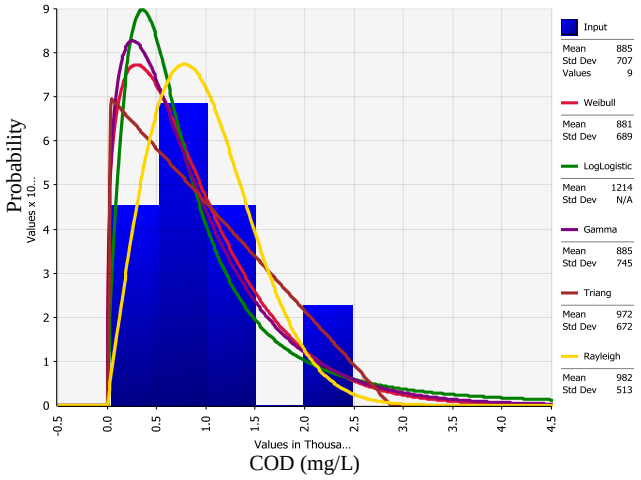
COD (mg/L)

Figure 5.1 Fit comparison of CDFs for daily COD concentrations for JMV Textiles, for top 5 distributions



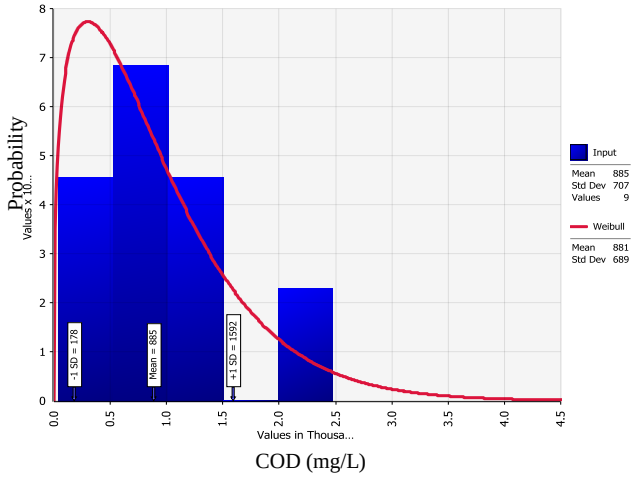
COD (mg/L)

Figure 5.2 CDF for daily COD concentrations for JMV Textiles, for top ranking distribution (Weibull)



COD (mg/L)

Figure 5.3 Fit comparison of PDFs for daily COD concentrations for JMV Textiles, for top 5 distributions



COD (mg/L)

Figure 5.4 PDF for daily COD concentrations for JMV Textiles, for top ranking distribution (Weibull)

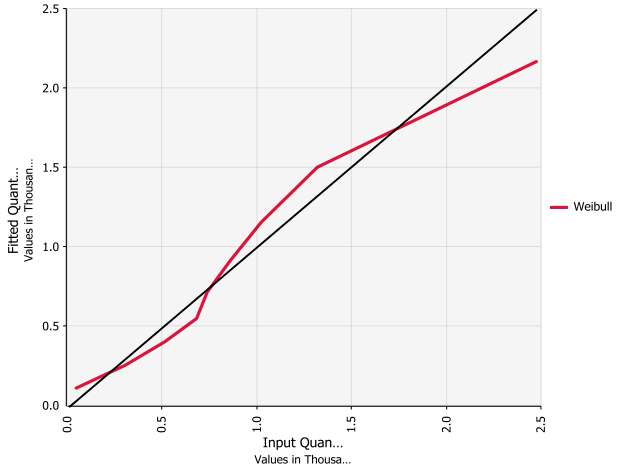


Figure 5.5 Q-Q plot for Weibull distribution

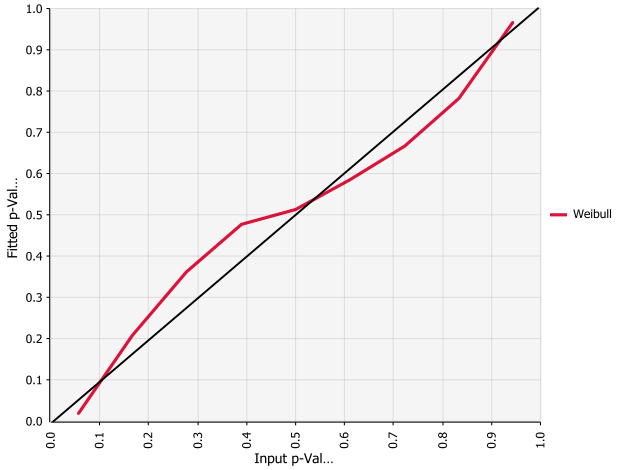


Figure 5.6 P-P plot Weibull distribution

5.4.4 Composition of surface run-off

Other studies on runoff quality focusing on case studies outside South Africa were also reviewed. The runoff quality found in other literature sources is presented in Table 5.6.

Table 5.6 Stormwater concentration levels for principal pollutants (Langeveld et al.,2012)

		Boogaard and Lemmen (2007)[a]	**Bratieres et al., (2008)[b]**	**Salvia-Castellvi et al. (2005)[c]**	**Fuchs et al. (2004)[c]**	**Daligault et al. (1999)[e]**	**Boogaard and Lemmen (2007)[a]**	**Bratieres et al., (2008)[b]**
		Dutch data mean (median-90 percentile	**Worldwide and Australian**	**Mean EMC St. Quirin (min-max)**	**Mean EMC Rte d'Esch (min-max)**	**Median (25-75 percentile**	**Dutch data mean (median-90 percentile**	**Worldwide and Australian**
TSS	mg/L	49 (20-150)	150	592 (30-500)	131 (30-300)	141 (74-280)	158 (11-458)	199 (25-964)
BOD	mg/L	6.7 (4.0-14)	-	335 (8-1 300)	30 (5-90)	13 (8-20)	10 (3-29)	17 (4-168)
COD	mg/L	61 (32-110)	-	1 152 (30-4 800)	138 (25-400)	81 (5-113)	68 (18-299)	121 (26-561)
TKN	mg/L	2.8 (1.7-5.2)	2.1	7.4 (1-24)	2.3 (0.6-7.8)	2.4 (2.1-5.8)	2.8 (1-12)	4.7 (1-50)
TP	mg/L	0.42 (0.26-0.97)	0.35	3 (0.3-12)	0.7 (0.2-2)	0.42 (0.24-0.70)	0.56 (0.3-4.7)	1.1 (0.3-19.1)
Pb	µg/L	33 (12-75)	140	80 (20-130)	50 (20-90	118 (46-239)	52 (2-210)	69 (4-404)
Zn	µg/L	194 (95-450)	250	3 330 (80-11 700)	1 170 (500-4 100)	275 (128-502)	607 (210-2 900)	146 (30-640)
Cu	µg/L	26 (10-47)	50	170 (40-500)	70 (30-200)	48 (28-110)	23 (7-59)	24 (6-52)
E.coli	#/100mL	3.4E+4 (1E+4-1E+5)	-	-	-	-	-	-

a. Dutch STOWA database (version 2.6, 2007), based on data of 10 monitoring projects in the Netherlands, residential and commercial areas, with *n* ranging from 26 (SS) to 169 (Zn).

b. 'Typical' pollutant concentrations based on review of worldwide (Duncan, 1999) and Melbourne (Taylor et al., 2005) data.

c. 2 monitoring locations in Luxembourg, residential areas, *n* = 11 per location. Location St. Quirin is reported to have significant illicit connections to the storm sewer.

d. ATV database, like Duncan (1999) partly based on the US EPA nationwide runoff programme (NURP), with *n* ranging from 17 (TKN) to 178 (SS).

e Brunoy: 55% educational and sporting infrastructures, 45% residential, Vigneux, residential, *n* = 30 per location.

Given the lack of rainfall intensity data, runoff sampling and runoff quality monitoring data for the Verulam catchment, estimating the runoff quality flowing into Verulam WWTP became a difficult task. The lack of description of such factors as land use, extent of impervious areas and hydrology and other relevant site characteristics of the study sites in some of the literature sources, made it impossible to find a catchment that was closely comparable to the Verulam catchment on which runoff volumes and composition would be based on. At the end the best available estimates for component for runoff composition were obtained from Langeveld et al. (2012). An average COD concentration of 81 mg/L was selected from Langeveld et al., 2012. The selected value was from the work of Fuchs et al. (2004). It is appreciated that COD concentration of runoff is site specific. This assumed value was used in this case because there was no estimate or measurement available to fill in this requirement to demonstrate the proposed methodology. This decision forms part of the assumptions made for the method to work and would remain a source of uncertainty until a correct value is found.

5.4.5 COD concentration in domestic wastewater

The approximate average COD for raw municipal domestic influent wastewater in South Africa is between 500 and 800 mg/L (WRC, 1994). A value of 800 mg/L was selected for the domestic wastewater in the Verulam WWTP catchment after evaluating the COD load balance within the catchment.

5.4.6 Composition of combined wastewater at the WWTP inlet

The variability of the composition of the influent wastewater received at Verulam WWTP during the year and for different years (2010, 2011 and 2012) is graphically displayed in box and whisker plots (Figure 5.8 to Figure 5.14). The box and whisker plots contain the following information: The median value shows that 50 percent of the data are larger than this value and 50 percent of the data are less than this value, the 25^{th} percentile or lower quartile shows that 25 percent of the data are less than this value and the 75^{th} percentile or upper quartile shows that 75 percent of the data are less than this value. The interquartile range (IQR) contains the values between the 25^{th} and 75^{th} percentiles and is the difference between the 25^{th} and 75^{th} percentiles. The bottom and the top whisker in the boxplot mark the minimum and maximum values respectively.

The marked minimum value is considered to be the smallest value within 1.5 times the IQR of the box while the marked maximum value is considered as the largest value within 1.5 times the IQR of the box. Outliers are values that lie more than 1.5 times the IQR from either end of the box while the outsiders are values that lie more than 3 times the IQR from ether end of the box (Tukey, 1977). The box and whisker plots for the influent wastewater composition data for the period of 2010 to 2012 are shown in

Figure 5.8 to Figure 5.14. Only maximum and minimum value for outliers and outsiders are plotted in the box and whisker charts.

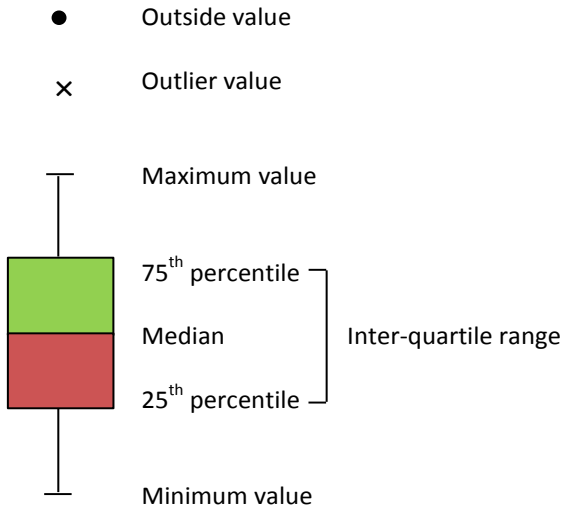


Figure 5.7 Example of box and whisker plox

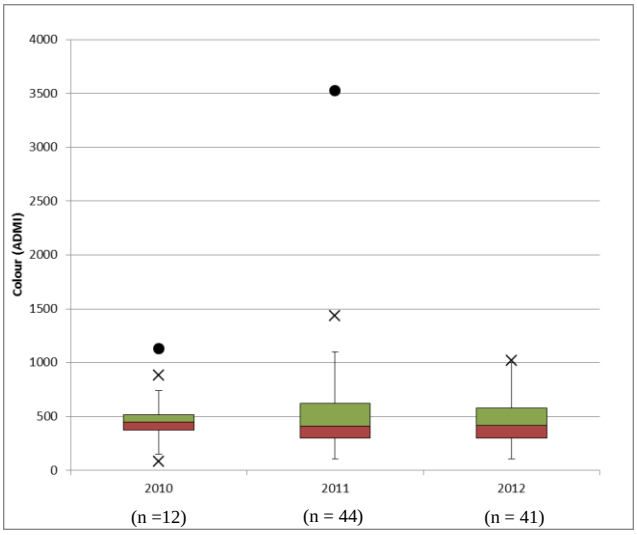


Figure 5.8 Variation of influent wastewater colour (2010-2012)

The number of influent wastewater samples collected for colour measurements were 12, 44 and 41 for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 475, 545 and 1121 ADMI respectively. The significant increase in the mean value in 2012 can be linked to the high colour measurements recorded during this period. The median values for the 3 consecutive years were 447, 410 and 415 ADMI. For the year 2010, 3 outlier values and 1 outside value were recorded while 2 outliers and 1 outside values are reported for 2011. 2 outlier and 3 outside values are reported for 2012. The maximum outliers recorded were 880, 1435 and 1020 ADMI, while the maximum outside values were 1130, 3530 and 21300 ADMI for the 3 consecutive years, respectively. The maximum outside value of 21 300 ADMI for 2012 was excluded from the boxplot to preserve the clarity of the boxplot chart. This extremely high value could be an indication of an unreliable laboratory measurement or a sudden discharge of wastewater with high concentration of dyes from the textile factory.

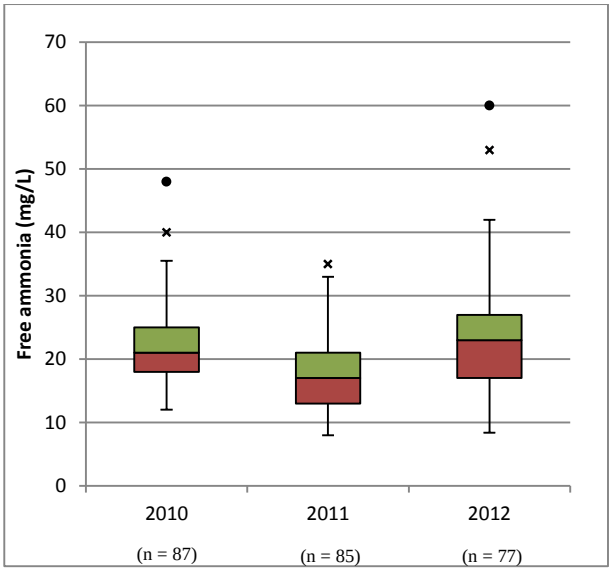


Figure 5.9 Variation of influent wastewater ammonia (2010-2012)

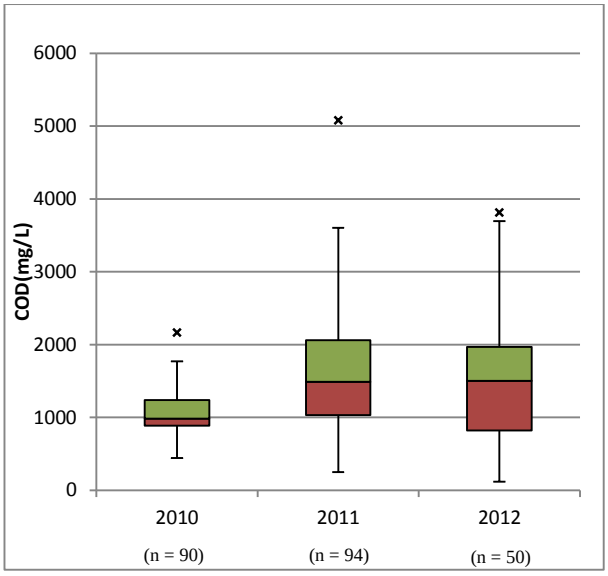


Figure 5.10 Variation of influent wastewater COD (2010-2012)

The number of influent wastewater samples collected for free ammonia measurements were 87, 85 and 77 for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 22, 18 and 24 mg/L respectively. The median values for the 3 consecutive years were 21, 17 and 24 mg/L For the year 2010, 3 outlier values and 1 outside value are reported for 2010 while 1 outlier and no outside values are reported for 2011. 1 outlier and 1 outside values are reported for 2012. The maximum outliers recorded were 40, 35 and 53 mg/L, while the maximum outside values was 48 and 60 mg/L for the year 2010 and 2012.

The number of influent wastewater samples collected for COD measurements were 90, 94 and 50 for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 1085, 1580 and 1547 mg/L respectively. The median values for the 3 consecutive years were 982, 1488 and 1504 mg/L For the year 2010, 6 outlier values and no outside values are reported for 2010 while 2 outlier and no outside values are reported for 2011. One outlier and no outside values are reported for 2012. The maximum outliers recorded were 2168, 5080 and 3816 mg/L for the 3 consecutive years, respectively.

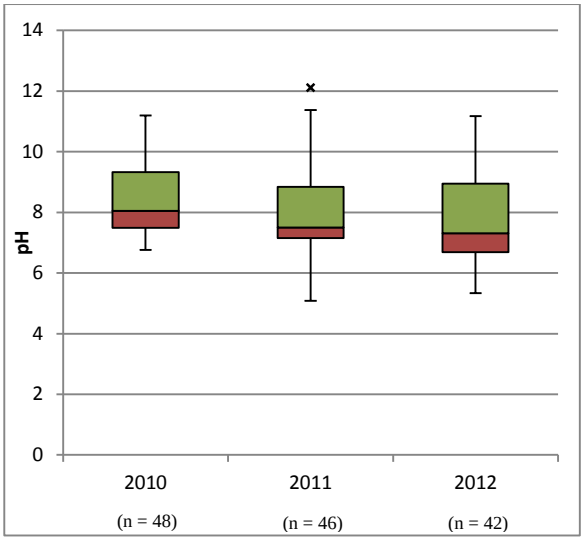


Figure 5.11 Variation of influent wastewater pH (2010-2012)

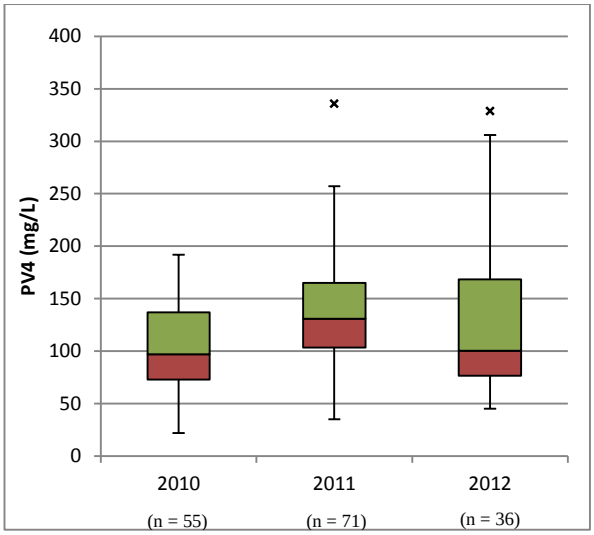


Figure 5.12 Variation of influent wastewater PV4 (2010-2012)

The number of influent wastewater samples collected for free ammonia measurements were 48, 46 and 42 for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 8 for all the years. The median values for the 3 consecutive years were 8, 8, and 7. For the year 2010 and 2012, no outlier or outside values were recorded. 3outlier and no outside values are recorded for 2011.The maximum outlier recorded in 2011 was a pH of 12.

The number of influent wastewater samples collected for PV4 measurements were 55, 71 and 36 for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 103, 132and 127 mg/L respectively. The median values for the 3 consecutive years were 97, 131 and 101 mg/L. For the year 2010 no outlier or outside values were recorded while 1 outlier and no outside values are reported for 2011. 1 outlier and no outside values were recorded for 2012. The maximum outliers recorded for 2011 and 2012 are 336 and 329 mg/L respectively.

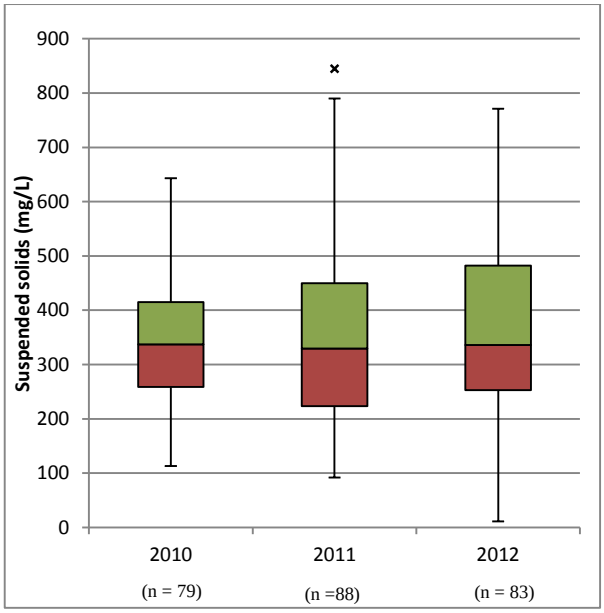


Figure 5.13 Variation of influent wastewater suspended solids (2010-2012)

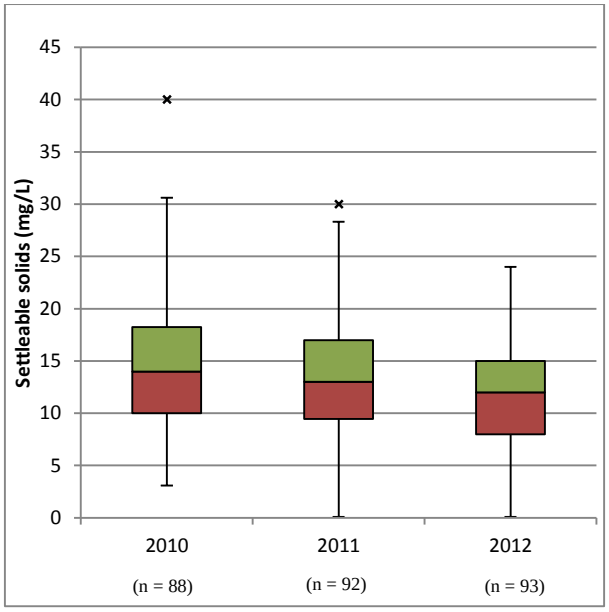


Figure 5.14 Variation of influent wastewater settleable solids (2010-2012)

The number of influent wastewater samples collected for suspended solids measurements were 79, 88 and 83 for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 353,344 and 365 mg/L respectively. The median values for the 3 consecutive years were 337,330 and 336 mg/L. For the year 2010 and 2012, no outlier and outside values were recorded. One outlier and no outside values were recorded in 2011. The maximum outlier recorded in 2011 is 885 mg/L.

The number of influent wastewater samples collected for settleable solids were 88, 92 and 93 mg/L for the years 2010, 2011 and 2012 respectively. The corresponding values for the mean were 15, 13 and 11 mg/L respectively. The median values for the 3 consecutive years were 14, 13 and 12 mg/L. For the year 2010, 5 outliers and no outside values were recorded, and for 2011 one outlier no outsiders values were recorded. No outlier and outside values were recorded in 2012. The maximum outlier values recorded in 2010 and 2011 are 40 and 30 mg/L respectively. A summary of the statistics of the influent wastewater composition is also presented in Table 5.7.

Table 5.7 Characteristics of influent wastewater received at the head of works in Verulam WWTP

Component (units)	Statistics	Year 2010	Year 2011	Year 2012
Colour (ADMI)	Mean	475	545	1121
	Range	80-1130	109-3530	108-21300
	No.of samples	12	44	41
Free ammonia (mg N/L)	Mean	22	18	24
	Range	12-48	8-35	8-60
	No.of samples	87	85	77
COD (mg/L)	Mean	1085	1580	1547
	Range	444-2168	248-5080	120-3816
	No.of samples	90	94	50
Settleable solids (ml/L)	Mean	15	13	11
	Range	3-40	0.1-30	0.1-24
	No.of samples	88	92	93
Suspended solids (mg/L)	Mean	353	344	365
	Range	113-643	92-845	11-771
	No.of samples	79	88	83
pH	Median	8	8	7
	Range	7-11	5.08-12.11	5-11
	No.of samples	48	46	42
PV4 (mg/L)	Mean	103	132	127
	Range	22-192	35-336	45-329
	No.of samples	55	71	36

Table 5.8 compares the average values of COD, Free ammonia, and total suspended solids for the Verulam WWTP influent wastewater to typical concentration values found in raw municipal wastewater with minor contributions of industrial wastewater as specified in Henze (2008).

Table 5.8 Typical composition of raw municipal wastewater with minor contributions of industrial wastewater (Henze, 2008) and average composition of Verulam WWTP influent

	Typical composition of raw municipal waste water with minor contributions of industrial wastewater				Average of Composition of Verulam WWTP influent		
					2010	2011	2012
Parameter	**Units**	**High**	**Medium**	**Low**	**Mean**	**Mean**	**Mean**
COD total	mg/L	1 200	750	500	1 085	1 580	1 547
Ammonia-N	mg/L	75	45	20	22	18	24
TSS	mg/L	600	400	250	353	344	365
VSS	mg/L	480	320	200	-	-	-
BOD	mg/L	560	350	230	-	-	-
TKN	mg/L	100	60	30	-	-	-

-No measurements were available to determine range or mean

The average of the measured influent wastewater COD falls in the range specified for high strength raw municipal wastewater with minor contributions of industrial wastewater. While the average values of the measured free ammonia and total suspended solids fall in the range specified for medium strength raw municipal wastewater with minor contributions of industrial wastewater.

5.4.7 COD load contributions in the Verulam WWTP catchment

The values of the COD load obtained for the year 2010 and 2011 are presented in Table 5.9.

Table 5.9: Annual Flow weighted COD contributions of major factories in the catchment for Verulam WWTP for the year 2010/11

	2010				2011			
Source	**Trade effluent (m^3/y)**	**Average COD (mg/L)**	**Trade effluent × Average COD (kg/y)**	**% contribution**	**Trade effluent (m^3/y)**	**Average COD (mg/L)**	**Trade effluent × Average COD (kg/y)**	**% contribution**
JMV	176 630	885	156 298	8.2	155 664	885	137 745	6.4
Nampak	86 391	2 333	201 560	10.5	118 874	2 333	277 346	12.9
Frimax Foods	29 594	1 993	58 981	3.1	34 775	1 993	69 307	3.2
Packo	19 949	1 203	23 999	1.3	22 283	1 203	26 806	1.2
Colgate Palmolive	16 362	4 910	80 344	4.2	12 108	4 910	59 455	2.8
Budget Soap	1 201	344	413	0.02	1 276	344	439	0.02
Industrial effluent			521 594	27.2			571 099	26.6
Domestic homes	1 740 444	800	1 392 355	72.2	1 971 704	800	1 577 363	73.4
Storm water infiltration	70 748	81	5 731	0.5	140 138	81	11 351	0.5
Total			**1 919 680**	**100**			**2 159 813**	**100**
Measured plant data	**2 400 698**	**1085**	**2 605 531**		**2 661 664**	**1580**	**4 205 514**	

The information presented in Table 5.9 shows that among the factories in the catchment, Nampak Tissue and JMV Textiles contribute the highest proportion of COD into Verulam WWTP with values for 2010 showing that 10.5% and 8.2 % of the COD load was from Nampak and JMV Textiles respectively. In 2011 the ranking of factories based on their contribution to the total COD load received at WWTP was similar to the ranking in 2010 and the contributions were 12.9% and 6.4 % for Nampak and JMV Textiles. The rest of the industrial COD load comes from the smaller factories, Frimax Foods, Budget Soap, Colgate Palmolive and Packo. Using the estimated average COD of 800 mg/L for domestic effluent the households in the Verulam catchment appear to have contributed contribute 72.5% and 73.0 % of the total COD received at the WWTP in 2010 and 2011 respectively. The corresponding contributions of the industrial effluent to the total COD load are approximately 27% for 2009 and 2010. The wastewater stream with the least COD concentration in the catchment is the stormwater infiltration. Strom water infiltration estimated to have an average COD concentration of 81 mg/L contributed less than 1 % of the total COD load in 2010 and 2011.

When the total COD load which was obtained by summing up the individual contributions from the factories, stormwater and the households as explained above, was compared to the value determined as the product of the total volume of the wastewater received and the average COD obtained from averaging measured influent COD data collected by the municipal laboratory, a discrepancy was observed. The two values from the COD loads did not match. The sum of the individual contribution to the COD load was less than the load determined using the wastewater volume and the measured influent COD. The source of this discrepancy can be attributed to several factors, with reliability of the estimates made and some of the historical data being the most obvious factors.

The source of this discrepancy was thought to be related to the following factors:

- The average COD concentration of the industrial effluent streams from the factories were obtained from a limited number of samples (<15 samples)
- The average COD concentration of domestic wastewater was estimated from literature (Ekama et al., 1996;WRC, 1994). The actual COD concentration of domestic wastewater could have been higher or lower than the estimated value.
- The average COD concentration of the stormwater infiltration was estimated by using a value from literature (Langeveld et al., 2012) .The actual COD concentration of stormwater infiltration wastewater could have been higher or lower than the estimated value.
- The volumes of storm water infiltration were obtained from an over simplified mathematical model backed by a number of assumptions

In the end only the COD fractionation results were taken from the catchment balance, partly due to the observed discrepancies in the total figures. The basic strategy behind all this was to obtain the best estimate of the overall composition from a combination of all the disparate bits of information. Thus the measured influent total COD is clearly more reliable than the catchment balance estimate; however the measurement gives no information at all about the COD fractionation.

5.4.8 COD fractionation of wastewater streams in the Verulam catchment

The results showed that the accuracy of the COD fractions for these two streams had an insignificant impact of the overall modelling results. The estimates of the COD fractions and their literature sources used for the industrial effluent streams in the Verulam WWTP catchment are presented in Table 5.10.

5.4.8.1 COD fractionation domestic effluent

The COD fractions obtained from Ekama et al. (1986) are presented in Table 5.10.

5.4.8.2 COD fractionation stormwater infiltration

The estimated COD fractions of stormwater are presented in Table 5.10.

5.4.8.3 COD fractions of combined influent wastewater

Table 5.10 presents a summary of the estimates of the COD fractions present in the different wastewater streams that combine and flow into Verulam WWTP.

Table 5.10 Estimates of COD fractions in industrial wastewater streams in the Verulam catchment

	Percentage of total COD of each factory					
Factory	**S_S**	**S_I**	**X_S**	**X_I**	**X_H**	**Reference**
JMV Textiles	48.9	1.3	29.6	20.1	-	Ubay Cokgor, 1999
Colgate Palmolive	24.4	4.9	46.3	24.4	-	Brownell et al., 1975; Wang, 2005
Budget Soap	24.4	4.9	46.3	24.4	-	Brownell et al., 1975; Wang, 2005
Packo	77.6	5.8	16.9	-	-	Ubay Cokgor, 1997
Nampak	33	28	5	33	-	El-Fadel.2012
Frimax Foods	77.6	5.8	16.9	-	-	Ubay Cokgor, 1997
Storm water	21.3	5.8	49.7	23.3	-	Zawilski et al., 2009
Domestic wastewater	20	5	62	13	-	Ekama et al., 1986

- COD fraction considered negligible

The COD fractions of the combined wastewater stream received at Verulam WWTP were calculated using the wastewater flows for 2009, 2010 and 2011, and COD fractions presented in Table 5.10. The result is given in Table 5.11.

Table 5.11 COD fractions of combined influent wastewater in the Verulam WWTP

	Percentage of total COD				
Year	**S_S**	**S_I**	**X_S**	**X_I**	**X_H**
2009	31	5	49	14	0
2010	31	5	50	14	0
2011	33	5	49	13	0
Domestic wastewater (Ekama et al., 1986)	20	5	62	13	0

There was no significant difference in the COD fraction results obtained for the years 2009, 2010 and 2011. When the estimated COD fractions were compared with those for South African domestic wastewater, the comparison showed that the combined wastewater received at Verulam WWTP contained more slowly biodegradable COD, X_S and less readily biodegradable COD, S_S than purely domestic wastewater. Although the catchment balance estimated the total COD as well as its fractionation, the eventual model only used the COD fractionation, taking the total COD measured at the head of works.

5.5 Conclusion

The following conclusions on the methods used to generate flow data in the catchment can be drawn from the results that were obtained:

- Multiple linear regression can be used to a certain extent to come up with a simplified relationship between rainfall and stormwater infiltration. However the simplified approach is supported by a series of assumptions which result in the over simplification of the actual relationship between rainfall and stormwater infiltration.
- Monte Carlo simulations may be used to generate missing data based on assumed similarity of probability distributions. In the case where there is limited or insufficient measured data to define the underlying probability distributions, as was the case in this study, the results obtained from the Monte Carlo simulations tend to be less reliable compared to cases where sufficient data is available for distribution fitting.

Considering the diverse nature of industrial activities, geographic differences, various socio-political realities and other factors, it is clear that the COD fractions of wastewater from industries are case-specific. Accurate COD fractionation for any stream can only be obtained by sampling the particular wastewater stream and doing analysis on the samples. However since it is difficult and time consuming to fractionate the COD of different wastewaters experimentally, especially industrial wastewater, it would be useful if it were possible to have a way of estimating COD fractions from case studies dealing with similar wastewaters. This was the premise to proceeding with this approach of COD fractionation.

Thus, the COD fractions of wastewater from industries similar to the ones identified in the Verulam WWTP catchment were used as estimates for COD fractions of wastewater streams in the Verulam WWTP catchment. This was done after making an assumption that wastewaters from the same type of industry would have similar COD fractions. The results of searching for and reviewing literature source on the subjected showed, among other things, that COD fractionation has not been done on all wastewater types especially those of industrial origin. No estimates of complete COD fractionation were

available for the wastewater from the soap and detergent industries.

The ultimate justification of using the results from the catchment balance with so many assumptions was the statistical outputs of the overall catchment and the modelling of the WWTP using the results from the catchment balance. If the WWTP model is able to predict the measure values, this would mean that the assumptions were good enough. Since the catchment balance incorporated the factory contributions, the impact of the factory is included in the model predictions.

6 MODELLING VERULAM WWTP

This chapter presents the modelling of the Verulam WWTP using ASM1. The COD fractionation results estimated using the catchment balance approach were used together with other influent wastewater properties to complete the influent wastewater characterisation at Verulam WWTP. The details of the modelling effort are presented in the following sections.

6.1 Introduction

The purpose of the model to be developed would be of limited use considering how it was put together. The immediate purpose would be to run simulations to show the compliance or non-compliance of the final treated effluent to the effluent discharge standards, when a factory is introduced into a particular catchment. These results would inform the process of granting or declining an effluent wastewater discharge permit to the factory that intents to discharge into WWTP catchment. The simulations of the model will show whether the WWTP will continue to meet the effluent standards or not.

The results from modelling Verulam WWTP will, to a certain extent, show the feasibility of developing a model for a municipal WWTP using the data collected for routine monitoring of the plant operations and other information available at the WWTP without carrying out additional measurements that are usually carried out when more accurate model calibration is required. The purpose of the entire evaluation was to enable modellers working for the municipality to be able to model WWTPs using the data available at the different WWTPs and a few additional specialized experiments. Thus, it was not necessary to achieve detailed highly accurate predictions of the dynamic process behaviour in the WWTP, but rather predictions of the WWTP's performance statistics. Due to lack of some information required for modelling, some steps outlined in commonly used calibration protocols discussed earlier were not carried out in this particular modelling project. Certain assumptions were made so as to be able to proceed with modelling of the WWTP. Justifiable deviations from what is recommended by Good Modelling Practice (GMP) guidelines are discussed where relevant.

6.2 Layout of Verulam WWTP

The site of Verulam WWTP is made up of an old plant and a new plant. The layout of the units at Verulam WWTP is shown on Figure 6.1.

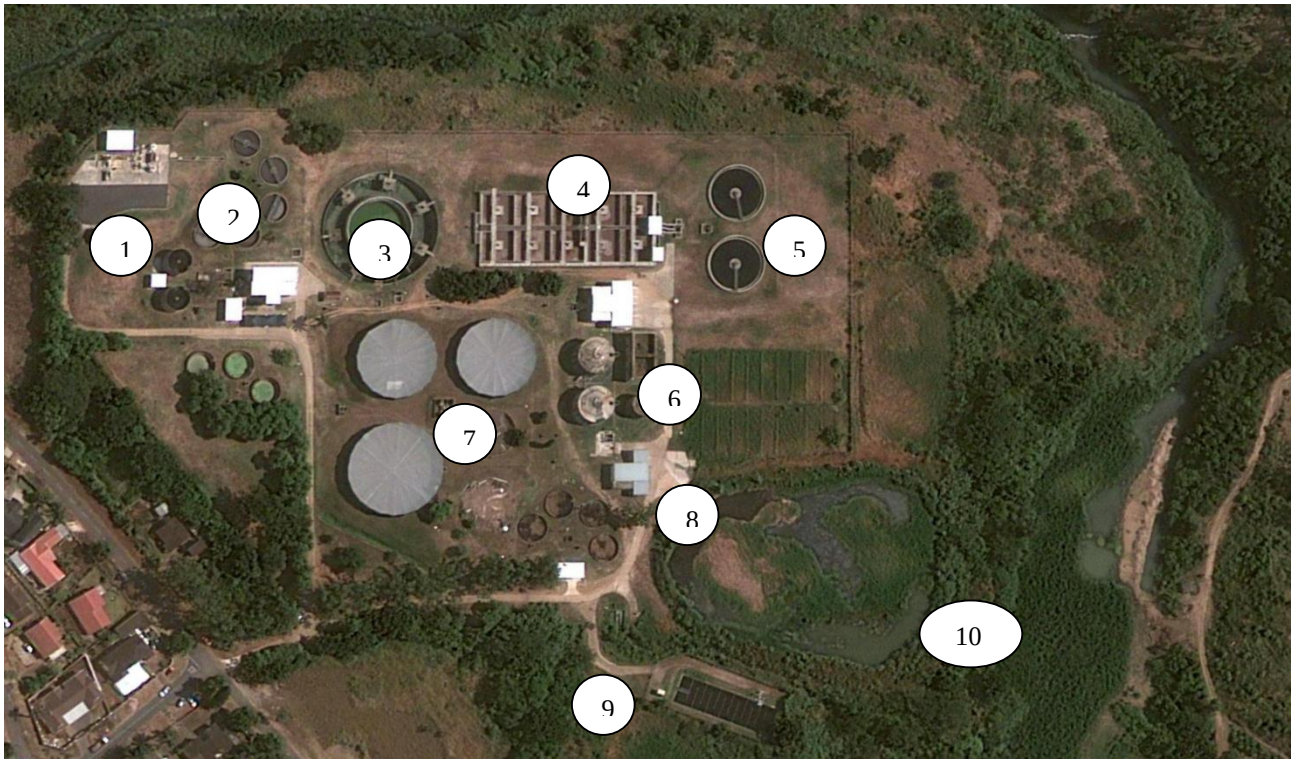


Figure 6.1 Aerial photograph of Verulam WWTP

1Inlet, screening and de-gritting	6 Anaerobic digesters
2 Primary settling tanks	7 De-commissioned trickling filters
3 Old 4 ML/d activated sludge plant	8 Chlorine contact tank
4 New 8 ML/d activated sludge plant	9 Treated effluent pond
5 Secondary clarifiers	10 River

The new activated sludge process has a design capacity of 8 ML/d. Before this new plant was built and commissioned, Verulam WWTP was made up of two plants, three high capacity trickling filters (7) and a 4 ML/d circular activated sludge plant (3). The trickling filters have since been decommissioned. The 4 ML/d activated sludge plant only operates when the influent wastewater exceeds 8 ML/d. Excess influent wastewater volumes are usually experienced during the rainy season. The excess influent wastewater is diverted from the inlet of the new 8 ML/d activated sludge plant to the 4 ML/d activated sludge plant. The treated effluent is chlorinated and pumped to a pond which discharges into the nearby river.

6.3 Process description of Verulam WWTP

The influent wastewater collected from the Verulam catchment enters the WWTP through a 600 mm diameter sewer pipe. The wastewater flows through a removable trash rack before going through the mechanical screens. This is done to protect the mechanical screens. The pumped works-domestic sewage is added before the wastewater passes through the automatic (10 mm bar gap) mechanically

raked retractable screens. Failure of the mechanical screens in position will cause flow to be diverted, due to the blinding of the screens, through the emergency bypass channel where there is a hand-raked (20 mm bar gap) emergency-bypass screen. A standby hand-raked retractable (20 mm bar gap) screen in the main channel is lowered into position in the event of failure and retraction of the mechanically raked screens. The removed screenings are dropped into a spiral conveyer that feeds the screenings to a washer which returns removed organics to the main channel and sends washed and compacted screenings to skip-storage. The wastewater is then passes to the grit removal facility.

6.3.1 Grit washing and removal

After screening, the wastewater flows down the concrete channel before the flow is split into the two vortex-degritters which remove the grit in the wastewater before it passes on to the next unit in the process. The washed grit is screw lifted from the base of the vortex-degritters and loaded to a skip.

6.3.2 Flow measurement and primary settlers

After the wastewater passes through the vortex degritters it enters the flow limiting control penstock that ensures that the flows entering the following process units never exceeds the design capacity of the plant. Excess stormwater flows are bypassed to the river through an overflow point upstream of the flow control penstock. A level sensor records times for which overflows occur. The wastewater that passes through the flow control penstock meets supernatant liquid (SNL) from the SNL sump before entering the distribution box for the five Dortmund primary settling tanks which separate the raw sludge from raw influent wastewater.

The raw sludge flows by gravity to the raw sludge pump station that feeds it to primary digesters. The overflow from the primary settling tanks flows by gravity to the activated sludge distribution chamber where two weirs in the chamber split the flow between the new 8 ML/d and old 4 ML/d activated sludge plants.

6.3.3 The new 8.5 ML/d activated sludge plant and secondary clarification facility

The 8 ML/d activated sludge plant was designed to be a 2-stage Bardenpho process, which can later be modified to a 5-stage Phoredox process (Cloete, 1997) by addition of an anaerobic cell upstream.

The standard Bardenpho process uses an anoxic cell at the head of the process followed by a standard BOD/nitrification process in an aerobic cell where BOD is converted to carbon dioxide, and ammonia to nitrates. Nitrate rich mixed liquor from the first aerobic cell is recycled to the head of the process. After the first aerobic cell another anoxic cell is used to reduce the dissolved oxygen and create de-nitrification. The final stage of the Bardenpho process is a re-aeration zone where the dissolved

oxygen concentration in the mixed liquor is increased to remove nitrogen gas and prevent phosphorus from being released in the final clarifier. The effluent then goes through another aerobic cell where the nitrogen gas is removed. The return activated sludge (RAS) is recycled from the secondary clarifier to the first anoxic cell.

The configuration of the activated sludge process at Verulam WWTP is different from the standard Bardenpho configuration. Nitrate rich mixed liquor from the first aerobic cell is not recycled to the head of the process. The configuration of the activated sludge process at Verulam WWTP is shown in Figure 6.2.

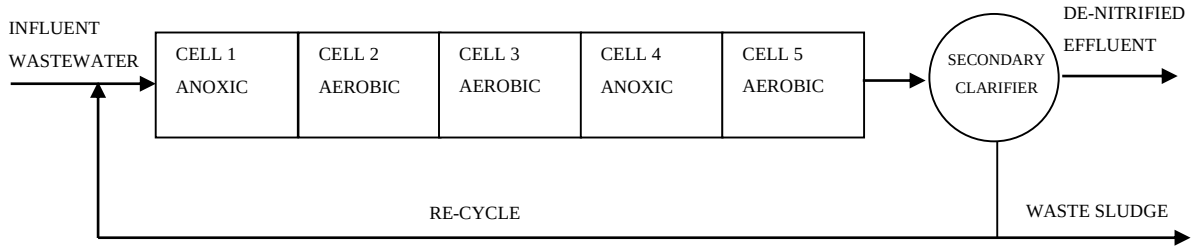


Figure 6.2 Configuration of Verulam WWTP

The aeration tank is made up of two identical lanes of five cells per lane. The first and fourth cells in each lane are anoxic. There is minimal turbulence in these cells, preventing biological settlement whilst keeping oxygen concentrations to a minimum with a low energy mixer. The second, third and fifth cells are aerobic, with 49 kW mechanical aerators in each cell.

A frequency inverter is used to set the rotational speed of each mechanical aerator. In cell 2, 3 and 5, the rotational speed of the aerators can be set to be proportional to the diurnal flow variation. As an alternative control option, dissolved oxygen measurement in cells 3 and 5 are recorded and compared with a set point, and the difference between the measured value and the set point is used by the frequency inverter to control the rotational speed of the mechanical aerators of cell 3 and 5 of each lane. The speed in cell 2 is manually set.

The return activated sludge is removed from the bottom of the secondary clarifiers by suction lift scrapers. It then flows, via pipe work and telescopic control valves, to the return activated sludge pump station sump. Two Archimedean screw pumps are used to return the activated sludge back into the central return sludge channel and then into the sludge lanes. Wasting of activated sludge is achieved through a gravity flow pipeline from the central return activated sludge channel. This waste activated sludge gravitates to the waste activated sludge (WAS) collection and dewatering facility.

6.3.3.1 The old 4 ML/d activated sludge plant

The 4 ML/d circular activated sludge plant has an initial anoxic zone with low energy mixer and then an aerobic zone with six mechanical aerators, and a central clarifier. The activated sludge overflows a weir at the end of the single circular lane and flows by gravity into the clarifier inlet chamber. Secondary effluent overflows the circumferential weir of the clarifier and flows by gravity to the chlorination facility. Settled biological sludge is removed from the bottom of the clarifier by suction lift scrapers. It then flows, via pipes and a telescopic control valve, into the return activated sludge sump that has a duty and standby submersible pump. The return activated sludge is pumped from this sump into a mixing chamber where it is mixed with the influent wastewater prior to entering the activated sludge reactor. The waste activated sludge portion is pumped from this sump to the WAS collection and dewatering facility.

6.3.3.2 The chlorination facility

The secondary effluent from the 4 ML/d and the 8 ML/d activated sludge plant clarifiers flows by gravity to the chlorination facility where the effluent is chlorinated in contact tanks before being discharged to the river via the treated effluent pond.

6.4 Materials and methods

The increased use of models in water management and increased co-operation between various players in the modelling field has resulted in the development of guidelines such as the Good Modelling Practice guidelines (STOWA/RIZA, 1999) to promote consistence in the assessment and comparison of simulation results. The IWA Task Group on Good Modelling Practice (GMP) has developed a framework to deal with the use of activated sludge models in modelling projects. The guidelines by the task group are based on the GMP Unified protocol and the GMP Application matrix (Rieger et al., 2012). The five steps of the GMP unified Protocol, which provide systematic approach for developing a process model are as follows:

1) Project definition
2) Data collection and reconciliation
3) Plant model set-up
4) Calibration and validation
5) Simulation and result interpretation

Effort was made to follow the guidelines of the GMP unified protocol in carrying out the modelling of Verulam WWTP. However, since the context of the modelling in this study was to rely on data collected for regular monitoring of the WWTP operations, alternative approaches had to be adopted in the modelling strategy. The methods adopted in each step recommended by the GMP unified protocol are presented in the following sections.

6.4.1 Project definition

The immediate purpose of the model developed would be to run simulations to show the compliance or non-compliance of the final treated effluent to the effluent discharge standards, when a factory is introduced into a particular catchment. Due to the data available for model the COD of the final effluent was the only parameter that could be used to evaluate the compliance of treated effluent to the discharge standards. The scope of modelling focused on the activated sludge process at Verulam WWTP. The expectations of the model would be to predict the WWTP's performance statistics rather than real time dynamics of an activated sludge system.

6.4.2 Data collection and reconciliation

The output of the data collection and reconciliation step is reconciled data for use in the subsequent steps of the modelling project. The desired quality and amount of data is closely related the purpose of the model. The input data has particular impact on the accuracy targeted in the model calibration step. The GMP guidelines highlight that data collection and reconciliation step is one of the steps that requires most of the effort in a modelling project and further emphasises the used of data of high quality in a process model (Rieger, 2013). In this modelling project, this particular step suffered the lack of some data that would have made it possible to adhere to the GMP guidelines.

6.4.2.1 Design and operational data

Design and operational data were obtained from the WWTP through consultation meetings with plant operators and the municipal engineers responsible for running Verulam WWTP. Historical plant records were reviewed for relevant data. Design specifications such as physical tank dimensions, piping and unit interconnections were provided by the process engineers in the form of drawings and process and instrumentation diagrams.

The operational data that were available were not entirely comprehensive. Several important variables that are usually required for model specification and calibration are not measured at Verulam WWTP. These include detailed sludge composition, TKN in influent wastewater and other process streams. Since the purpose of the study was to evaluate how far a WWTP can be modelled with limited information, the next step of setting up the model was taken even under the absence of some information.

The sizes of the units at Verulam WWTP are presented in Table 6.1. Operational data obtained from historical records from the WWTP are presented in Table 6.2.

Table 6.1 Design data of Verulam WWTP

Unit	No of units (-)	Dimensions of each unit (m)	Total Capacity (m^3)
Primary Clarifier	5	Diameter 10.3, Depth 8.5	970
ASU Cell 1	1	14 × 14 × 4.5	1 764
ASU Cell 2	1	14 × 14 × 4.5	1 764
ASU Cell 3	1	14 × 14 × 4.5	1 764
ASU Cell 4	1	14 × 14 × 4.5	1 764
ASU Cell 5	1	14 × 14 × 4.5	1 764
Secondary Clarifier	2	Diameter 21, Depth 3	1 030
Volume of recycle channel	2		884

Table 6.2 Operational data for Verulam WWTP obtained from plant records (2010-2011)

Variable	Unit	Average value	No. of measurements
Design average influent flow average	m^3/d	6 035	727
Influent wastewater pH	-	8*	94
Influent settleable solids	mg/L	14	180
Influent wastewater COD	mg/L	1 340	184
Activated sludge waste flow average	m^3/d	180	31

*Median

6.4.2.2 Influent characterisation:

In order to run dynamic simulations showing the dynamics occurring on a daily basis in the WWTP there was need to prepare a dynamic input file that represents the influent wastewater received by the WWTP. To prepare the dynamic ASM1input- the following was carried out:

- The probability distribution models fitted to the flow and COD data collected from the factories in the catchment were used to generate daily flows for the factories and average daily COD values for 2010 and 2011.
- Daily flow volumes of infiltration were obtained using the simplified storm water model derived from regression analysis. The corresponding average daily COD values for infiltration were assumed to be the average COD of infiltration obtained from Langeveld et al. (2012).
- The daily flow volumes of domestic water were obtained as the difference between the total measured wastewater flow and the sum of the wastewater flow of the factories and infiltration. The corresponding average daily COD values for domestic wastewater were obtained from assuming a normal distribution for the daily COD values for domestic wastewater with an average COD of South African domestic wastewater obtained from WRC, (1994).

- In order to determine the concentrations of the COD fractions for the input file, a matrix of the COD fractions obtained from the catchment balance (Chapter 5) was multiplied by the average daily total COD from each of the contributors to give combine component fluxes which were then divided by the total flow rate to give the concentration of COD fractions in the dynamic input file.
- The values of the rest of the ASM1 components in the input file were obtained using the methods presented in Chapter 5.

6.4.2.3 Kinetic and stoichiometric parameters:

Default values of the ASM1 parameters obtained from Henze et al. (1987) were used for the activated sludge model before adjustment of model parameters was considered.

6.4.2.4 Biological characterisation

In a typical modelling project aimed at developing a simulation model for a WWTP, a measuring campaign would be carried out to capture the daily or weekly dynamics of the flows and composition of the influent wastewater, effluent wastewater and other streams in the WWTP. This is recommended by the calibration protocols discussed in previous sections. However in this particular case the measuring campaign was not done, since the objective was to evaluate the success of modelling using the available data. The available measurements did not capture daily or weekly variations of the composition of the influent wastewater and other streams of the wastewater treatment process. In some cases, less than 10 measurements of a wastewater variable within one month were the only available measurements. Data from the year 2011 was chosen for the plots because it had the least gaps compared to other years. Figure 6.3 to Figure 6.6 show variations of influent wastewater properties over a whole year. The wastewater properties plotted are free ammonia, COD, settleable solids and total suspended solids concentrations. Important influent wastewater composition variables that are not measured but are usually tested for when modelling WWTPs include total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen.

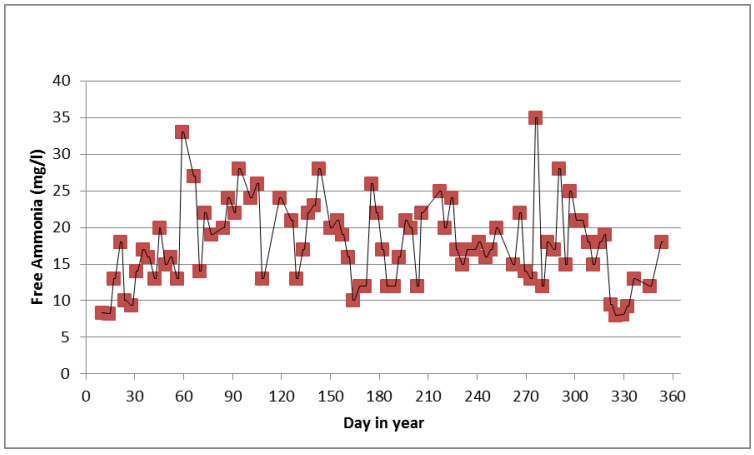


Figure 6.3 Measured free-ammonia in influent wastewater at Verulam WWTP for the year 2011

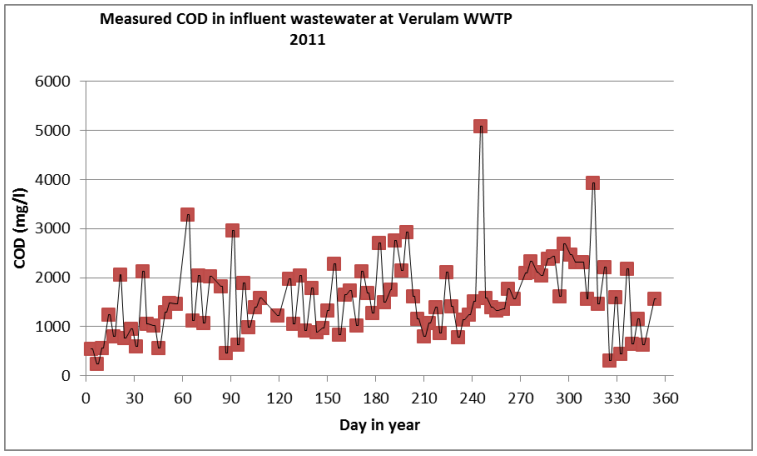


Figure 6.4 Measured COD in influent wastewater at Verulam WWTP for the year 2011

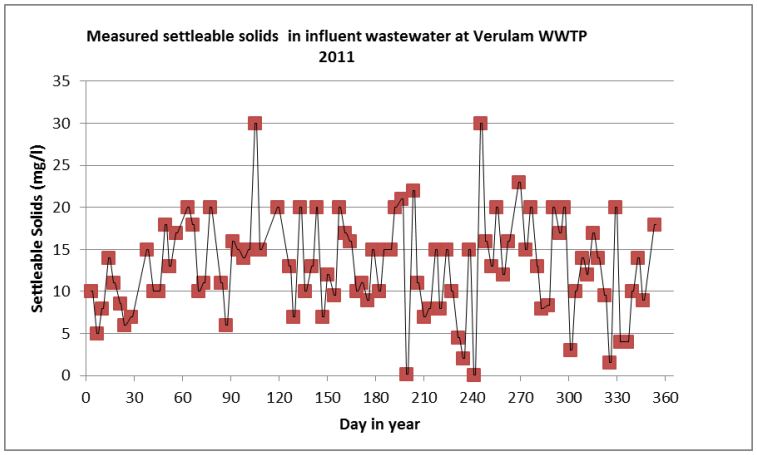


Figure 6.5 Measured settleable solids in influent wastewater at Verulam WWTP for the year 2011

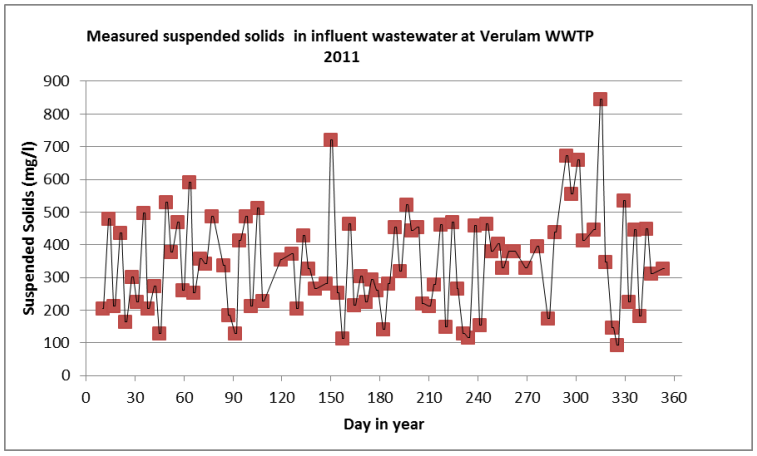


Figure 6.6 Measured suspended solids in influent wastewater at Verulam WWTP for the year 2011

The dynamics of effluent wastewater composition were also not captured for daily or weekly intervals, but variations of wastewater composition are presented for the whole year. Figure 6.7 to Figure 6.11 presents the variation of some of the composition variables of effluent waster at Verulam WWTP. The wastewater composition variables that are plotted are COD, suspended solids, nitrate and nitrite nitrogen, TKN and total nitrogen.

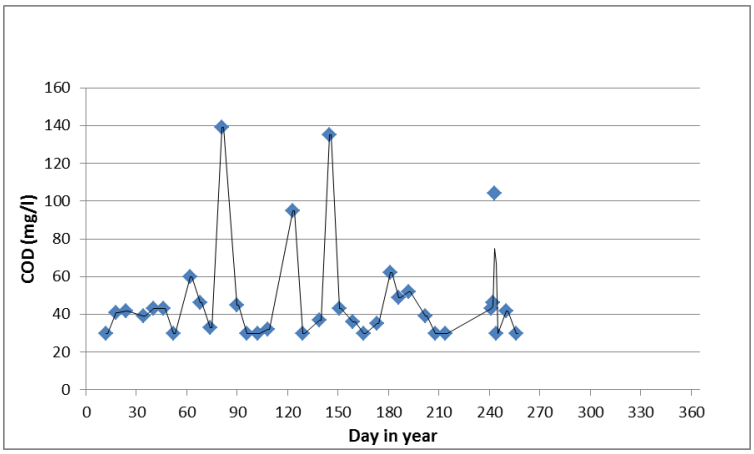


Figure 6.7 Measured COD in final effluent wastewater at Verulam WWTP for the year 2011

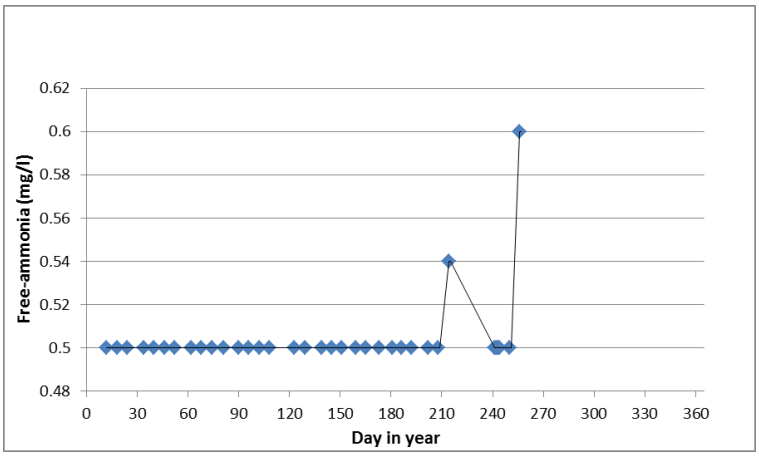


Figure 6.8 Measured free-ammonia in final effluent at Verulam WWTP for the year 2011

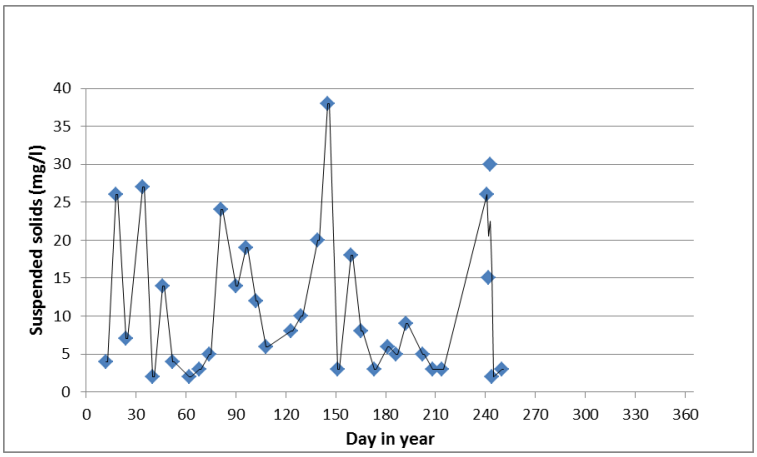


Figure 6.9 Measured suspended solids in final effluent at Verulam WWTP for the year 2011

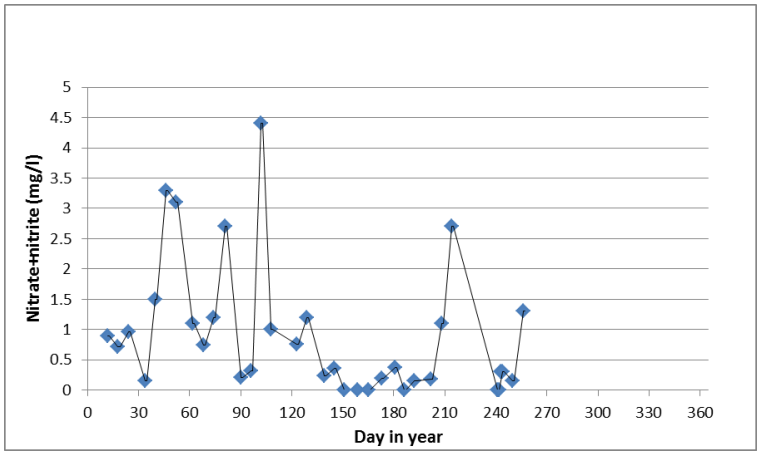


Figure 6.10 Measured (nitrate+nitrite) in final effluent at Verulam WWTP for the year 2011

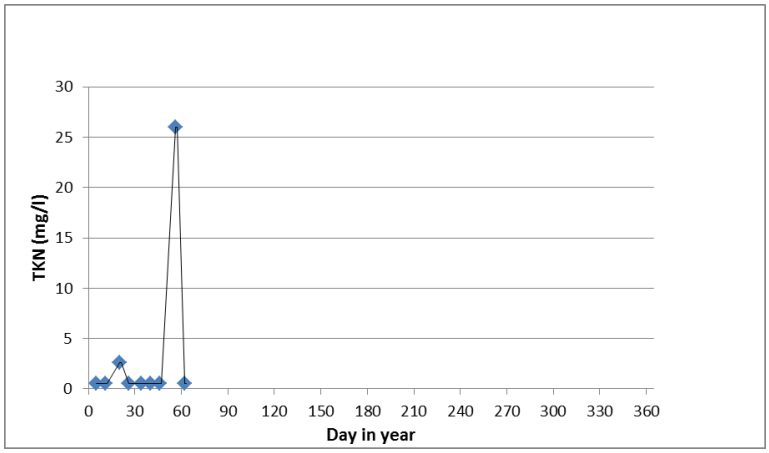


Figure 6.11 Measured TKN in final effluent at Verulam WWTP for the year 2010

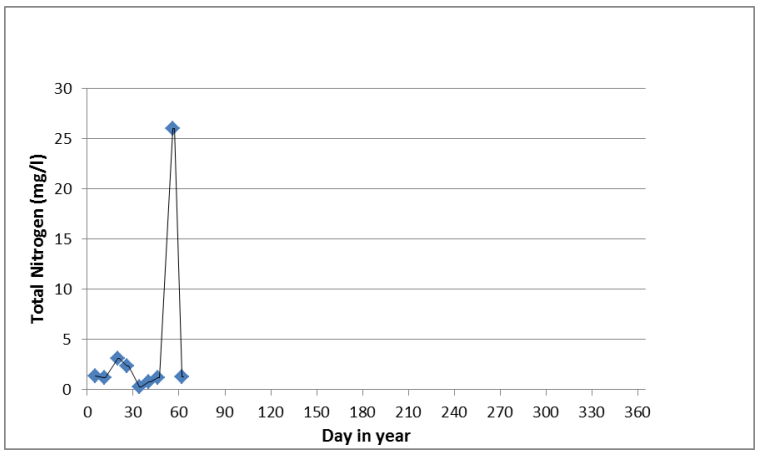


Figure 6.12 Measured Total Nitrogen in final effluent at Verulam WWTP for the year 2010

Figure 6.7 to Figure 6.12 show that during the last 3 months of the year 2011 no data was collected for the selected wastewater composition variables and that for the year 2010 TKN and TN were only measured for the first two months of the year. The reason for discontinuing these measurements was

cost saving.

The measured COD in the final treated effluent (Figure 6.7) was less than 60 mg/L most of the time. Only 5 out 35 measurements indicate CODs higher than 60 mg/L. The measured free ammonia (Figure 6.8) in the final effluent was less than or equal to 0.5 mg/L for 30 out of 32 measurements. The analytic methods used to measure free ammonia in the final effluent from Verulam could not detect concentrations less than 0.5 mg/L; hence the constant concentration of 0.5 mg/L for the first 210 days of the year, on the plot. The measured concentrations of suspended solids in the final effluent (Figure 6.9) were less than 40 mg/L and nitrate + nitrite (Figure 6.10) were less than 4.5 mg/L. No measurements were available for TKN and TN for the year 2011. Data from the year 2010 was plotted to illustrate the variation and sparcity of measurements of these variables. The measurements for these variables were only available for the first 2 months of the year. The limited measurements show that the TKN and TN (Figure 6.12) measured in the final effluent is less than 3 mg/L except for one measurement in February, which is suspected to be erroneous.

6.4.2.5 Sludge concentrations

At the Verulam WWTP activated sludge samples are routinely collected from the aeration tanks Cell 2 and Cell 3 (Figure 6.2) and from the recycle stream returning activated sludge to the aeration basin. The samples from the aeration tanks were tested for nitrate, nitrite, pH and suspended solids. The return activated sludge was tested for suspended solids. The average values of results from sludge analysis for

the year 2010 are presented in Table 6.3.

Table 6.3 Analysis results of sludge samples collected from the activated sludge unit at Verulam WWTP

Sludge source	Suspended solids (mg/L)		Nitrate (mg N/L)		Nitrite (mg N/L)		pH	
	No. of samples	Average	No. of samples	Average	No. of samples	Average	No. of samples	Median
Cell 2	85	5 513	78	1.5	78	<0.1	57	7.4
Cell 3	87	5 607	79	0.9	76	<0.1	59	7.3
Recycle	39	10 462						

The suspended solids concentration in the activated sludge unit (Cell 2 and Cell 3) appear to be approximately half the concentration of suspended solids in the recycled return activated sludge underflow from the secondary clarifiers. The measured concentration of nitrite in the aerobic cells, Cell 2 and 3 is less than 0.1 mg/L for more than 95 % of the time while the average nitrate concentration were 1.5 and 0.9 mg/L for Cell 2 and Cell 3 respectively. The corresponding median values for the measured pH were 7.4 and 7.3. The variation of suspended solids concentrations in Cell 2 and 3 for the year 2010 are shown in Figure 6.13 and Figure 6.14.

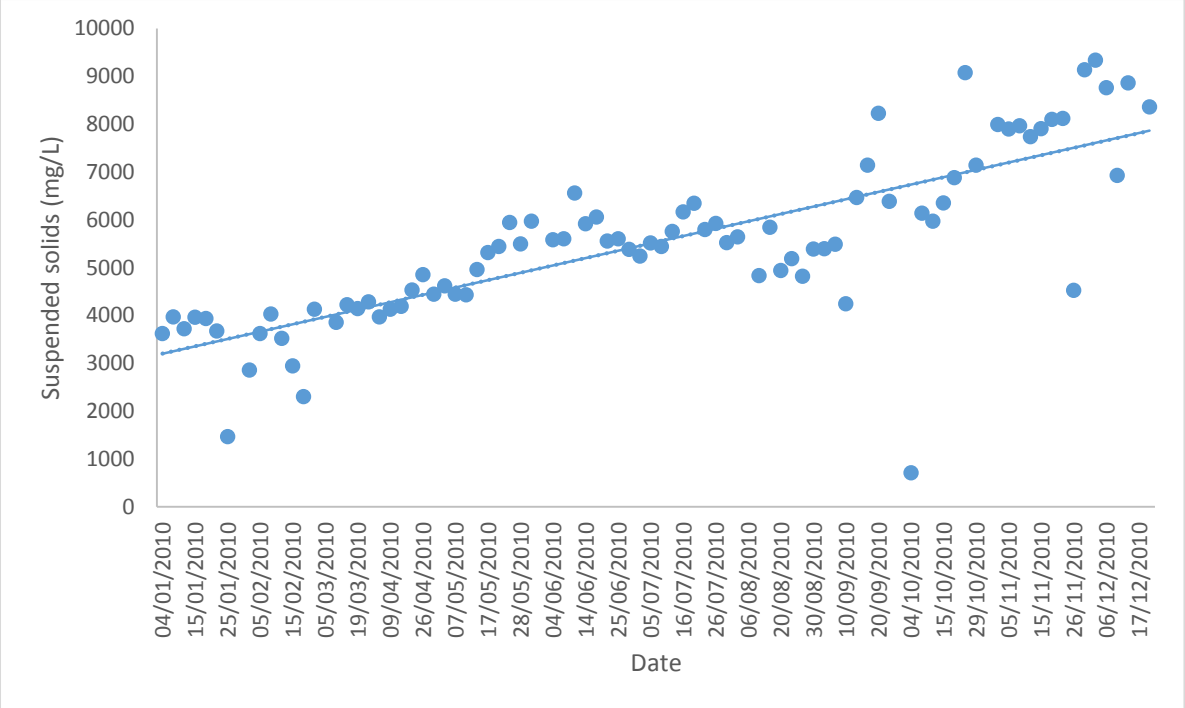


Figure 6.13 Suspended solids concentration in Cell 2 in Verulam WWTP for the year 2010

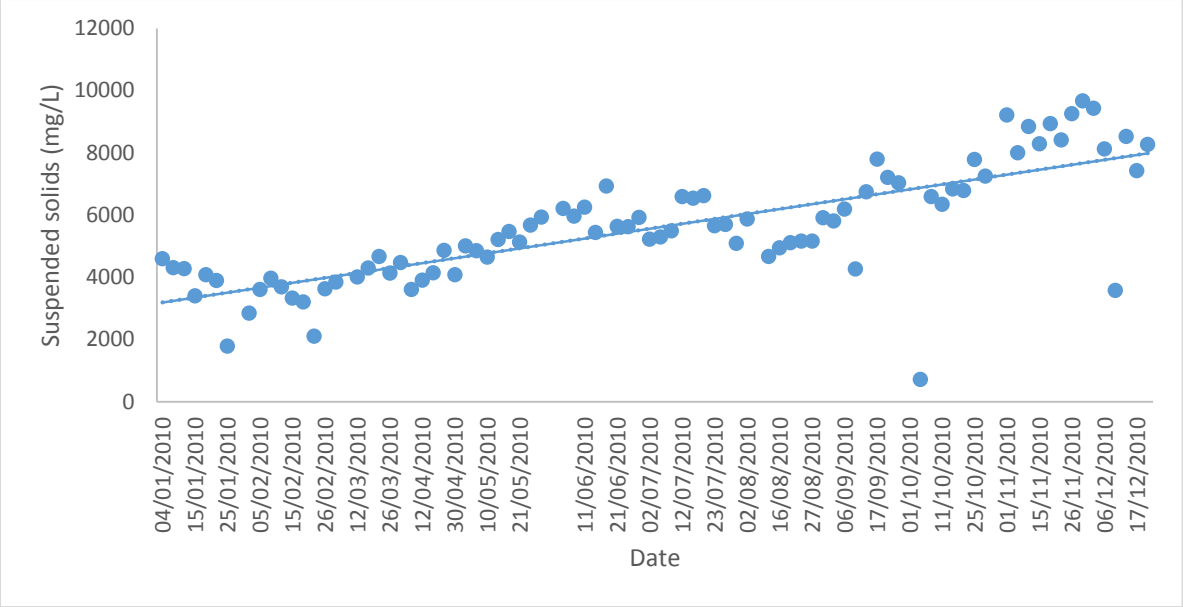


Figure 6.14 Suspended solids concentration in Cell 3 in Verulam WWTP for the year 2010

The plots of mixed liquor suspended solids (MLSS) for 2010 in Cell 2 and 3 exhibit an upward trend from the beginning of the year to the end of the year. In some cases a plot of MLSS against time provides a rough assessment of how stable the process is for steady-steady calibration. Based on Figure 6.13 and Figure 6.14 the overall trend of concentration of MLSS shows a rise with time suggesting that the activated sludge process might not have been operating close to steady-state. On the other hand it could be related to how sludge was being wasted from the process during this period. The exact reason for the observed MLSS variation with time, could not be ascertained from the plant historical records.

6.4.2.6 Additional information on WWTP operation

The supernatant liquid (SNL) from the digesters is supposed to be mixed with raw influent wastewater before the primary clarifiers. The WWTP was designed to handle a maximum of 400 m^3/d of supernatant liquid. However mass balances around the plant, show that during the times when the digesters and filtration process were running before 2010, the average volume of supernatant was 150 m^3/d. Digester supernatant often introduces ammonia loads and other substances to the wastewater treatment process. During the period of 2009, 2010 and 2011, Verulam WWTP experienced operational problems on the digesters that resulted in periods when no supernatant liquid was pumped to the activated sludge process. In the period simulated in the model the SNL was not being recycled to the process.

6.4.2.7 Summary of available information

During data collection for modelling, certain aspects are important. These include data frequency, the use of average values for steady-state operation, and accuracy of mass balances. These aspects of data collection are linked to the purpose of the model. Average values of measurements are sufficient for steady-state modelling and reliable if the plant was operating at steady-state during the period the measurements were made. Accurate mass balances will result in more reliable model simulations.

On comparing the data that were available for modelling in this study against the data requirements that are generally required for modelling the activated sludge process according to the summary compiled in Rieger, (2012), the aspects affected by lack of measurements their impact on modelling are summarised in Table 6.4. It is evident that some measurements that would have resulted in a more accurate model calibration and simulations are not measured currently at Verulam WWTP. Thus, the following sections serve to indicate how far the modelling exercise could be carried forward under conditions where some measurements are not available, and highlight the impact they have on the modelling results. The reason of carrying forward with the modelling exercise was to identify crucial short comings and to demonstrate idea of how a WWTP model could be used in the context of effluent discharge permitting and at the end make recommendations on how the whole protocol maybe carried out with the least amount of data gathering required in the context of an organisation such as eThekwini municipality.

Table 6.4 Comparison of data requirements for modelling WWTPs and data that was available in the Verulam WWTP

Data Requirements	**Data availability in Verulam WWTP case study**			**Comment or impact on modelling project**
	All data available	**Some data available**	**No data available**	
Influent and other input flows		YES		Flow measurements are available but some flow meters were faulty thus making it difficult to determine a correct flow balance.
Influent organics and suspended solids (COD, TSS, VSS,)		YES		VSS not measured, VSS affects modelling of sludge production
Influent nutrients (TKN, ammonium nitrogen, P, PO_4 - P)		YES		TKN, P and PO_4 - P are not measured. P removal and nutrient balance cannot be carried out.
Influent COD, N and P fractions			YES	COD, N and P fractionation must be carried out for IWA ASM-type models.
Alkalinity of influent wastewater and effluent wastewater			YES	This has no impact on modelling nutrient removal in ASU.
Tank volumes, depths and layouts, flow connections and hydraulic behaviour, equipment (aerators, mixers, pumps), P& I-Diagram, main characteristics of the sludge treatment train		YES		Information on the hydraulic behaviour of the process was not available.
DO control strategy and set points, pumping set-points/ flow splits, other control strategies		YES		DO is measured in two of the aerobic cells. DO in other cells is not measured, thus there are no measured DO values to compare with the model predictions.
Effluent organics: (COD, BOD_5, TSS)		YES		BOD_5 is not measured in the effluent. The main focus appears to be on the COD.
Effluent nutrients: TKN, ammonium nitrogen, nitrate and nitrite, P, PO_4 - P		YES		Not enough data are measured thus it is impossible to calibration of nutrient removal.
Mixed liquor MLSS, MLVSS		YES		MLVSS is not measured, prediction of sludge production and mass balancing cannot be carried out accurately.
Total P of mixed liquor			YES	DO control, aerobic sludge age
Flow of waste activated sludge (WAS); MLSS of WAS	YES		YES	A flow meter is available to measure WAS and the laboratory samples and analyses for MLSS.

6.5 Configuring the model in WEST

The WEST configuration representing the Verulam WWTP is presented in Figure 6.15. After setting up the configuration of the WWTP, sub-models were assigned to the different units in the configuration.

Thereafter simulations were run and evaluated.

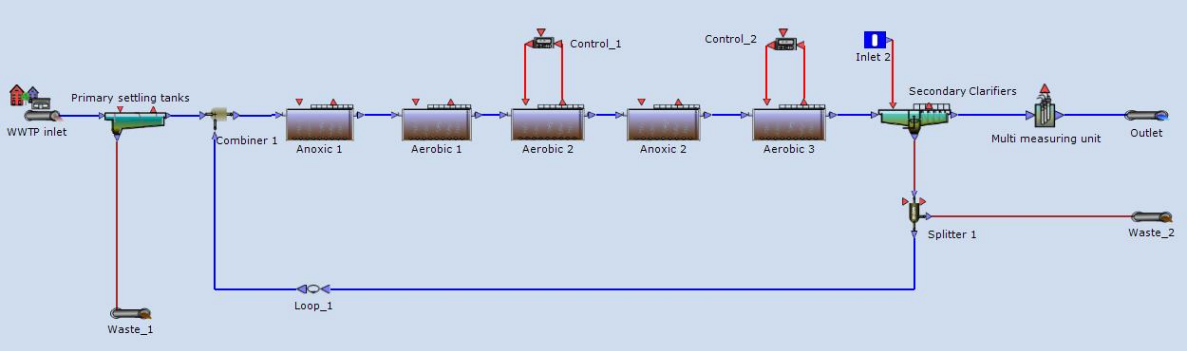


Figure 6.15 Configuration of Verulam WWTP in WEST software

The configuration consists of the major units of the WWTP, the activated sludge unit (ASU) and the two secondary settlers. The primary settlers are configured as one unit since it is assumed that they operate in the same way. This assumption was also extended to the configuration of secondary clarifiers; they were configured as one unit. Combiners and splitters have been added to combine and split flows, respectively. A measuring unit was added to the WWTP configuration to measure the composition of the final treated effluent. The model blocks used to construct the configuration are listed in Table 6.5.

Table 6.5 WEST Block models for Verulam WWTP

Block	Description
WWTP inlet	Inlet of influent wastewater to the WWTP
Primary settling tanks	Combination of 5 primary clarifiers
Combiner 1	Combiner of influent wastewater and recycled activated sludge
Anoxic 1	First anoxic cell of activated sludge unit
Aerobic 1	First aerobic cell of activated sludge unit
Aerobic 2	Second aerobic cell of activated sludge unit
Anoxic 2	Second anoxic cell of activated sludge unit
Aerobic 3	Third aerobic cell of activated sludge unit
Control_1	Dissolved oxygen controller in first aerobic cell
Control_2	Dissolved oxygen controller in second aerobic cell
Inlet 2	Inlet for solids concentration data
Secondary clarifiers	Combination of 2 secondary clarifiers
Multi measuring unit	Unit measuring composition of the final effluent
Outlet	Outlet of final effluent
Splitter 1	Splitter of secondary clarifier underflow
Loop_1	Loop break introducing time delay for simulations
Waste_1	Outlet of primary clarifier underflow
Waste_2	Outlet of wasted activated sludge

The sub-model assigned to the primary settlers was a primary point settler (WEST Models Guide, 2014), while the activated sludge unit cells were modelled as fixed volume activated sludge units. Proportional integral derivative (PID) controllers were used to model the controllers in the aerobic cells of the activated sludge unit. The secondary settler model (WEST Models Guide, 2014) was used to model the secondary clarifiers.

6.5.1 Control of DO concentration in the activated sludge unit

The oxygen in the activated sludge unit is supplied by mechanical aerators. Mechanical aerators are made up of an impeller attached to a motor mounted above the aeration tank concrete structure. During operation the turning impeller entrains air from the atmosphere and mixes the air with the wastewater or mixed liquor. This in turn creates high air-to-water-exchange-surface-area which results in more oxygen being dissolved in the mixed liquor. In most cases the design of the mechanical aeration system has an inverter to control motor speed that will receive input from a transmitter that measures dissolved oxygen (DO) concentration in the activated sludge unit. Lower DO concentration will induce the motor to operate at higher speed and thus increase the amount of oxygen introduced to the activated sludge unit.

The activated sludge unit at Verulam WWTP is made up of aerobic and anoxic cells. The control of the dissolved oxygen concentration in the aerobic cells is crucial for the process to treat wastewater efficiently. The concentration of dissolved oxygen has significant influence on the behaviour of heterotrophic and autotrophic active microorganisms that are present in the activated sludge. Many control strategies involving DO concentration have been proposed for the activated sludge process (Spanjers et al.,1996), but their evaluation is difficult partly due to the variability of influent, complexity of biological and biochemical phenomena and lack of standard evaluation criteria (Holenda et al., 2008).

The biological nitrogen removal consists of nitrification and de-nitrification. This is meant to take place in different cells in the activated sludge unit. In the WWTP model, the correct environment or conditions need to be created in each cell in order to match the actual activated sludge unit. The nitrification process depends on the dissolved oxygen concentration in the activated sludge unit. Hence the dissolved oxygen concentration is an important control parameter to be considered when creating the right environment in the units making up the WWTP model.

In the aerobic cells the oxygen should be high enough for the microorganism to degrade or utilise organic matter and convert ammonia to nitrate. On the other hand high dissolved oxygen concentration in the recycle makes de-nitrification less efficient and high DO concentrations mean high airflow rate and high energy consumption which is costly for the WWTP. WWTPs usually have a DO concentration control strategy to ensure that all process take place in the correct cells in the activated sludge unit. The DO control philosophy at Verulam WWT is summarised in Table 6.6 .

Table 6.6 Dissolve oxygen control philosophy at Verulam WWTP

Cell No.	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
Conditions	Anoxic	Aerobic	Aerobic	Anoxic	Aerobic
Description of conditions in cell	No aeration, minimum turbulence preventing biological settlement whilst keeping oxygen concentrations to a minimum	Aeration using 49 kW mechanical aerators, rapid mixing.	Aeration using 49 kW mechanical aerators, rapid mixing.	No aeration, minimum turbulence preventing biological settlement whilst keeping oxygen concentrations to a minimum	Aeration using 49 kW mechanical aerators, rapid mixing.
Process control option 1 (diurnal flow control)		9 set-points are used by the SCADA to control the aerator proportionally to the diurnal flow variations.	9 set-points are used by the SCADA to control the aerator proportionally to the diurnal flow variations.		9 set-points are used by the SCADA to control the aerator proportionally to the diurnal flow variations.
Process control option 2 (DO control)			DO is measured in the cell, compared with SCADA set point and the difference is used to control the mechanical aerator		DO is measured in the cell, compared with SCADA set point and the difference is used to control the mechanical aerator

6.5.1.1 Option 1 Aerator control based on diurnal flow variations

The control of aeration in cells 2, 3 and 5 in the activated sludge unit based on the diurnal flow variation is set up in the supervisory control and data acquisition (SCADA) system so that the SCADA system automatically selects slower aerator speeds at night and faster speeds during the peak day period according to a pre-set diurnal flow pattern.

6.5.1.2 Option 2 Aerator control based on DO measurement in cell 3 and 5

In this option the dissolved oxygen concentration is measured by probes in cell 3 and cell 5. The measured value is compared with the set point for each cell. The set point for the dissolved oxygen concentration in cell 3 is 1.0 mg/L and in cell 5 it is 2.0 mg/L. A PID controller will then adjust the rotational speed of the mechanical aerators in the cells to achieve the DO set points. This automated control of aerator speed will enable the treatment to respond to COD loading variation.

The sampling interval for the DO control is between 0 to 60 minutes on the SCADA. A setting of 15 minutes, means that the PID controller will sample the DO and compare the measured signal with the set point and then implement a correction to the aerator rotational speed once every 15 minutes. The plant records at Verulam WWTP showed that option 2 was the preferred option at Verulam WWTP.

6.6 Model calibration

Even though mathematical models are simplified representations of complex systems they still have to describe the key aspects of the real system being modelled (Rieger, 2012). Calibration of the model is required until simulation results match observed data to within a pre-defined error range. Model calibration is an iterative process. In a typical model calibration procedure when the model simulations do not match the measured data, due to data quality, data availability and plant model set-up, the modeller is required to go back to the data collection and reconciliation step where specific additional measurements may be done or to go back to the plant model set-up where the plant model set up may be revised. Going back and correcting previous modelling steps is preferred to adjusting bio-kinetic parameters of the model (Rieger, 2012).

One of the recommended procedures for calibration is to start by calibrating the hydrodynamics of the plant which have high impact on diurnal variations of the dissolved concentrations. After the hydrodynamics, influent wastewater or recycle stream characteristics can be modified to fit sludge production. This step is aimed at establishing the correct solids retention time (SRT) for the system (Rieger, 2012). At this stage, if simulations do not match measured data to the required accuracy, modifying the plant model set-up may be considered. After this stage, in cases where more complex clarifier models than the simple point settler or ideal clarifier model have been used, parameters of the clarifier model are adjusted as required. Aeration sub-model parameters are then adjusted if necessary. The last parameters to be considered for adjusting are the bio-kinetic parameters. The adjustment of bio-kinetic parameters must be accompanied by a plausible bioprocess reasons (Rieger, 2012).

Various calibration protocols (Vanrolleghem et al., 2003; Hulsbeek et al., 2002; Langergraber et al., 2004) are available for reference. These calibration protocols were reviewed and are presented and discussed in Appendix D. Effort was made to follow calibration guidelines for the WWTP, however the lack of information prevented one from carrying out some of the recommended steps. Such areas have been highlighted, the impact on the modelling results discussed and where required recommendations have been made. One of the actions that could not be done was carrying out more measurements to improve certain calibration steps. The reason for this is that the scope of the project, which was driven by lack of resources, was to show how much useful modelling work could be carried out by municipality engineers using the data available to them. Hence where critical information

was missing, this has been highlighted and recommendations made.

The purpose of the model in this study which might appear as not being completely calibrated when compare to a typical modelling study where most of the required data is available, was to illustrate that with a certain amount of plant data and information about factories and households within a catchment of a WWTP, one can use this information to put together a simplified model of the WWTP, that can predict, in simple terms the impact on treated effluent quality, of introducing a new factory into that catchment or a significant change in the pollutant loads from the contributors in the catchment. Thus, the value in carrying out the modelling within the current background supported by assumptions was to show the steps that can be followed, highlight critical areas that require information in order to obtain improved and more acceptable results and demonstrate the proposed protocol structure and how it can be used in the discharge permitting process in a municipality.

The assumption and lack of data introduces uncertainty, but this does not take away the value of the demonstration of the concept. It was envisaged that the recipient of the protocol would then apply this protocol in their context by following the proposed procedure, taking into account the critical data requirements highlighted and the recommendations to produce a WWTP model fitting their context, while still relying on data collected for regular WWTP monitoring to a certain point before critical or intensive measurements are required.

A steady-state calibration was attempted before evaluating the dynamic predictions of the WWTP model.

6.6.1 Steady-state calibration

Characterisation of the main flows was carried out before steady-state calibration was done. An exercise to evaluate the performance of the flow meters at the WWTP was carried out at Verulam WWTP in order to collect flow data for developing a steady-state flow balance. Daily flow totals were collected over a period of 1 month in July 2010. There was no SNL being recycled to the activated sludge system. The averages of daily totals of flow at different measuring points of the WWTP obtained from the exercise are presented in
Figure 6.16.

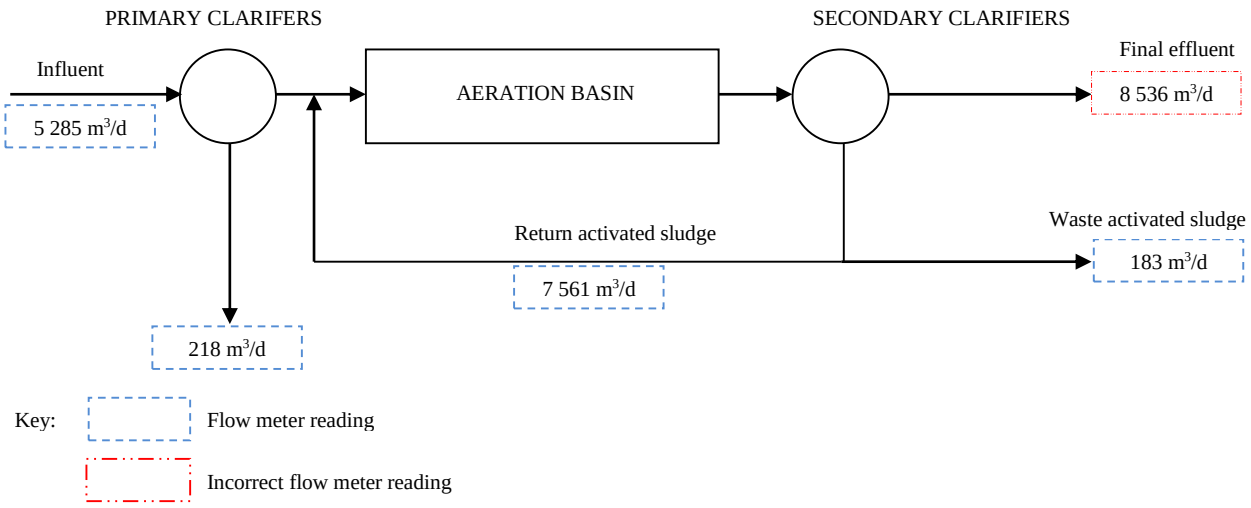


Figure 6.16 Flow meter readings at Verulam WWTP in July 2010

The findings from this exercise showed that the final effluent flow meter was giving out incorrect readings. The reading of the final effluent flow meter showed values that were higher than the influent flow coming into the WWTP that was measured by a calibrated flow meter at the WWTP inlet. The flow meter readings from the rest of the flow meters were accepted, even though there were minor calibration issues with one of the flow meters for the return activated sludge. This meter was suspected to have been calibrated in the wrong units. The meter was however reading properly thus it was easy to resolve the issue. A mass balance calculation was done after excluding readings from the final effluent meter and the estimated steady-state flow of final effluent was 4 882 m^3/d.

After the flow balance a steady-state calibration was attempted using the configuration developed for the WWTP. The main objective of the steady state calibration was to fit the modelled sludge properties to the sludge properties that are measured at Verulam WWTP. It is important to have an accurate account of the sludge mass inventory in the activated sludge process and to have an accurate estimate of sludge age and the solids retention time (SRT) (Melcer, 2003). For reliable simulation studies, 95% accuracy is recommended for SRT simulated by the model (Brdjananivic et al., 2000; Meijer et al., 2001). The SRT can be evaluated on the basis of the P, TSS or COD balances on the process.

P and COD balances could not be carried out around the activated sludge process due to lack of measurements on the waste activated sludge stream and primary sludge. COD is only measured on the influent wastewater and final effluent. Phosphorus is not measured in the influent, waste activated sludge and primary sludge. A TSS balance, based on the limited measurements available established that the WWTP was not running at steady-state. The suspended solids concentrations measured in Cell 2 and Cell 3 for 2010 shown in Figure 6.13 and Figure 6.14 respectively, exhibit and upward trend

through the year, suggesting unsteady-state operation. Further investigations on the SRT used at Verulam WWTP revealed that the removal of dewatered sludge from the site of the WWTP was determining how much sludge was being wasted from the process as compared to running the process based on a set SRT. Delayed removal of de-watered sludge from the WWTP to disposal sites, due to issues related to the contracts between the municipality and external service providers resulted in inconsistent sludge wasting resulting in unsteady operations of the activated sludge system. Furthermore the SRT could not be accurately calculated from the available measurements since the MLSS are not measured in Cell 1, 4 and 5. Furthermore the TSS in the primary effluent and secondary clarifiers are not measured thus the total sludge mass in the activated sludge process could not be estimated.

On this background, the attempted steady calibration was limited to trying to predict the average TSS measured in Cell 2, Cell 3 and waste activated sludge after ensuring that the flows in the model matched the measured flows in the WWTP. The steady-state influent wastewater flowrate was obtained by averaging the recorded dynamic influent data. The average wasted sludge volume and composition was obtained from historical operational data of the WWTP. If measured and model predicted results do not match during a steady-state calibration, the parameters responsible for the long-term behaviour in the activated sludge system need to be adjusted in order for model predicted results to fit the measured results. The parameters recommended for adjustment are decay coefficients, b_H and b_A and the influent inert particulate COD, X_I (Petersen et al., 2000).

After ensuring that the flow balance of the model matched that of the WWTP, the concentrations of the total suspended solids predicted by the model in Cell 2, Cell 3 and waste activated sludge were compared with the measured values. The model predicted less suspended solids than what is measured in the WWTP. To solve this problem, values of b_H and b_A were adjusted from their default values but there was no significant improvement in the predicted results, thus and the default values of b_H and b_A were adopted again. The results of the attempted steady state calibration are presented in Table 6.7.

Table 6.7 Results of attempted steady-state calibration

	Measured value (mg/L)	**Model predicted value with no adjustment of parameters (mg/L)**	**Model predicted value with COD fractions adjustment (mg/L)**
TSS in waste activated sludge	10 462	2 340	6 305
TSS in Cell 2	5 513	1 489	4 145
TSS in Cell 3	5 607	1 472	4 140

When the fractionation of particulate COD used in the steady state calibration was changed there was a significant increase in the TSS concentrations predicted by the model. At this point in the model calibration process, this result is an indicator that X_I might have been underestimated in the catchment balance model. The steady state COD fractionation used in the initial steady state run, before adjusting any model parameters of the model are shown in Table 6.8 together with set of COD fraction in which X_I was increased to see the effect on the solids balance in the model. The particulate inerts X_I were increase to 60 % and particulate slowly biodegradable COD X_S was reduced to 15 %.

Table 6.8 Average COD fractionation of influent wastewater for steady state calibration

COD fraction	% of total COD	
	Before adjustment	**After adjustment**
S_S	20	20
S_I	5	5
X_S	62	15
X_I	13	60

Adjusting the COD fractions increased the suspended solids in Cell 2 and 3 significantly. The values predicted by the model are shown in the last column of Table 6.7. This result showed that the fraction of X_I in the influent wastewater had more effect on the sludge production in the process, than the model parameters b_H and b_A. However since there were many uncertainties and assumption in the COD fractionation and the model itself, it was difficulty to fix the values of X_I and X_S in the influent charaterisation based on these results of the attempted steady-state calibration. The ideal situation would be that after identifying a possible underestimation of X_I or X_S in the combined influent received at the inlet of the WWTP, one would take steps back and adjust the catchment balance model such that the value of X_I is changed to the more suitable value. It was not possible to identify which contributor's COD fractions should be adjusted from the information that was available.

Furthermore the ideas presented above would be more appropriate to follow if the WWTP was operating under steady conditions. Since it was established that the plant was not operation at a stable SRT from the MLSS measurements in Cell 2 and Cell 3 and the investigations carried out on the sludge wasting in the process at Verulam WWTP. It would be unsuccessful to calibrate the model based on the averages of the available measurements.

6.6.2 Dynamic calibration

After attempting the steady-state calibration, dynamic simulations were run and assessed for dynamic calibration of the model. The dynamic simulations were run with default ASM1 kinetic parameters presented in Table 6.9.

Table 6.9 Default ASM1 model parameters used for dynamic modelling of Verulam WWTP (Henze, 1987)

Symbol	Default value at (20 ºC)	Unit
Y_A	0.24	g cell COD formed/(g N oxidised)
Y_H	0.67	g cell COD formed/(g COD oxidised)
μ_H	6.0	/day
μ_A	0.08	/day
K_S	20.0	g COD/m^3
K_{OH}	0.5	g O_2/m^3
K_{OA}	0.4	g O_2/m^3
K_{NO}	0.50	g NO_3-N/m^3
b_H	0.62	/day
η_g	0.8	dimensionless
η_h	0.40	dimensionless
k_h	3.0	g slowly biodegradable COD/ (g cell COD·day)
K_X	0.03	g slowly biodegradable COD/ (g cell COD·day)
K_{NH}	1.0	g NH3-N/m^3
K_{OA}	0.4	g O_2/m^3
k_a	0.08	m^3·COD /(g·day)

Figure 6.17 shows the comparison between 200 days of model-predicted and measured values of COD in the final treated effluent from the Verulam WWTP. There was one process model aspect which had a significant effect on the treated effluent quality, and that was the efficiency of the final clarifiers, since any suspended solids in the final effluent contribute directly to the COD. The only measured data available that provided any information about this were the measured effluent total suspended solids. The COD agreement is not a perfect match but is close to the measured values, apart from the very high peak predicted at around 100 days and lower predicted value on some days. The predicted high COD value at around 100 days was due to high TSS concentration from the secondary clarifiers. There is clearly an inconsistency between the reported measured COD and measured TSS values at this point, a high TSS in the clarifier overflow must be accompanied by a high COD in reality but this was not the case in the measured data that was available for modelling. The trend of the predicted COD appears to show the expected effect of high TSS in the clarifier overflow, on the COD of the final effluent. Figure 6.18 shows how the predicted final effluent COD values vary with TSS values measured in the final effluent.

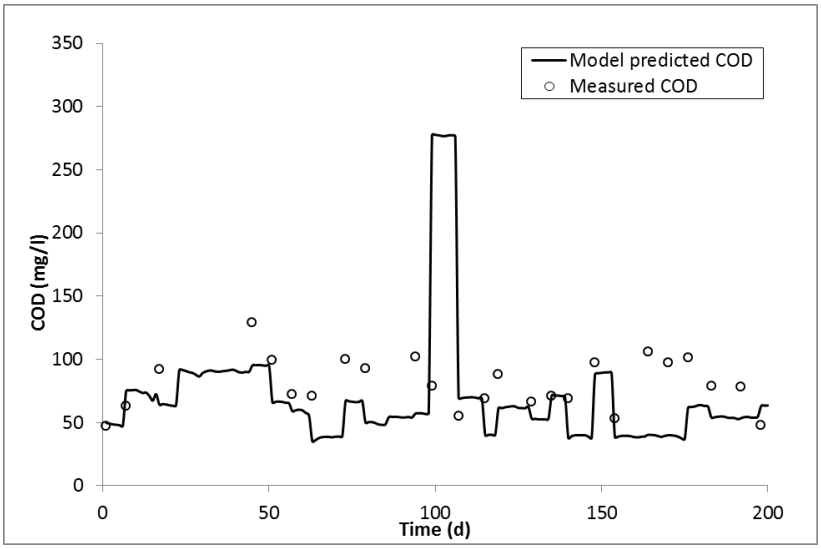


Figure 6.17 Measured and predicted final effluent COD concentration for the Verulam WWTP

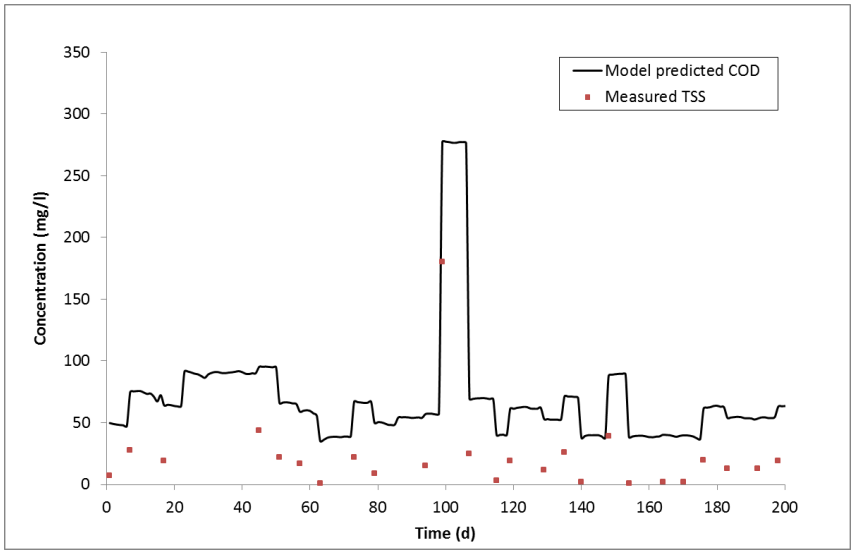


Figure 6.18 Model predicted final effluent COD and measured final effluent TSS concentrations

Since the catchment balance and the wastewater treatment process model, taken together, form a probabilistic model, the evaluation of the predictions form the model was carried out on a statistical basis by comparing the prediction by the model with measurements on a cumulative probability basis, rather than a day-by-day basis. This is consistent with the envisaged use of the model, which would be to predict the probable cumulative impact of a factory's effluent on the quality of treated wastewater being returned to the environment. Figure 6.19 presents the COD comparison on a cumulative frequency basis. The agreement is almost good up to the 95% level, and the discrepancy thereafter is largely a result of the almost certainly incorrect measurement previously noted. The overall observation was that the model-predicted COD values were lower than the measured COD values.

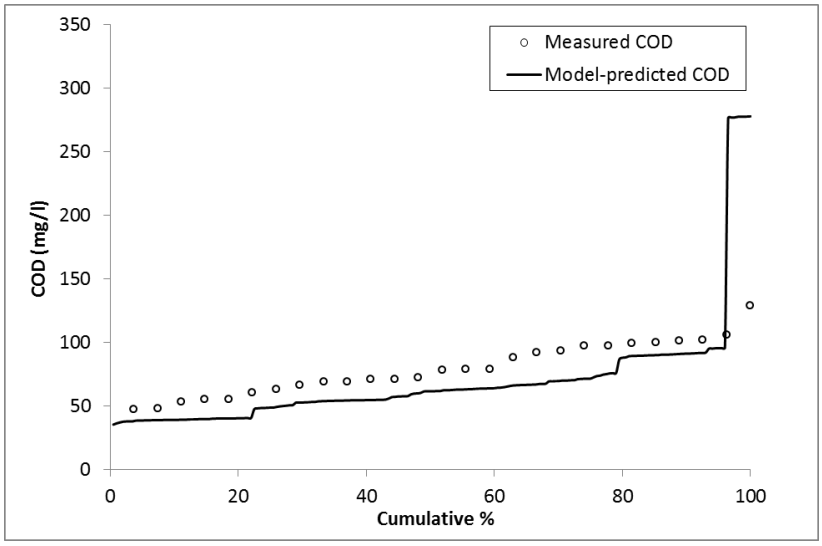


Figure 6.19 Cumulative frequency plot for measured and predicted final effluent COD for the Verulam WWTP

To improve the match between model-predicted and measured final effluent COD, the COD fractionation of the influent wastewater was adjusted. The proportion of S_I was increased from 5% to 7 % and X_S was reduced from 62% to 60 %. The reason for increasing S_I fraction in the influent is that the model-predicted final effluent COD was lower than expected and the cause could be the underestimation of the S_I fraction in the influent. The results obtained after this adjustment of COD fractions are shown in Figure 6.20 and Figure 6.21. The match between the model-predicted and measured final effluent COD values improved after increasing the S_I fraction suggesting that the S_I estimate obtained from the catchment COD balance was too low. There was no significant change observed in the model's prediction of ammonia concentration in the final effluent, after the influent wastewater COD fractions were adjusted.

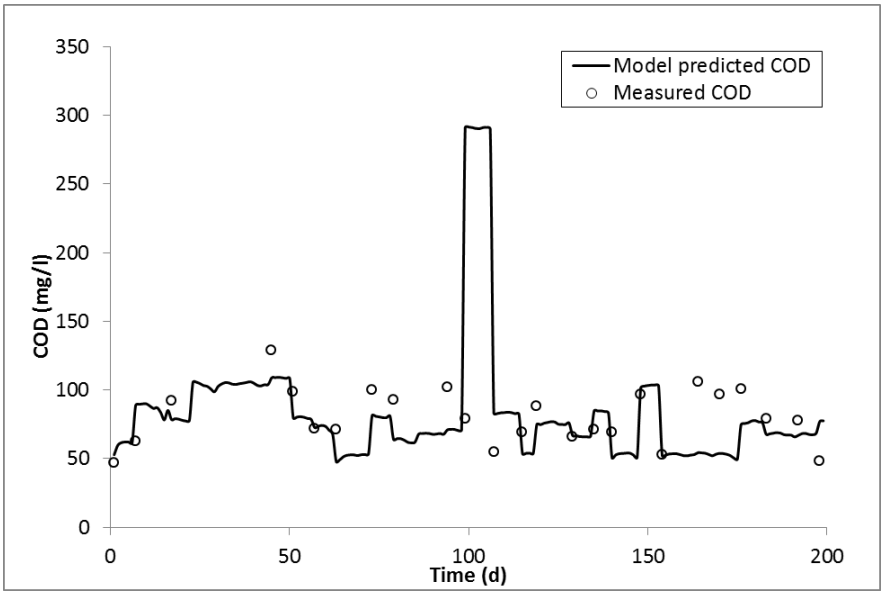


Figure 6.20 Measured and predicted final effluent CODs for the Verulam WWTP after adjusting COD fractions

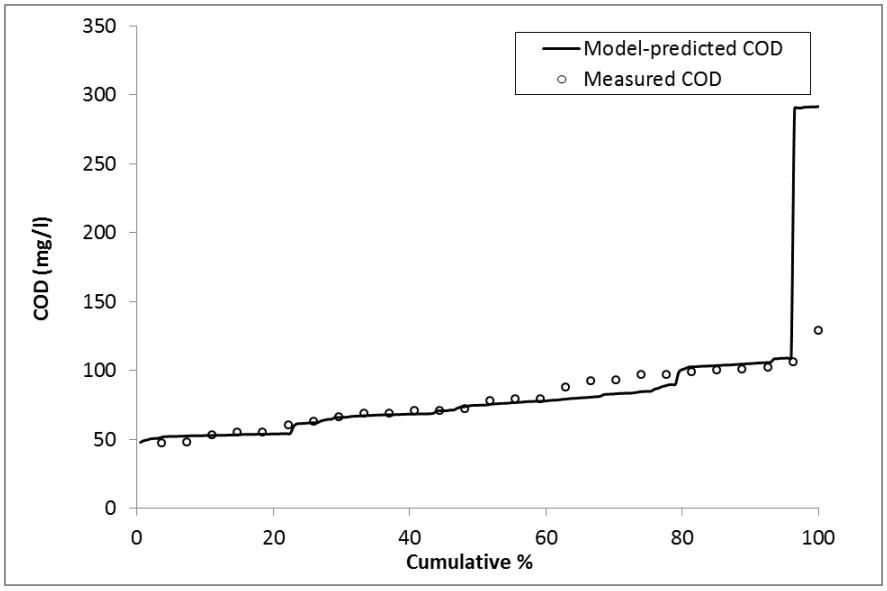


Figure 6.21 Cumulative frequency plot for measured and predicted final effluent COD for the Verulam WWTP after adjusting COD fractions

Figure 6.22 shows a plot comparing the measured and model predicted ammonia in the final effluent coming from the WWTP after adjusting COD fractions and adopting values resulting in Figure 6.21. The agreement between the model predicted and measured values is acceptable except for some peaks observed in the predicted values. The evaluation of the predicted values is done conservatively in this case since the measurements appear to mostly be at the lower detection limit of the method used to measure ammonia in final effluent. Hence it is not clear how to assess the model's prediction accuratly.

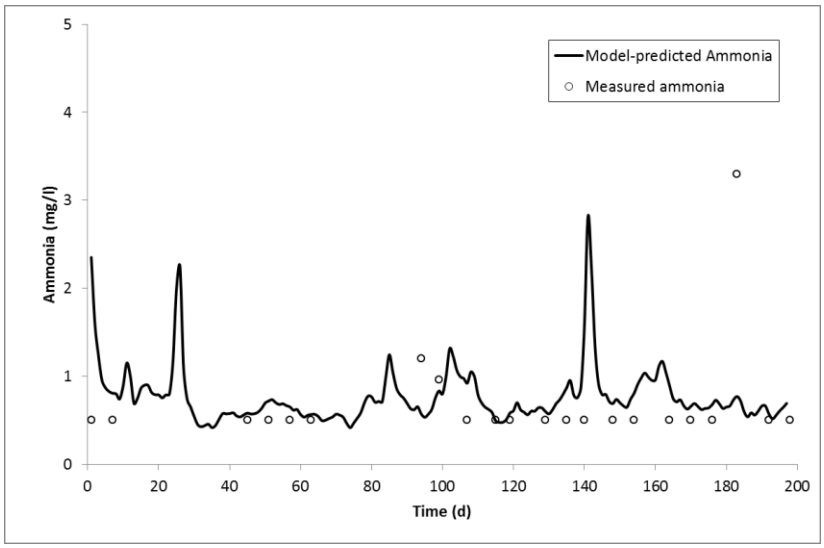


Figure 6.22 Measured and predicted final effluent ammonia for the Verulam WWTP after adjusting COD fractions

Figure 6.23 presents the comparison of model-predicted and measured ammonia in the final effluent on

a cumulative frequency basis.

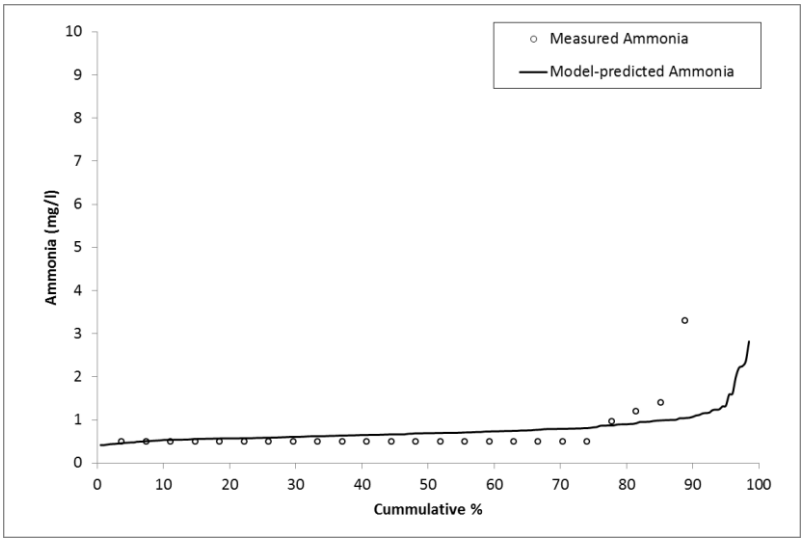


Figure 6.23 Cumulative frequency plot for measured and predicted final effluent ammonia for the Verulam WWTP after adjusting COD fractions

The agreement is very good up to the 85% level, and the discrepancy thereafter is largely due to the very high values of ammonia concentration predicted at the beginning of the simulation period and the peaks that appear in the model prediction shown in Figure 6.22. Model parameters were not adjusted to change the fit of final effluent ammonia.

6.6.3 Discussion of model calibration

The typical aim of model calibration for WWTPs is to obtain a set of model parameters that results in acceptable predictions of the final treated effluent, sludge production and the internal concentration dynamics of the WWTP being modelled (Gernaey et al., 2004). In this modelling exercise which was far from an ideal WWTP modelling case with respect to the available measured data, some of the typical calibration steps could not be executed. P and COD balances could not be carried out around the activated sludge process due to lack of measurements on the waste activated sludge stream and primary sludge in order to establish the correct SRT for steady-state calibration. The MLSS measurements on two of the compartments, in the ASU further suggested unsteady operation of the WWTP serving as a warning on calibrating the model based on steady-state. The bio-kinetic model parameter were not adjusted in the attempted calibration process due to the fact that there was significant uncertainty in the different steps taken to put together the model. A series of assumptions were made in putting together the model hence adjusting bio-kinetic model parameters was not going to fix issues such as lack of measured data. The only adjustments that were made during the dynamic calibration were adjusting the proportion of S_I from 5 % to 7 % and X_S from 62 % to 60 %. This resulted in an acceptable match between the cumulative frequency plots between the measured and model predicted final effluent COD.

The deviation of the calibration from the procedures recommended by other researcher in activated sludge modelling calibration such as Petersen et al. (2002) and Hulsbeek et al. (2002), was done due to the need to demonstrate the proposed purpose of such a model. Therefore the required level of calibration for this model was reduced to practical applicability in this specific context instead of scientific exactness.

6.7 Scenario analysis-Evaluation of the impact of factory effluent on the operation of the Verulam WWTP

The intended purpose of the WWTP model was to evaluate the impact of industrial effluent from factories, on the operation of the WWTP, particularly the compliance of the final treated effluent quality to the standard set for the WWTP. This is particularly important when granting permits to new factory requesting to discharge in a WWTP catchment. At Verulam WWTP the final treated effluent COD must be 75 mg/L or less for 90% of the time. In the event that a new factory applies for a discharge permit in this catchment, the municipality would require assurance that the final treated effluent will still be compliant to the required quality standard. To demonstrate how the WWTP model could be used in such a case, two types of scenarios were created and run in the model for evaluation. However, due to limited information, the assessment of WWTP performance was limited to final effluent COD.

A series of assumptions were made at different stages of developing the WWTP model. Despite these assumptions the preliminary results given by the model allowed demonstrating the concept on the basis that the developed model formed a baseline on which effects of changing the wastewater treatment load could be evaluated. With improved data availability more accurate results can be obtained. Based on the assessment carried out for granting discharge permits, the required level of accuracy from the model is lower than that required to predict the short term dynamics of the process. Thus, the impact on compliance was evaluated by comparing the cumulative plots of simulation results rather than comparing a time series against another. This is in line with the assessment carried out by the municipality for permitting purposes. The municipality requires to know whether the final treated effluent would be compliant for 90% of the time.

Input files representing the composition of influent wastewater for two types of scenarios were prepared and used to run simulations on the WWTP model. The two types of scenarios that were simulated were the following:

- Increasing influent wastewater load of the WWTP by introducing a factory into the WWTP catchment
- Reducing the influent wastewater load of the WWTP by removing the contribution of factory effluent within the WWTP catchment

The rational of running a scenario in which a new factory comes into the catchment of the WWTP is that the municipality needs to know the impact on effluent quality compliance of introducing a new factory into the catchment before granting a discharge permit. The rational for running a scenario where a factory is removed from the catchment is that there has been cases in eThekwini Municipality where problematic factories have moved from one WWTP catchment to another, resulting in a change in the final treated effluent compliance in the previous catchment and the new catchment.

The first type of scenario that was simulated was the operation of the WWTP with an additional factory producing the same volumes of wastewater and similar characteristics to the Nampak factory in the catchment. Nampak contributes the highest COD load among the factories in the catchment. The aim of running this scenario was to evaluate the COD compliance of the final treated effluent COD after an increase of the COD load in the catchment.

In order to evaluate the effect of reducing COD load in the WWTP catchment, on the COD compliance of the final treated effluent COD two scenarios were run in the model. The first scenario was made up by removing the contribution of the Nampak factory and then assessing the COD of the final treated effluent. The second scenario was made up by removing the contribution of JMV Textiles factory from the catchment and assessing the final treated effluent COD

6.7.1 Preparation of input files for scenario analysis

For the scenarios used to evaluate increased load on the WWTP performance, the input files representing the combined influent wastewater to the WWTP were prepared by adding the volume of the additional wastewater into the catchment and the concentrations of the COD fractions to the input file used to establish the baseline behaviour of the WWTP. For the scenarios evaluating reduced load on the WWTP, the volumes and the concentration of the COD fractions of the factories were subtracted from the input file representing the total combined influent wastewater going into the WWTP. It should be pointed out that in the scenario analysis only the volume and the concentrations of COD fractions of the wastewater could be reduced or increased for the factories. It was impossible to remove or add the contribution of factories to other wastewater components ($X_{BA,}$ X_P, X_{ND}, S_{ALK}, S_{NO}, S_{NH} and S_O) since these are not measured directly on the industrial effluent stream. $X_{BA,}$ X_P and S_{NO} were considered negligible (Henze et al., 2000; Henze, 2008). The values for X_{ND}, S_{ALK}, S_{NH} and S_O were kept the same in the input files used for the simulations. In the ideal case, for a more comprehensive analysis of the overall impact of introducing an additional industrial wastewater stream a more detailed characterisation of that stream will be required and this will in turn evoke the comprehensive prediction of the impact from the model.

6.7.2 Simulation results for different scenarios

The simulation results for the different scenarios are presented in Figure 6.24 to Figure 6.26. Figure 6.24 and Figure 6.25 show how the cumulative frequency plots of the COD values of the final treated effluent change when the load on the WWTP is increased due to the presence of a new factory and reduced by taking out a factory from the catchment.

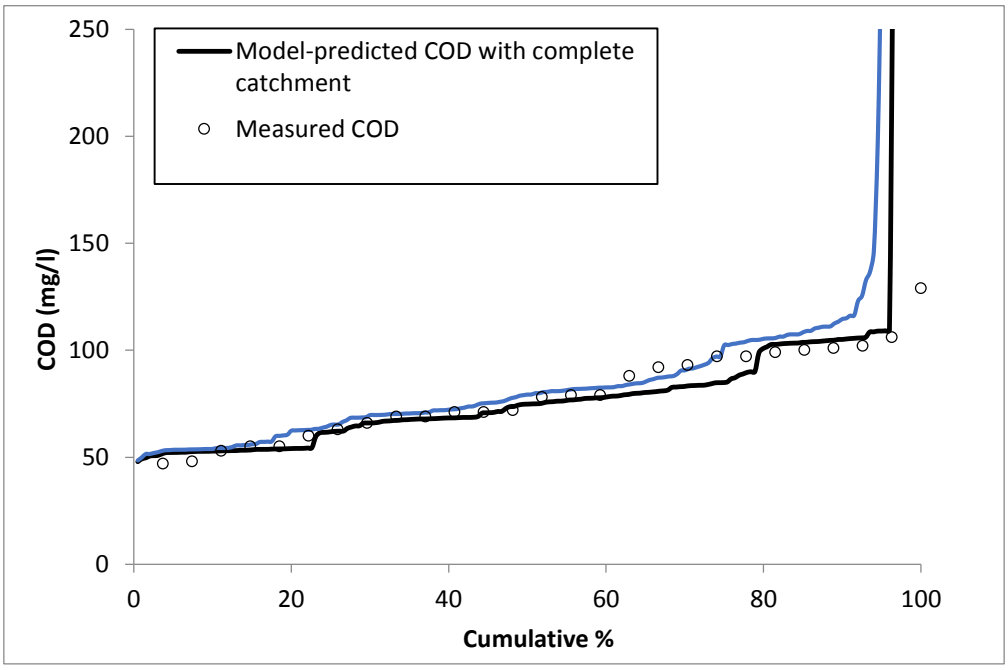


Figure 6.24 Comparison of cumulative frequency plots for final effluent COD when load is increased

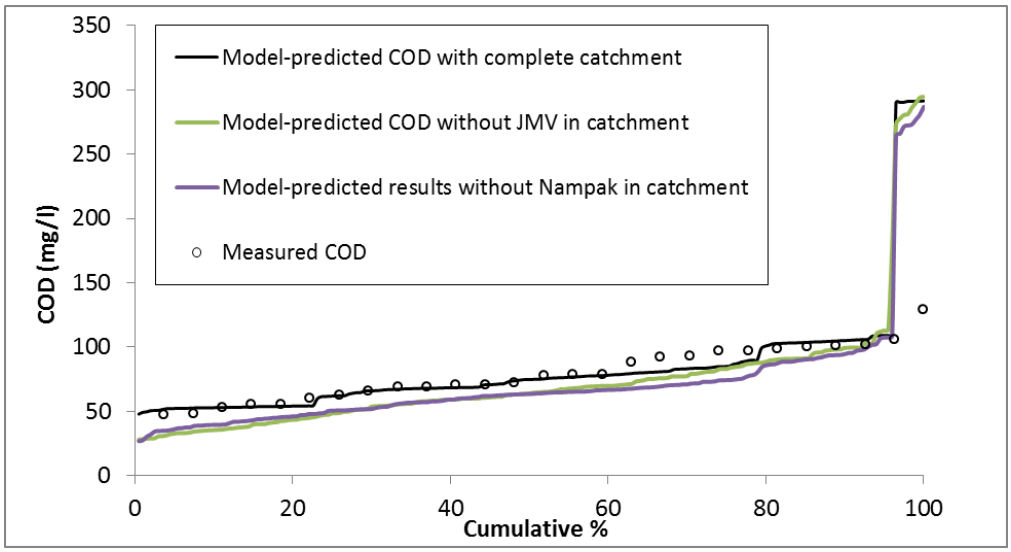


Figure 6.25 Comparison of cumulative frequency plots for final effluent COD when load is reduced

Figure 6.24 shows that if a new factory with similar volumes and effluent properties to Nampak is introduced into the catchment the COD values of the final treated effluent will increase and Figure 6.25 shows that if JMV Textiles or Nampak factories are removed from the WWTP catchment the COD values of the final treated effluent will decrease. However the evaluation goes beyond the observed change in COD values. What is of concern to the Pollution Control department of the municipality is how the increase will affect the compliance of the treated effluent to the quality standards set for the particular WWTP. Figure 6.26 shows how compliance of the final treated effluent COD changes in the different scenarios, and how it compares to the measured COD and the model predictions based on the initial complete catchment. The final effluent COD of wastewater from Verulam WWTP must be 75 mg/L or less for 90% of the time.

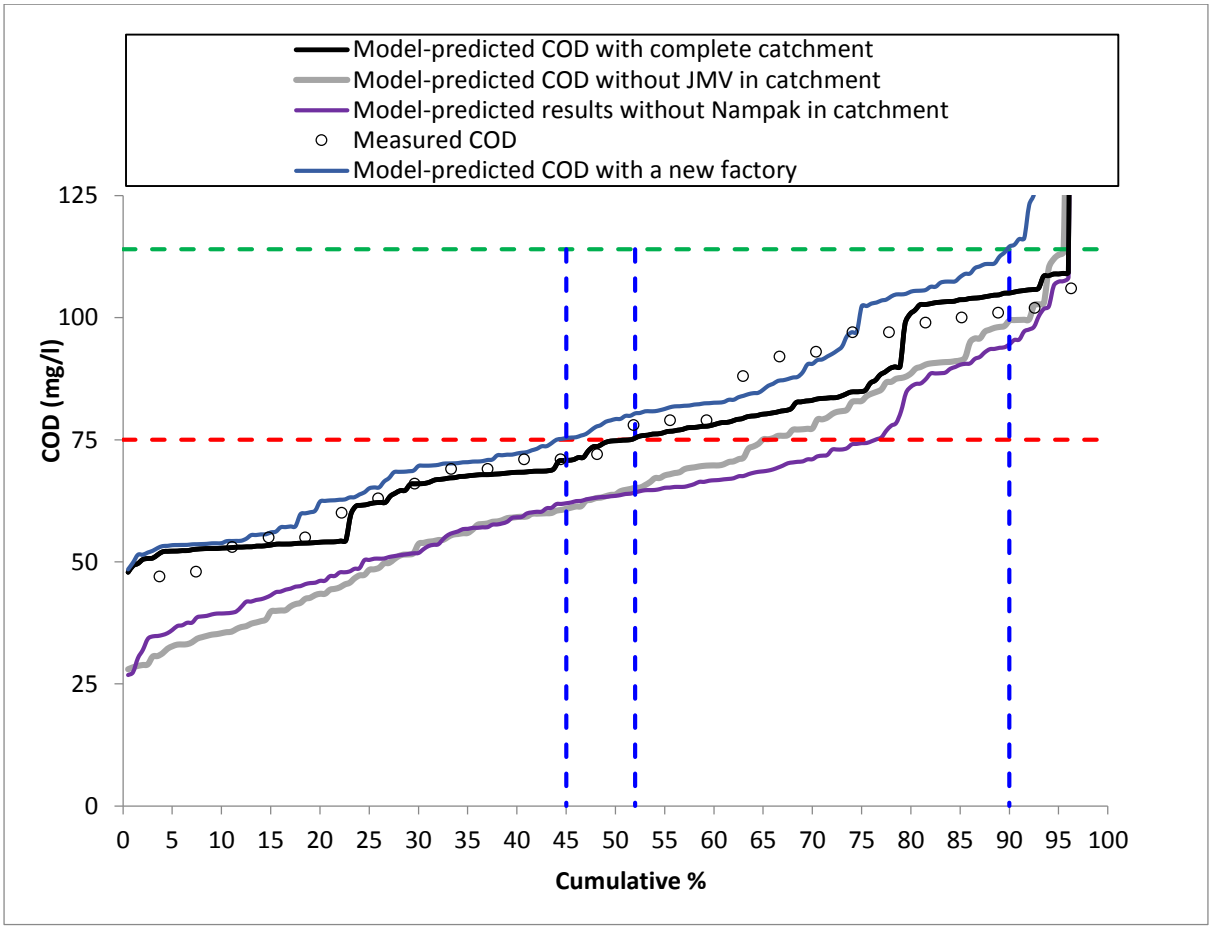


Figure 6.26 Cumulative frequency plots for final effluent COD for various scenarios

Figure 6.26 shows that the measured final effluent COD is equal to or less than 75 mg/L for approximately 50% of the time. The model predicts the same. Introducing a new factory into the WWTP catchment would reduce the compliance of the final treated effluent to the required treated effluent quality, from a compliance of 50% to 45 % of the time. Removing JMV Textiles and Nampak from the catchment shows that the final effluent COD will be equal to or lower than 75 mg/L for more than 65% of the time and 75 % of the time respectively. This indicates an improvement in compliance of the final effluent quality.

Such an assessment, carried out using the WWTP plant model would provide information to the decision maker during the process of considering whether to grant a discharge permit or not to a new factory seeking to discharge into that particular WWTP. Furthermore the impact of reducing the load on industrial effluent on the WWTP can also be evaluated using the WWTP model. However it must be pointed out that processes and mechanisms of the activated sludge process are complex. Hence the impact of changing the wastewater load on the WWTP has effects on other components, such as the TSS, ammonia, and phosphorus. Thus, to establish the complete impact on the WWTP when the volume and composition of influent wastewater changes, more measurements can be carried out on the influent into the WWTP and the final effluent, and a more sophisticated model calibration can be carried out. In this study, the demonstration of how the WWTP model can be used as a tool for evaluation, was limited to the final treated effluent COD, because the measure of compliance in Verulam is based on final treated effluent COD. While the demonstration of the concept in this study has focused on a narrower scope due to limitations in resources and measured data, it must be emphasized that with more measured data and more detailed model calibration, more accurate predictions can be obtained from the WWTP model. However for the purpose of permitting, evaluating the impact on compliance based on cumulative plots as done above is adequate as compared highly accurate dynamic model predictions.

6.8 Uncertainties in Verulam WWTP model

In the case of modelling Verulam WWTP, the approach to assessing uncertainty was focused on identifying the significant uncertainties that would affect the ability of the model to be reliable for its purpose as a tool to assess the impact of industrial effluent on WWTP performance. Due to the scope of work in this study, in-depth uncertainty analysis is not presented. There was deliberate focus on the methodology used to come up with influent wastewater characteristics for the WWTP model since a number of assumptions were made in this area.

The amount and quality of data available for modelling Verulam WWTP were a significant source of uncertainty. During model calibration, it was observed that the predicted values of the final effluent COD were lower than the measured values. This was corrected by increasing the combined influent wastewater S_I fraction from 5% to 7%. This was an indication that the catchment balance approach underestimated the S_I fraction from the contributors in the catchment. However using the available information there was no way of knowing which contributor's S_I fraction needed to be increased and to what values. The calibration process provided a means to identify the source of uncertainty. This uncertainty could be reduced by having more accurate COD fractions of the different contributors of wastewater in the WWTP catchment. Furthermore the calibration procedure that was followed did not follow all the steps recommended in key publications on activated sludge modelling calibration such as Hulsbeek et al. (2002), Petersen et al. (2002) and Sin et al. (2005) due to missing data.

During the setting up of the model, the model parameters for the ASM1 model were not adjusted from their default values. It is possible that the presence of industrial effluent and temperature variations may affect kinetic parameters of the model such that their true values for particular activated sludge unit are different from the default values recommended in Henze et al. (1987). The different model kinetic parameters may have a strong or weak influence on the model's predictions. This type of uncertainty was not evaluated in this study due to the scope of the dissertation and limited time to explore the complex subject of quantifying the relevant uncertainty. Methods do exist for quantifying the uncertainty in mathematical modelling (Sin et al., 2011; Belia et al., 2009) and they include sensitivity analysis, scenario analysis, Gaussian error propagation and other methods.

6.9 Conclusion – Modelling of Verulam WWTP

The steps for developing a model for Verulam WWTP were presented. Results of the COD fractionation based on the catchment balance approach, historical laboratory measurements and estimation of other components from literature sources were used to put together a dynamic input file that represents the influent wastewater received at the WWTP, after respirometry-based COD fractionation did not work.

The resulting input file was used in simulations on the WWTP model developed on the WEST platform and the results were evaluated. Before calibrating the WWTP model recommendations of calibration protocols for WWTP models were reviewed to guide the calibration procedure. However the recommended calibration procedures could not be applied directly and completely to this particular modelling project due to the lack of measured data required in the recommended steps.

The typical aim of model calibration for WWTPs is to obtain a set of model parameters that results in acceptable predictions of the final treated effluent, sludge production and the internal concentration dynamics of the WWTP being modelled (Gernaey et al., 2004). In the case for Verulam WWTP, P and COD balances could not be carried out around the activated sludge process due to lack of measurements on the waste activated sludge stream and primary sludge. COD is only measured on the influent wastewater and final effluent. Phosphorus is not measured in the influent, waste activated sludge and primary sludge. A TSS balance, based on the limited measurements available established that the WWTP was not running at steady-state and further investigations on the SRT used at Verulam WWTP revealed that the process was not being controlled based on a set value of the SRT. Furthermore the SRT could not be accurately calculated from the available measurements since the MLSS are not measured in Cell 1, 4 and 5 and TSS in the primary effluent and secondary clarifiers are not measured.

The attempted steady-state model calibration gave insight to the possibility that the value of X_I estimated for the influent wastewater could have been low. However it was not possible to correct the influent wastewater COD fractionation at this point since there were many other factors that were uncertain in the model itself and the influent characterisation. Model calibration was carried out further without the needed adjustments identified in the steady-state calibration.

After running dynamic simulations on the model, the only adjustments that were made during the dynamic calibration were adjusting the proportion of S_I from 5 % to 7 % and X_S from 62 % to 60 %. This resulted in an acceptable match between the cumulative frequency plots between the measured and model predicted final effluent COD. The bio-kinetic model parameters were not adjusted in this model. Considering the methods used to arrive at this influent characterisation there was no basis to adjust the model parameters, but the modelling results were accepted as a good starting point for modelling the WWTP. The model's predictions after the aforementioned adjustment of COD fractions, was satisfactory to demonstrate how the model can be used as a tool to evaluate the impact of introducing a new factory into a WWTP catchment during an assessment of issuing out a discharge permit to the factory. Furthermore, it was shown how the model can be used to assess the impact of reducing the load on the WWTP. While the demonstration was limited to evaluation of compliance of the final treated effluent COD, since this is the main criteria at Verulam WWTP, the methodology can be extended to other wastewater components on a calibrated model.

It should be pointed out that, while the model was able to predict the final effluent COD to an acceptable match, even though the identified uncertainty could not be reduced or eliminated, the need for a reliable steady-state and dynamic calibration of such a model still remains an important step to be taken in order to archive a more accurate WWTP model. In this case the model managed to work and allow demonstration of the proposed concept. From the modelling results it can be concluded that, the reasonable form of assessment of the model's performance appears to be assessing on a statistical basis as compared to day-by-day basis. Thus the impact of different scenarios on the final effluent quality was evaluated based on the cumulative frequency plots. The required level of calibration for this model was practical applicability as compared to accurate scientific exactness.

The proposed methodology can be used to evaluate the impact on the operation of the WWTP. The fact that the impact of the different scenarios on the compliance of the final effluent COD to set standards can be determined, means that if one was trying to use the model to set the discharge limits for a factory in this particular catchment, the compliance of final effluent COD to the WWTP discharge permit would form part of the criteria used to issue the effluent discharge permit, since it is clear that factories can

contribute to non-compliance of final effluent COD. In the actual discharge permit granted to JMV it was assumed that COD would not be a limiting factor. JMV Textiles was issued a discharge permit which was based on colour of the discharged effluent. As mentioned earlier, the permit for JMV Textiles was issued hurriedly before the methodology presented in this study was complete. This was rather unfortunate that the criterion chosen to base the limits of the discharge permit was colour, not effluent COD. The assessment carried out using the WWTP model shows that the assumption that COD would not be a limiting factor may have been incorrect. The methodology shows that industrial effluent COD has significant impact on compliance of the final treated effluent from Verulam WWTP. Uncertainties in the model mean that it cannot be stated categorically that it was incorrect, but at the least more investigation should have been carried before granting the permit.

In the beginning of the entire research project, it was envisaged that the assessment of the impact of factory effluent, would be carried out using the model developed in the study and then the results would inform the process of setting the limits in the discharge permit. The results of the model for the different scenarios show that a well calibrated WWTP model would be a useful tool in such an exercise.

7 CONCLUSION

The objective of this study was to propose a means of improving the assessment of the impact of industrial effluent on the performance of WWTPs for the purpose of evaluation of factories which apply for permits to discharge industrial effluent into municipal wastewater treatment plants. The proposed means was a WWTP model, which is a new concept in relation to the permitting process. The context of the modelling further introduced complexities to the task of modelling. The proposed WWTP was developed in a context of limited measurements and resources. Hence, from the beginning, the aim was to obtain a simple model rather that a complex model aiming for scientific exactness. A wide scope at the beginning of the project, limited resources and missing data drove the candidate to impossible limits during the pursuit of the objective of the study.

The aim of influent wastewater characterisation in the study was to obtain a representation of wastewater components and volumes required for modelling using ASM1. The most challenging step was to obtain COD fractions present in the combined influent wastewater received at the WWTP. The batch test recommended in Wentzel et al. (1995) was used to estimate the COD fractions, X_{BH}, S_S and S_I. The OUR profiles of the respirograms obtained from the batch test differed from results obtained in a similar study by Wentzel et al. (1999). The OUR profiles obtained could not be interpreted accurately using the modified UCT model (Dold et al., 1991), resulting in unreliable COD fractionation results which also came with poor percentage COD recoveries which were either too low or too high, when compared to the acceptable range of 95- 105% (Wentzel et al., 1995). An explanation of the unexpected OUR profiles, could be the hydrolysis of slowly biodegradable substrate present in the wastewater taking place in a manner that is not accurately described by the UCT model that is used for interpretation. Furthermore when the performance of the DO probe, during respirometry experiments carried out on purely domestic wastewater from another WWTP was compared with the performance when Verulam wastewater was used, it was concluded that the presence of industrial effluent in wastewater interfered with the ability of the DO probe to measure DO concentration accurately.

The results obtained from this study could not be compared in detail with findings from other researchers since it was clear that the method had not worked well. However a brief comparison of the COD fraction results obtained from the batch test at Verulam WWTP with results from two South African WWTPs (Wentzel et al., 1995), highlighted that experimental results were probably out of the expected range. Furthermore the composition of the 24 hour flow-weighted wastewater samples collected at Verulam WWTP varied significantly from day to day.

Since influent characterisation is a crucial step in modelling wastewater water treatment plants, as highlighted in many publications (Hulsbeek et al., 2002; Roeleveld et al., 2002 and others). The study proposed a catchment balance supported by advanced statistical methods for handling missing data and peer reviewed publications (Henze et al., 2000; Henze, 2008; Henze et al., 1987; Zawilski et al., 2009; Langeveld et al., 2012; WRC, 1994; Ubay Cokgor; 1999; Brownell et al., 1975; Wang 2005; Ubay Cokgor, 1997; El-Fadel, 2012; Ekama et al., 1986 and others) as a source of some of the missing data required to achieve complete influent wastewater characterisation. Stormwater infiltration, domestic wastewater from households and industrial wastewater from six factories were identified as the main sources of wastewater in the Verulam WWTP. Volumes of stormwater infiltration and domestic wastewater water are not measured in the catchment. Monthly averages of volumes of industrial wastewater from the six factories were available from municipal records. Complex run-off models such as ACRU (Schulze, 2004) could not be used to generate stormwater volumes in this catchment since the models require significant amounts of information as input and detailed physical characterisation of catchment, which were not available. Consequently a simplified model was used to predict the storm water infiltration after establishing the relationship between rainfall and the wastewater volumes measured at Verulam WWTP. The data of the monthly volumes of the wastewater for the six factories were used to generate estimates for daily flows for the factories using statistical theory of distribution fitting and Monte Carlo simulations and statistical theory relating the sampling distribution of the sample mean and population variances on the limited available measurements. Since the volume of the combined wastewaters is measured at the WWTP, after determining stormwater filtration and industrial wastewater volumes, the domestic wastewater volume was estimated from a catchment flow balance. The flow balance showed that the influent wastewater from Verulam WWTP consists of approximately 20 % industrial effluent and 80% domestic effluent, by volume.

The composition of the streams identified in the catchment were required to complete the catchment balance. The key composition parameters were the COD fractions of the wastewater streams since the ultimate aim of the catchment balance was to use the wastewater flows and the COD fractions in the respective streams to estimate the COD fractions in the combined influent wastewater at the WWTP. The average COD concentration of stormwater was estimated from Langveld et al. (2012) and the COD fractions were estimated from the study by Zawilski et al. (2009). The average COD of South African domestic wastewater was obtained from Ekama et al. (1986) together with corresponding COD fractions. The daily average COD values of each industrial wastewater stream were generated from the limited available measurement using distribution fitting and Monte Carlo simulations. While the COD fractions for industrial wastewater were obtained from different literature sources (Ubay Cokgor; 1999; Brownell et al., 1975; Wang 2005; Ubay Cokgor, 1997; El-Fadel, 2012; Ubay Cokgor; 1997). With the aforementioned information, a catchment COD balance allowed the estimation of the combined wastewater COD fraction for Verulam WWTP. The COD fractions of the combined influent wastewater

obtained from the catchment balance approach were S_S = 31% S_I = 5% X_S = 49% X_I =14% X_{BH}=0, for 2009; S_S = 31% S_I = 5% X_S = 50% X_I =14%, for 2010 and S_S = 33% S_I = 5% X_S = 49% X_I =13%, for 2010 suggesting that the COD fractions do not vary significantly on average.

The value of obtaining estimates, in particular COD fractions of the industrial wastewater effluent, from literature, in the methodology, is that obtaining COD fractions experimentally is complex and difficulty process. If knowledge of the core business of the factory producing a wastewater stream is adequate to lead one to obtain reliable estimates of the COD fractions from literature or studies that have characterised that type of wastewater, this would be an advantage, especially in a model such as the one in this study. The success of the methodology, based on such estimates would mean that it would be much easier to evaluate factories for discharge permits using the WWTP model, because the need for highly accurate COD fractionation based on experiments would be removed. This would allow the municipality to carry out evaluations based on WWTP model, since one of their key constraints is lack of capacity to carry out detailed COD fractionation of wastewater samples.

The principle behind the catchment balance approach was to use the limited available knowledge and measured data with respect to the characteristics and volumes of the wastewater released by the major contributors to the WWTP catchment to estimate the composition of the combined wastewater stream received by the WWTP, with special focus on the COD fractionations. While the approach was associated with uncertainty due to assumptions that had to be made, since a lot of data was missing, the aim of adopting and applying the methodology was to demonstrate that with reasonable assumptions, and a limited data set, adequate results could be obtained. It should be noted that the goal of the modelling was to provide a statistical description of the system outputs rather than to give outputs that correspond to the actual daily variations experienced at the WWTP. Thus, the WWTP model results (output of WWTP model) were presented and evaluated on a statistical basis. The evaluation assessed how well the statistical description of the model output was matching that of measurements taken at the WWTP. This proved to be an appropriate method for evaluating the compliance of the treated effluent to set effluent standards. This means the proposed methodology can be used in the discharge permitting system.

The fitting of probability distribution functions to the available data and Monte Carlo simulations were used to fill in gaps in data and to generate some of the required flow and composition data. The following conclusions can be drawn from the different stages of the methodology of the catchment balance approach:

- Multiple linear regression analysis can be used to estimate the relationship between rainfall and stormwater infiltration.

- Monte Carlo simulation can be used to logically represent the contribution of factory effluent in a WWTP catchment, on a statistical basis.
- The Weibull probability distribution was the best distribution to describe the flows of wastewater from all the factories in the Verulam catchment. This probability distribution is recommended for similar future investigations.
- The results of searching for and reviewing literature sources for the COD fractionation of wastewater showed that COD fractionation has not been undertaken on many wastewater types especially those of industrial origin. No estimates of complete COD fractionation were available for the wastewater from the soap and detergent industries.

After completing influent characterization a model of Verulam WWTP was developed based on ASM1. The plant configuration was set up on the WEST platform. The historical plant data measured for plant monitoring purposes was used to develop the model and also to try and calibrate the model. Guidelines for good modelling practice (Rieger et al., 2012) were reviewed and effort was made to follow the guidelines but the lack of measurements forced deviations from guidelines at some stages of the modelling. Balancing sludge production and knowing the SRT with 95% accuracy (Brdjannovic et al., 2000) is important for reliable simulations in a model. P and COD balances could not be carried out around the activated sludge process due to lack of measurements on the waste activated sludge stream and primary sludge. COD is only measured on the influent wastewater and final effluent. Phosphorus is not measured in the influent, waste activated sludge and primary sludge. A TSS balance, based on the limited measurements available established that the WWTP was not running at steady-state and further investigations on the SRT used at Verulam WWTP revealed that the process was not being controlled based on a set value of the SRT and that the SRT was not constant. Thus the attempted steady state calibration was reduced to trying to match the average solids concentrations measured in some of the cells of the ASU. After running dynamic simulations on the model, and adjusting only the proportion of S_I from 5 % to 7 % and X_S from 62 % to 60 %, the model's prediction of the treated final effluent COD showed an acceptable match between the cumulative frequency plots of the measured and model predicted final effluent COD. The bio-kinetic model parameters were not adjusted in this model. Influent wastewater and treated effluent nutrients such as TKN, P, PO_4-P are not measured hence the model could not be calibrated for nutrient removal. The reason why there is less attention on these parameters, especially in the final treated effluent is that compliance of the treated effluent quality is accessed based on the COD concentration at this particular WWTP.

The resulting model, with the simple calibration, was able to allow the demonstration of how the impact on compliance of final treated effluent of introducing a new factory in a WWTP catchment, could be assessed. Furthermore The ASM1 model, originally designed for the activated sludge process treating domestic water proved to be capable of modelling the activated sludge process at Verulam WWTP which receives a combined influent (domestic and industrial wastewater).

The success of the modelling exercise which used the influent characterisation based on the catchment balance approach provided a deeper insight in the subject of WWTP modelling for permitting purposes. Therefore the methodology, with all its assumptions, can be recommended for use as a tool for assessment and to suggest priorities for future investigations related to discharge permit assessments.

The ultimate justification of using the results from the catchment balance with so many assumptions and uncertainty was that the frequency distribution of treated effluent quality from the combined catchment plus WWTP model showed a satisfactory correspondence with the distribution of plant measurements. A significant feature of the catchment balance methodology is that the influence of each factory is already represented in the wastewater characterisation, albeit in a very approximate form. The evaluation of the factory effluent for the purpose of setting the permit conditions thus becomes just a special case of the process of improving the model to represent specific issues in the catchment, rather than a separate modelling process as envisaged in the original project proposal.

A noticeable shortfall in the methodology presented in this thesis is the quantification of the uncertainty associated with every assumption that went into the model. This was a subject that could not be tackled in this dissertation due to scope of work and limited resources. However, the main outcome of the modelling exercise appears to match the observed uncertainties in the actual WWTP outputs. More extensive uncertainty analysis would further ascertain the confidence that one must have in the model's prediction. There was no way of avoiding making assumptions, and the main justification for these assumptions is that the WWTP model was able to predict the measured values of variables of the WWTP well enough.

Recommendations

While dynamic modelling studies have been carried out at some of the WWTPs owned by eThekwini Municipality, the full potential of dynamic modelling and simulation of activated sludge plants as a decision making tool for improving plant operations, is not being utilized. It is recommended that the methodology outlined in this thesis be taken further through more studies to bring it to a point where it can be used by municipalities to improve the compliance of the final treated effluent from WWTPs to the set standards. Further studies that recommended should focus on

- Quantifying the uncertainty associated with the different steps in the methodology

- Improving data collection with the focus on COD fractions of the sources of wastewater in the catchment of WWTPs
- Improving the stormwater runoff and infiltration models
- Increasing the amount of measured data available for fitting probability distribution functions
- Detailed model calibration guided by Good Modelling Practice guidelines

The above recommendations will aim to address the gaps identified in this particular study. It should be noted that the current study has shown that there is no need to derive or apply complex models for influent characterisation and COD fractionation in particular, to achieve acceptable results. Thus the recommended further studies must aim to address the gaps with limited complexity to ensure that the methodology can be of practical use to municipalities running WWTPs.

A follow-up project (WRC K5/2221) has been initiated, which will provide a vehicle for continuing the development of WWTP modelling. How it is conducted will be informed by the experiences gained in this project. The proposed methodology and deliverables were formulated to address several aspects that include further research in the following subjects:

- Investigation of more robust and reliable laboratory methods for wastewater characterisation.
- The further development of influent wastewater characterisation using a combination of catchment balance and laboratory measurements.

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APPENDICES

Appendix A Modules in trade effluent discharge permit application form

Module 1 Permit holder details

The details required in this module include business details of the enterprise, the date on which the enterprise started operating, information on any upgrade in production and the date of the initial discharge to the sewer system. Information on the land use zoning as per Town planning Scheme (residential or commercial) must be provided. Any assessment that may be relevant to wastewater disposal such as an Environmental Impact Assessment should be stated. A map or sketch showing the location of the enterprise in relation to its external environment such as roads, residential areas, rivers and other geographical features must be submitted.

Module 2 Process and plant details

A process flow sheet made up of process block diagrams is required in Module 2. Each block representing a unit in the process should be accompanied by details describing the inputs and outputs of the unit, major equipment used in the unit and the key functions of the unit. The link between the process blocks should be clearly shown. All discharge points must be marked. In situations where the enterprise is complex, further simplified block diagrams which break down the complex process into smaller component unit processes may be requested. A colour coded drainage plan is required. During the preparation of the process block diagram the applicant needs to identify potential or present environmental impact aspects and list them in an "Aspect Register" before comparing and prioritising in order of significance. Provision should be made for the management of some of the identified environmental aspects in the Emergency response and Contingency Plans that are submitted with the application. Material and Safety Data Sheets (MSDS) for all substances used, produced and stored on site must also be kept in an easily accessible place on site. Production details such as production capacity, whether the process is batch or continuous and any new process changes should be provided in this module.

Module 8 Waste management

In Module 8 the applicant is required to identify all types of waste generated in each process block. A waste audit will identify the source and types of waste produced. The amount of waste and the hazard level should be provided. The main pollutants should be identified and their concentrations estimated. The applicant is then required to provide waste management systems for the wastes identified through the process block assessment.

Module 10 Trade effluent discharges to sewer from site or via road haulage

In module 10 the applicant is required to identify and describe the composition of effluent to be discharged. The volumes of effluent and the concentration of the identified components must be reported. A sampling point where a representative sample or well mixed sample of the final effluent going to the sewer must be identified and the method used to obtain a representative sample must be described in detail. In the case where the enterprise is already generating effluent, representative samples of the effluent must be analysed by an International Organisation for standardization (ISO) certified or acceptable laboratory. An approximate concentration range must be identified for each parameter. If the permit applicant has not begun operating the plant and hence is unable to obtain samples for analysis, it is their duty to conduct research and give the best estimate of the likely concentration range.

The applicant is required to identify components in the effluent that may cause a risk of corrosion to the sewer infrastructure, toxicity or hazard to municipality staff, detrimental effect on the wastewater treatment plant processes, nuisance to neighbours, environmental bio-accumulation and provide details on the nature of their impact. Intermittent or short releases such as those resulting from batch production, cleaning operations, plant startup, shutdown, and scheduled maintenance must be presented. If these releases differ from ordinary process wastewater, the composition should be specified. All effluent pre-treatment methods currently applied or proposed to be applied on site to ensure that the final trade effluent discharge to sewer complies with legal standards should be presented. The standard of treatment required depends on the emission limit values set in the permit for the criteria pollutants. If current discharge levels are higher than the limit prescribed in the permit then the permit holder is required to identify appropriate technology and install additional treatment.

The applications for trade effluent discharge permit are considered by the Pollution and Environment Department of eThekwini Water and Sanitation. The permit applicant has the right to appeal and to make representation before a tribunal to ensure a fair administrative procedure. The eThekwini Water and Sanitation Authority charges a fee for processing applications for discharge permits in line with the sewage disposal bylaws. In each catchment area users who discharge high volumes or high strength effluent are identified and monitored regularly to ensure compliance with water quality requirements set in the sewage disposal bylaws. Noncompliance is addressed by issuing warnings to the non-complying users and legal prosecution in more severe cases.

Appendix B Interpretation of results from the aerobic batch test

The typical OUR profile that is obtained from the aerobic batch test is shown in **Error! Reference source not found.**. An increase of the OUR is observed from the start of the test when the amount of readily biodegradable COD S_S present is not limiting the growth of biomass. This is followed by a sharp decrease in OUR, when the readily biodegradable COD is depleted. After this period the readily biodegradable COD that being utilised is only available due to the hydrolysis of slowly biodegradable COD X_S. The OUR measured during the period of non-limited growth is due to the utilisation of both S_S and X_S.

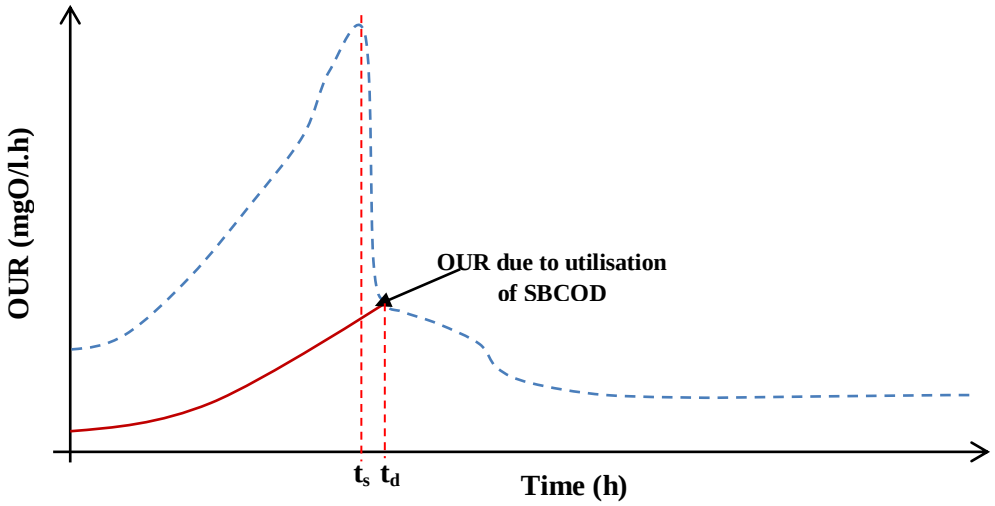

Figure B.1 Typical OUR profile for aerobic batch test on raw wastewater **showing OUR utilisation of the slowly biodegradable COD**

From this respirogram and the simplified UCT model the following information can be obtained

- The heterotrophic active biomass Z_{BH} present in the water
- The readily biodegradable COD S_S
- The wastewater heterotrophic maximum specific growth rate on RBCOD $\hat{\mu}_H$
- The wastewater heterotrophic maximum specific growth rate on SBCOD K_{MP}
- COD recovery

The heterotrophic biomass specific death rate, b_H and the heterotroph yield, Y_{ZH} need to be determined from separate experiments or values may be assumed from literature sources of similar experimental work. In this study the value of b_H and Y_{ZH} were taken as 0.62/d and 0.66 mgCOD/mgCOD. The source of these values was (Wentzel et al., 1995).

Table B.1 The simplified UCT model (Dold et al., 1991) for the conditions present in the aerobic batch

i COMPOUND → / **↓ j PROCESS**	**Z_{BH}**	**Z_E**	**Z_I**	**S_{ads}**	**S_{enm}**	**S_{bs}**	**S_{us}**	**O**	**PROCESS RATE, ρ_j**
Aerobic growth of Z_{BH} on S_{bs}	1					$\frac{-1}{Y_{ZH}}$		$-\frac{(1-Y_{ZH})}{Y_{ZH}}$	$\mu_H \cdot \frac{S_{bS}}{K_{SH}+Sb_S} \cdot Z_{BH}$
Aerobic growth of Z_{BH} on S_{ads}	1			$\frac{-1}{Y_{ZH}}$				$-\frac{(1-Y_{ZH})}{Y_{ZH}}$	$K_{MP} \cdot \frac{S_{ads}/Z_{BH}}{K_{SP}+S_{ads}/Z_{BH}} \cdot Z_{BH}$
Death of Z_{BH}	-1	f_E			1- f_E				$b_H \cdot Z_{BH}$
Adsorption of S_{enm}									$K_A S_{enm} Z_{BH}(f_{MA}- S_{ads}/ Z_{BH})$
Stoichiometric constants Y_{ZH} – Heterotrophic yield f_E –Endogenous residue f_{MA}- Max. ratio S_{ads}/ Z_{BH}	(M COD. L^{-3}) Active heterotrophic biomass	(M COD. L^{-3}) Endogenous mass	(M COD. L^{-3}) Inert mass	(M COD. L^{-3}) Adsorbed slowly biodegradable substrate	(M COD. L^{-3}) Enmeshed slowly biodegradable substrate	(M COD. L^{-3}) Readily biodegradable soluble substrate	(M COD. L^{-3}) Un-biodegradable soluble substrate	(M COD. L^{-3}) Oxygen	Kinetic constants μ_H -heterotrophic max. specific growth rate on S_{bs} K_{SH} –heterotrophic half saturation on S_{bs} K_{SP} -heterotrophic half saturation on S_{ads} b_H -heterotrophic specific death rate K_A -S_{enm} specific adsorption rate

Theory for determining heterotrophic active biomass Z_{BH}

From the simplified UCT model shown in **Error! Reference source not found.** the rate of growth of heterotroph biomass is given by equation B.1

$$\frac{dZ_{BH}}{dt} = growth\ on\ RBCOD + growth\ on\ \ SBCOD + death$$

$$\frac{dZ_{BH}}{dt} = \hat{\mu}_H \cdot \frac{S_{bS}}{K_{SH}+Sb_S} \cdot Z_{BH} + K_{MP} \cdot \frac{S_{ads}/Z_{BH}}{K_{SP}+S_{ads}/Z_{BH}} \cdot Z_{BH} - b_H \cdot Z_{BH} \qquad [B.1]$$

It can be accepted that during the initial stages of the batch test, (before the readily biodegradable COD is depleted and the OUR drops precipitously) $S_{bs} >> K_{SP}$ and $S_{ads}/Z_{BH} >> K_{SP}$ (Wentzel et al., 1995), therefore:

$$\frac{dZ_{BH}}{dt} = (\mu_H + K_{MP} - b_H) \cdot Z_{BH} \qquad [B.2]$$

Separating variables and integrating and solving equation B.2 yields the active organism concentration at a time t, ($Z_{BH(t)}$;mgCOD/L) in terms of the initial active organism concentration ($Z_{BH(t)}$;mgCOD/L) ,time (t, in h) and the net specific growth rate,($(\hat{\mu}_H + K_{MP} - b_H)$;d). The factor 24 converts time t in hours to days.

$$Z_{BH(t)} = Z_{BH(0)} e^{(\hat{\mu}_H + K_{MP} - b_H)t/24} \qquad [B.3]$$

The OUR at a time t is a function of $Z_{BH(t)}$ and the net specific growth rate:

$$OUR_{(t)} = \frac{1-Y_{ZH}}{Y_{ZH}}(\hat{\mu}_H + K_{MP}) \cdot Z_{BH(t)} / 24 \quad [B.4]$$

Substituting equation B.3 for $Z_{BH(t)}$ in equation B.4 and taking natural logarithms yields:

$$\ln OUR_{(t)} = \ln\left[\frac{1-Y_{ZH}}{Y_{ZH}}(\hat{\mu}_H + K_{MP}) \cdot Z_{BH(t)} / 24\right] + (\hat{\mu}_H + K_{MP} - b_H) \cdot t / 24 \quad [B.5]$$

This equation represents a straight line with:

$$\text{Slope} = (\hat{\mu}_H + K_{MP} - b_H) \cdot t / 24$$

$$\text{Y-intercept} = \ln OUR_{(t=0)} = \ln\left[\frac{1-Y_{ZH}}{Y_{ZH}}(\hat{\mu}_H + K_{MP}) \cdot Z_{BH(t)} / 24\right]$$

From the plot of ln $OUR_{(t)}$ versus time in hours, the influent active heterotrophic biomass $Z_{BH(0)}$ can be obtained as shown in equation B.6

$$Z_{BH(0)} = \frac{e^{(y-\text{intercept})} \cdot 24}{\frac{1-Y_{ZH}}{Y_{ZH}} \cdot (slope \cdot 24 + b_H)} \text{ mgCOD/L} \quad [B.6]$$

The biomass yield Y_{ZH} and the death constant b_H are determined from experiment.

Heterotroph maximum specific growth rate on SBCOD, K_{MP}

The S_S concentration is calculated from the concentration of oxygen utilised in its degradation. This requires the OUR before the precipitous drop to be separated into its S_S and X_S contributions, which is equivalent to separating the overall growth rate $(\hat{\mu}_H + K_{MP})$ into its $\hat{\mu}_H$ and K_{MP} components.

In terms of the UCT-model, growth of heterotrophic micro-organisms on readily biodegradable substrate, and slowly biodegradable substrate, is independent. The only thing that separates them is the respective maximum growth rates on the two substrates. The oxygen uptake rate, OUR (mgO_2/L.h), of the two growth processes are given by equation B.7 and B.8.

$$OUR_{RBCOD(t)} \cdot 24 = \frac{1-Y_{ZH}}{Y_{ZH}} \cdot \hat{\mu}_H \cdot Z_{BH(0)} \cdot e^{(\hat{\mu}_h + K_{MP} - b_H)t/24} \quad [B.7]$$

$$OUR_{SBCOD(t)} \cdot 24 = \frac{1-Y_{ZH}}{Y_{ZH}} \cdot K_{MP} \cdot Z_{BH(0)} \cdot e^{(\hat{\mu}_h + K_{MP} - b_H)t/24} \quad [B.8]$$

Where:

Y_{ZH} = Yield coefficient for heterotroph (mg COD/mg COD)

$\hat{\mu}_H$ = Maximum specific growth rate of heterotroph on readily biodegradable substrate (/d).

K_{MP} = Maximum specific growth rate of heterotrophs on slowly biodegradable substrate (/d).

$Z_{BH(0)}$ = Initial concentration of heterotroph (mg COD/L).

b_H = Lysis and decay rate for heterotroph (/d).

Before the precipitous decrease the total OUR, $OUR_{(t)}$, is the sum of the two growth processes, equation B.7 and B.8. When RBCOD is depleted the OUR shows the precipitous decrease and if this occurs at $t = t_d$ h, K_{MP} can be calculated from equation B.9.

$$K_{MP} = \frac{OUR_{SBCOD(t=t_d)} \cdot 24}{\frac{1-Y_{ZH}}{Y_{ZH}} \cdot Z_{BH(0)} \cdot e^{(\hat{\mu}_H + K_{MP} - b_H)\cdot(t=t_d)/24}} \quad \text{[B.9]}$$

Where:

$OUR_{SBCOD(t=td)}$ = OUR value due to utilisation of X_S only, immediately following the precipitous drop i.e. at $t=t_d$

(t_d) =The time immediately following the precipitous drop in OUR in h

$(\hat{\mu}_H + K_{MP} - b_H) \cdot t / 24$ = the slope of the ln $OUR_{(t)}$ vs. time *(h)* plot.

Heterotroph maximum specific growth rate on RBCOD, $\hat{\mu}_H$

The maximum growth rate is calculated from the value for K_{MP} derived earlier and the slope of the *ln OUR* versus time plot as shown in equation B.10.

$$\hat{\mu}_H = slope \cdot 24 - K_{MP} \quad \text{[B.10]}$$

Determination of the influent RBCOD concentration

Knowing K_{MP} and $\hat{\mu}_H$, the OUR_{SBCOD} can now be calculated and subtracted from OUR_{total} to give the OUR_{RBCOD}. The RBCOD then is given by $1/(1-Y_{ZH})$ times the area between the observed OUR and the theoretical OUR_{SBCOD} from the start of the batch test t=0 to the precipitous drop $t=t_d$:

$$RBCOD = \frac{1}{1-Y_{ZH}} \int_{t=0}^{t=d} \left(OUR_{total} - OUR_{SBCOD}\right) \cdot dt \text{ mgCOD/L} \quad \text{[B.11]}$$

The RBCOD concentration can be found by doing the integration in equation B.11 graphically, i.e. determining the area between the two curves in the OUR plot.

COD analysis

The principle of the experiment is that organic matter is oxidized by a mixture of boiling chromic and sulphuric acids. A sample taken before and after the OUR experiment is refluxed in strong acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed. The oxidisable matter is then calculated in terms of the oxygen equivalent.

Appendix C Results of distribution fitting on wastewater-flow data for factories in Verulam WWTP catchment

Table C.1 Ranking of probability distributions fitted to daily average trade effluent volumes for JMV Textiles

Rank	Distribution	Chi-squared statistic
1	Weibull	3.2727
2	Beta general	4.9697
3	Gamma	9.2121
4	Inverse Gaussian	9.2121
5	Log normal	9.2121

Table C.2 Ranking of probability distributions fitted to daily average trade effluent volumes for Nampak

Rank	Distribution	Chi-squared statistic
1	Weibull	5.2222
2	Betageneral	7.1667
3	Erland	7.1667
4	Gamma	7.1667
5	Inverse Gaussian	11.8333

Table C.3 Ranking of probability distributions fitted to daily average trade effluent volumes for Frimax

Rank	Distribution	Chi-squared statistic
1	Triangular	10.2778
2	Weibull	10.667
3	BetaGeneral	12.2222
4	LogLogistic	12.2222
5	Erlang	13.3889

Table C.4 Ranking of probability distributions fitted to daily average trade effluent volumes for Packo

Rank	Distribution	Chi-squared statistic
1	Rayleigh	3.8824
2	LogLogistic	4.7059
3	Pearson6	5.9412
4	Erlang	6.3529
5	Gamma	6.3529
6	Weibull	6.3529

Table C.5 Ranking of probability distributions fitted to daily average trade effluent volumes for Colgate Palmolive

Rank	Distribution	Chi-squared statistic
1	Triangular	3.6667
2	BetaGeneral	5.2222
3	Gamma	6.0000
4	Weibull	6.0000
5	Erlang	9.1111

Table C.6 Ranking of probability distributions fitted to daily average trade effluent volumes for Budget Soap

Rank	Distribution	Chi-squared statistic
1	Weibull	1.3333
2	BetaGeneral	4.0556
3	Erlang	7.1667
4	Gamma	7.1667
5	Inverse Gausss	11.0556

Distribution fitting results for daily average flow data from JMV Textiles

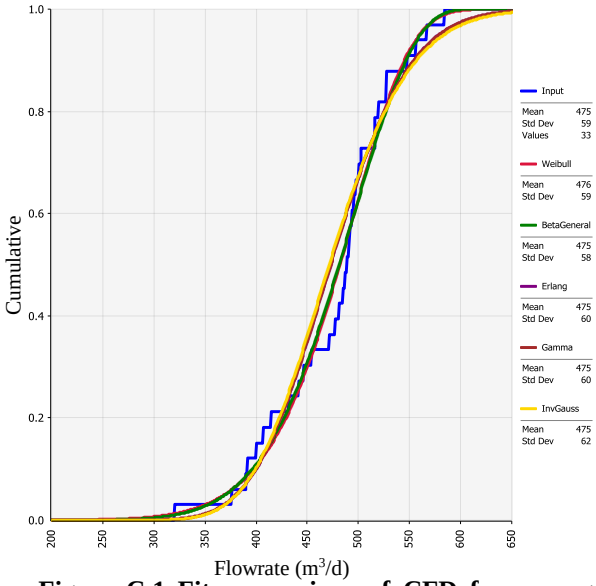

Figure C.1 Fit comparison of CFD for average daily flows for JMV Textiles, for top five distributions

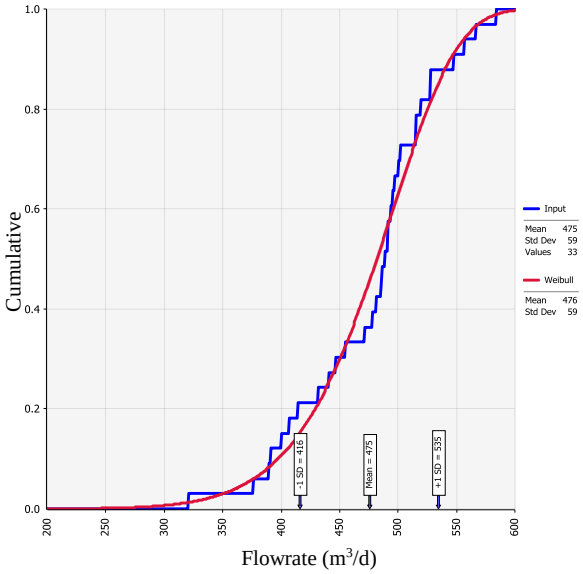

Figure C.2 CFD for average daily flows for JMV Textiles, for top ranking distribution (Weibull)

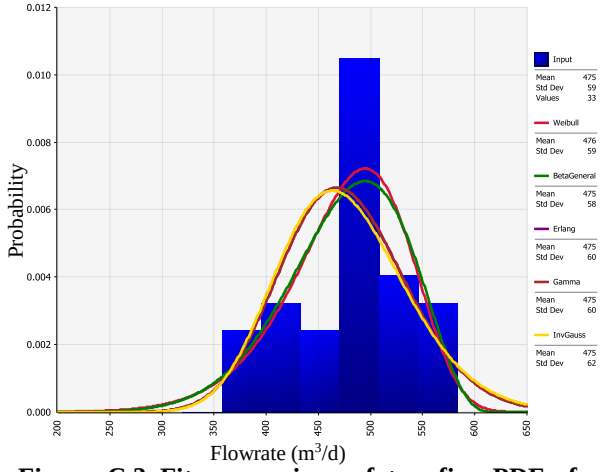

Figure C.3 Fit comparison of top five PDFs for JMV Textiles daily average flows

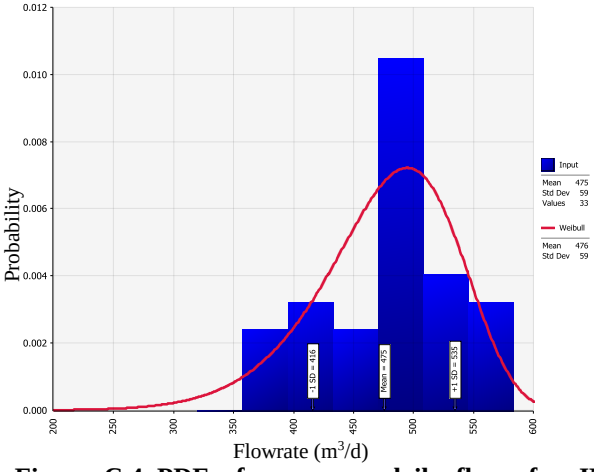

Figure C.4 PDF for average daily flows for JMV Textiles, for top ranking distribution (Weibull)

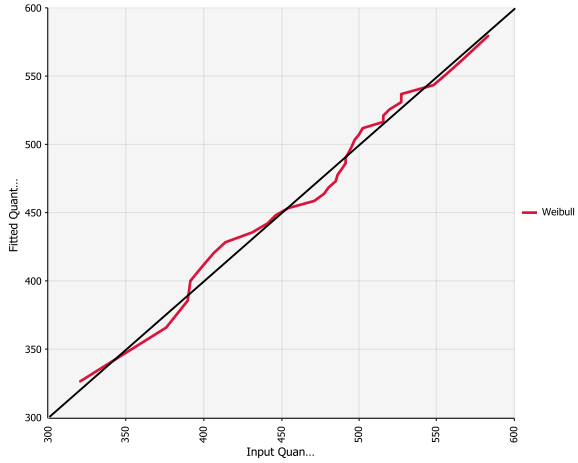

Figure C.5 Quantile-Quantile plot for JMV Textiles daily average flows

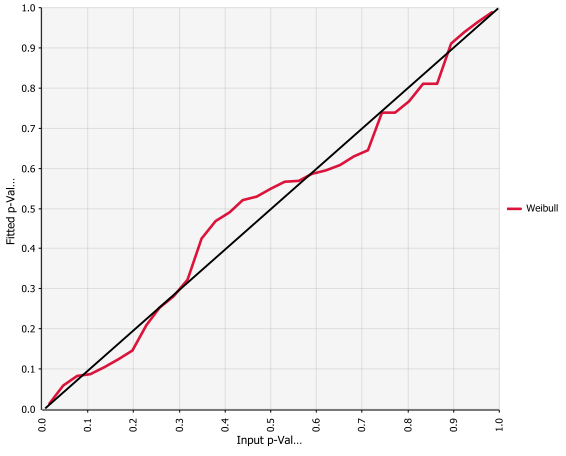

Figure C.6 Probability-Probability plot JMV Textiles daily average flows

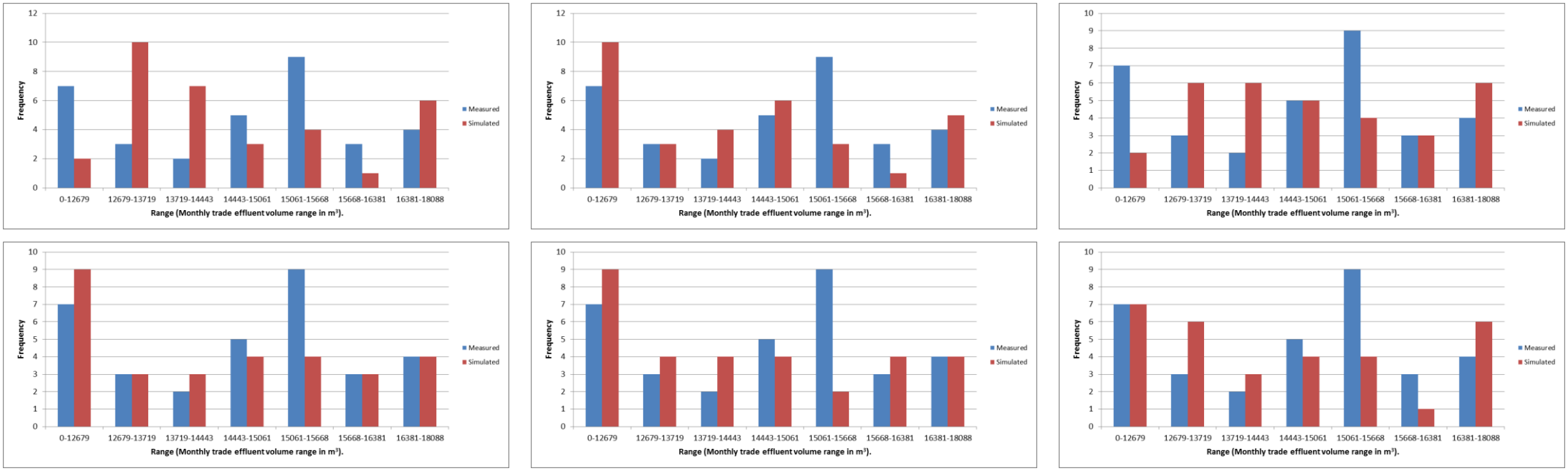

Figure C.7 Distribution of measured and simulated monthly trade effluent volumes-JMV Textiles

Distribution fitting results for daily average flow data from Nampak

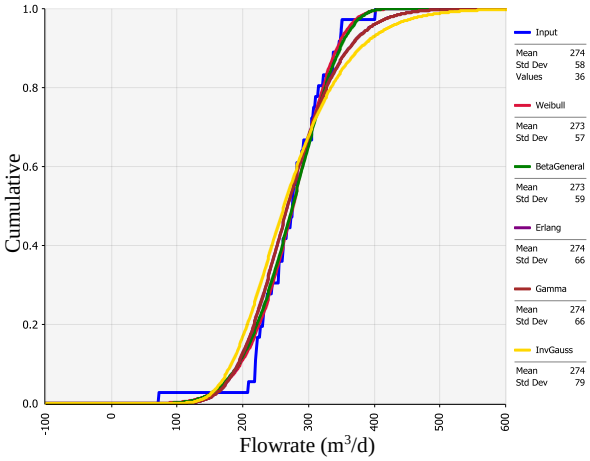

Figure C.8 Fit comparisons of CDFs for daily average flows for Nampak, for top 5 distributions

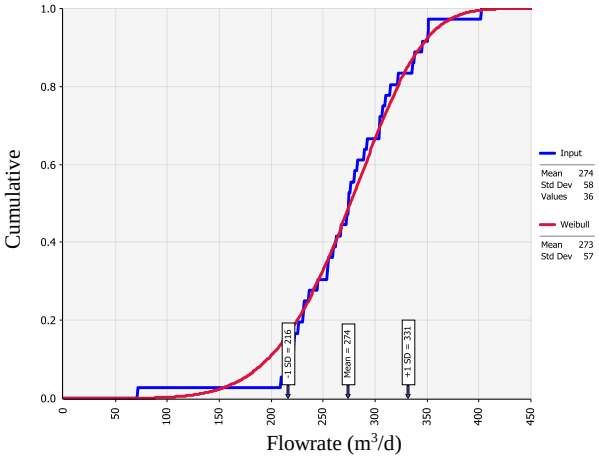

Figure C.9 CDF for daily average flows for Nampak, for the top ranking distribution (Weibull)

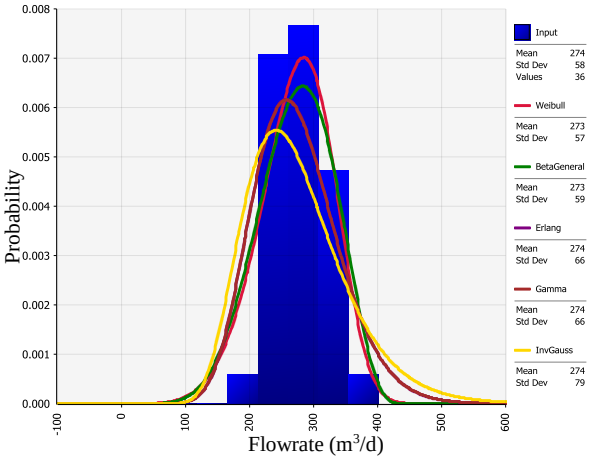

Figure C.10 Fit comparisons of PDFs for daily average flows for Nampak, for top 5 distributions

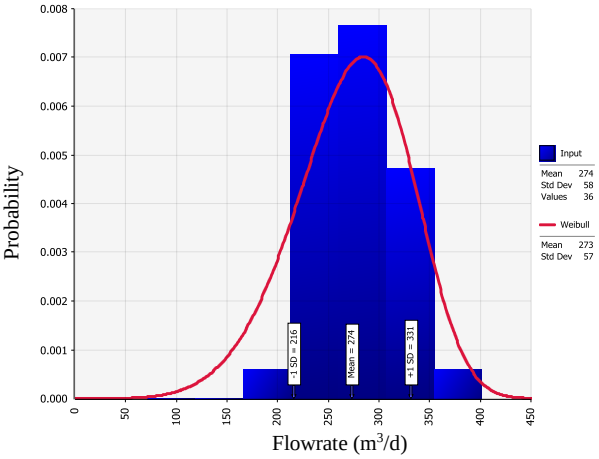

Figure C.11 PDF for daily average flows for Nampak, for the top ranking distribution (Weibull)

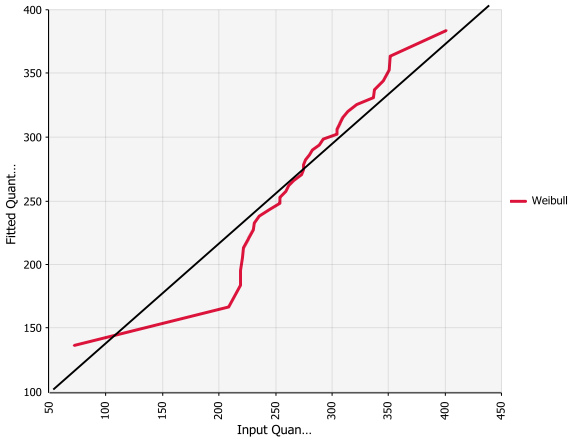

Figure C. 12 Q-Q plot for Weibull distribution

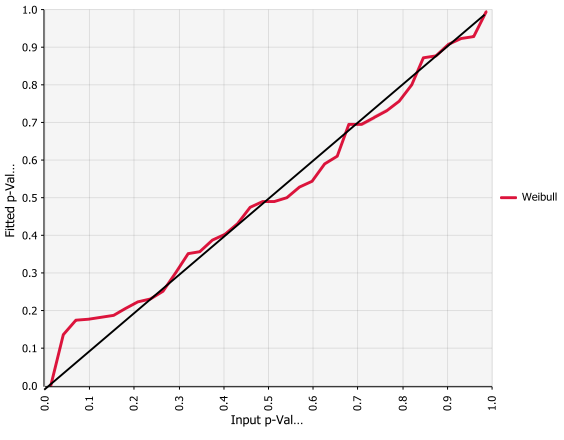

Figure C. 13 P-P for Weibull distribution

Distribution fitting results for daily average flow data from Frimax Foods

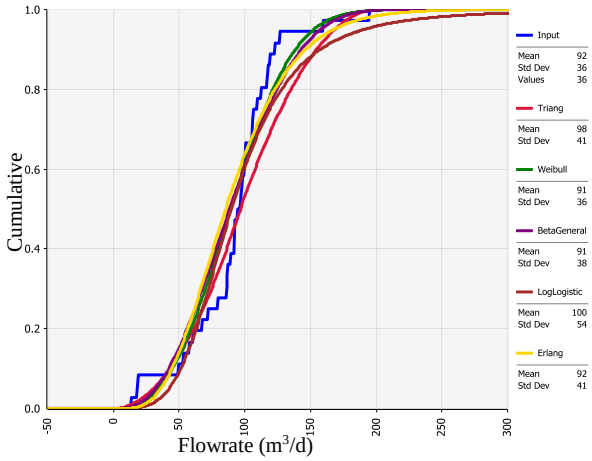

Figure C.14 Fit comparisons of CDFs for daily average flows for Frimax Foods, for top 5 distributions

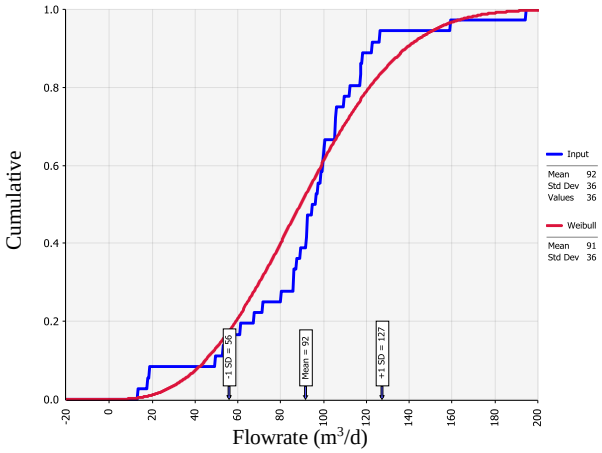

Figure C.15 CDF for daily average flows for Frimax Foods, for the top ranking distribution (Weibull)

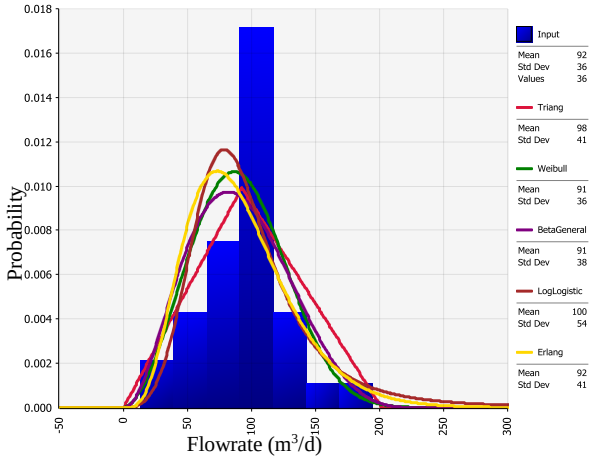

Figure C.16 Fit comparisons of PDFs for daily average flows for Frimax Foods, for top 5 distributions

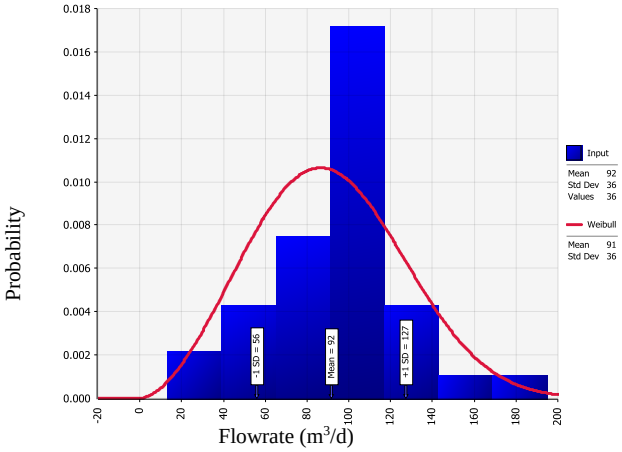

Figure C.17 PDF for daily average flows for Frimax Foods, for the top ranking distribution (Weibull)

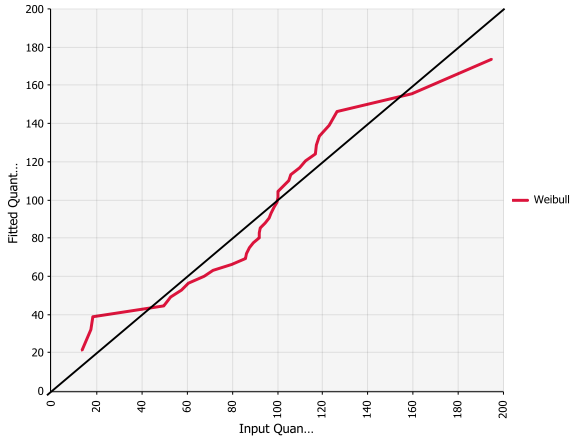

Figure C.18 Q-Q plot for Weibull distribution

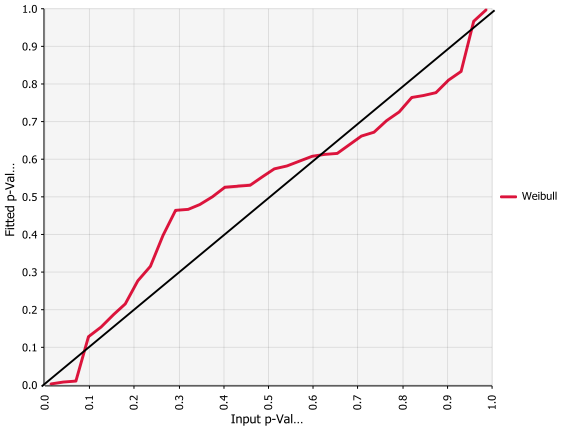

Figure C.19 P-P plot Weibull distribution

Distribution fitting results for daily average flow data from Packo

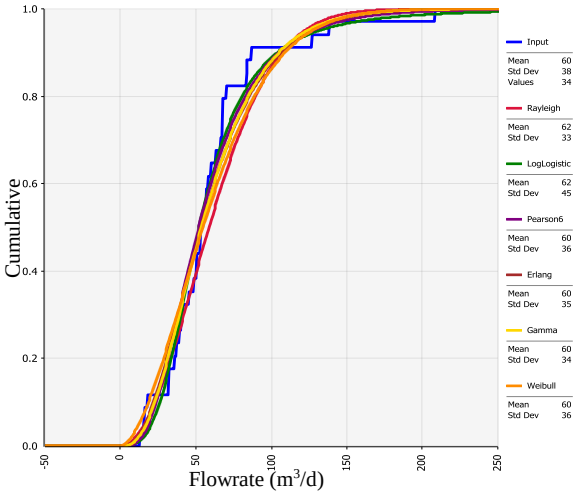

Figure C.20 Fit comparisons of CDFs for daily average flows for Packo, for top 5 distributions

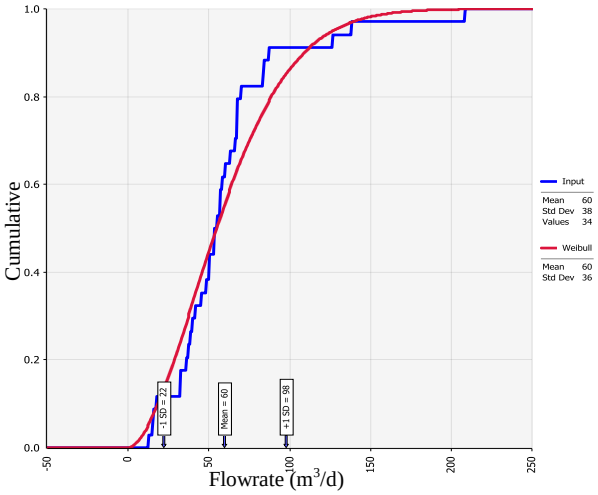

Figure C. 21 CDF for daily average flows for Packo, for the top ranking distribution (Weibull)

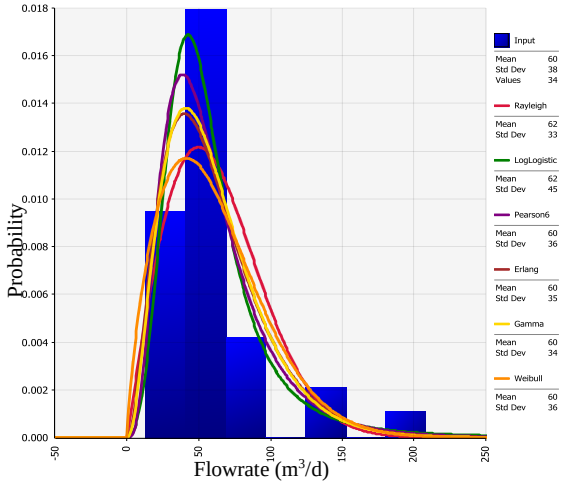

Figure C.22 Fit comparisons of PDFs for daily average flows for Packo, for top 5 distributions

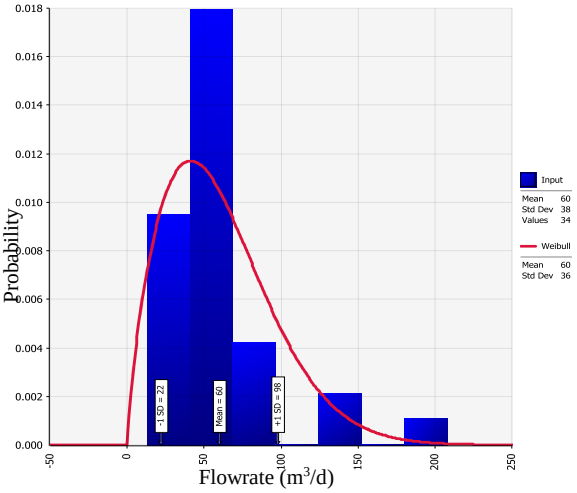

Figure C.23 PDF for daily average flows for Packo, for the top ranking distribution (Weibull)

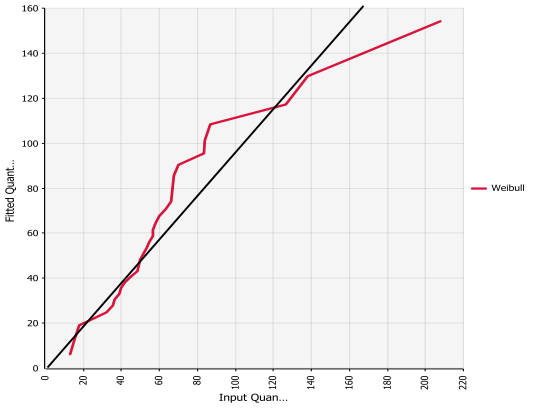

Figure C.24 Q-Q plot for Weibull distribution

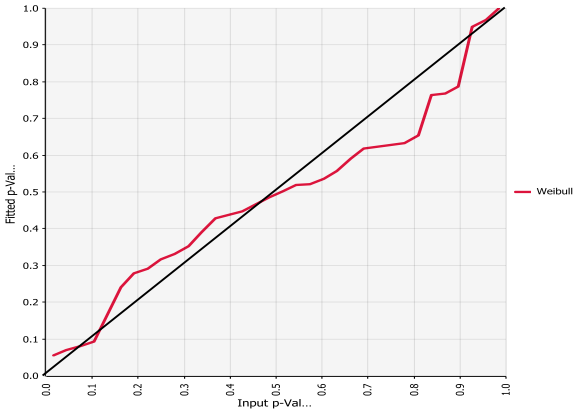

Figure C.25 P-P plot Weibull distribution

Distribution fitting results for daily average flow data from Colgate Palmolive

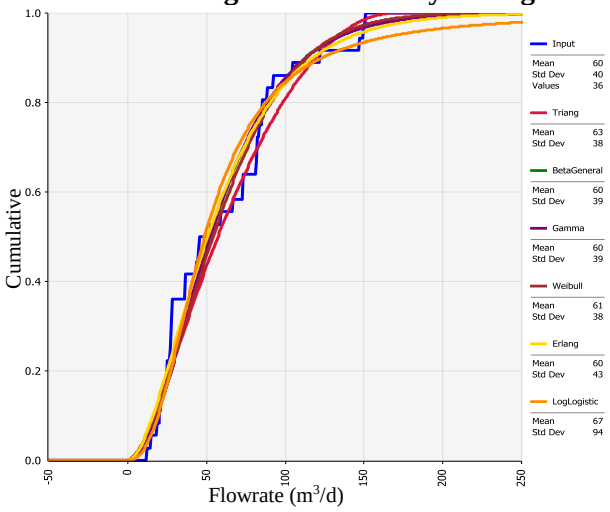

Figure C.26 Fit comparisons of CDFs for daily average flows for Colgate Palmolive, for top 5 distributions

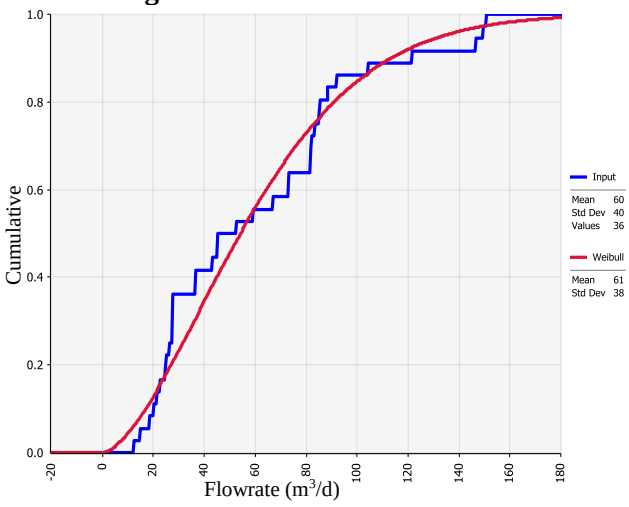

Figure C.27 CDF for daily average flows for Colgate Palmolive, for the top ranking distribution (Weibull)

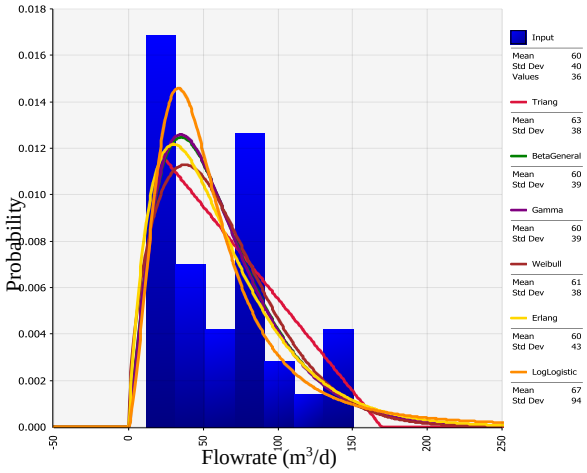

Figure C.28 Fit comparisons of PDFs for daily average flows for Colgate Palmolive, for top 5 distributions

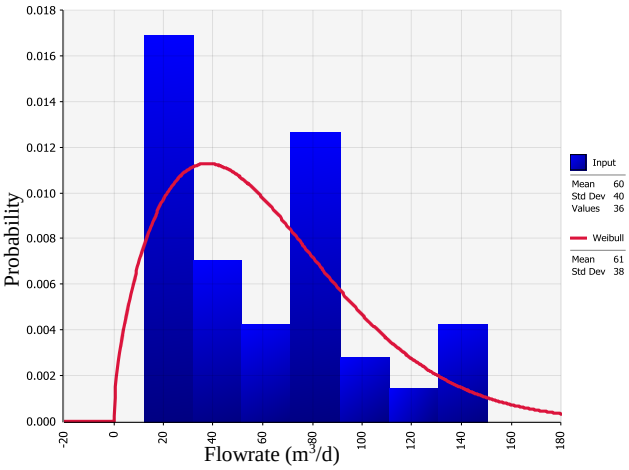

Figure C.29 PDF for daily average flows for Colgate Palmolive, for the top ranking distribution (Weibull)

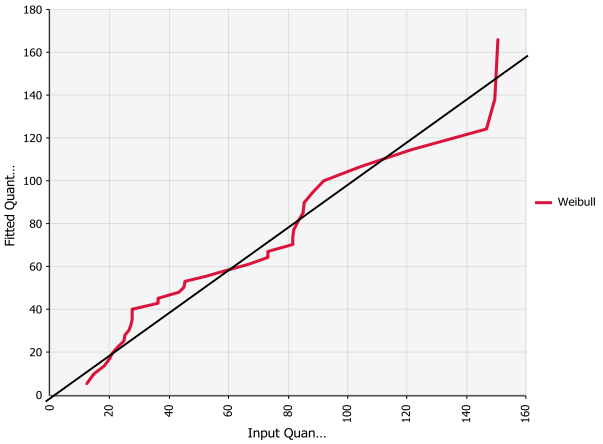

Figure C.30 Q-Q plot for Weibull distribution

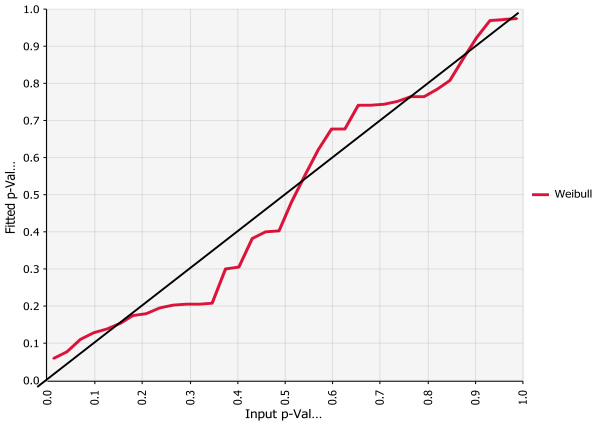

Figure C.31 P-P plot Weibull distribution

Distribution fitting results for daily average flow data from Budget Soap

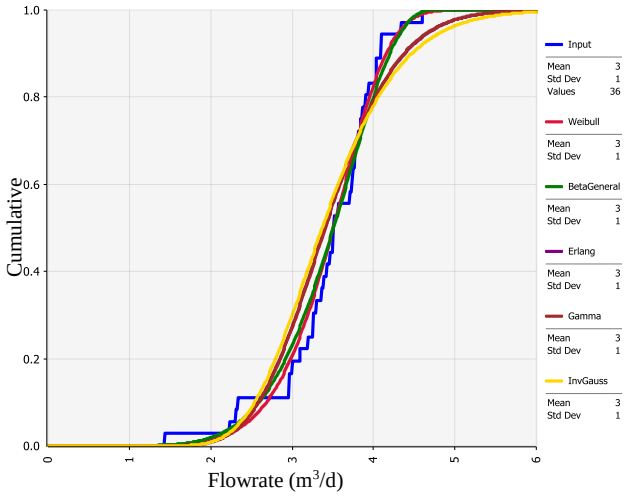

Figure C.32 Fit comparisons of CDFs for daily average flows for Budget Soap, for top 5 distributions

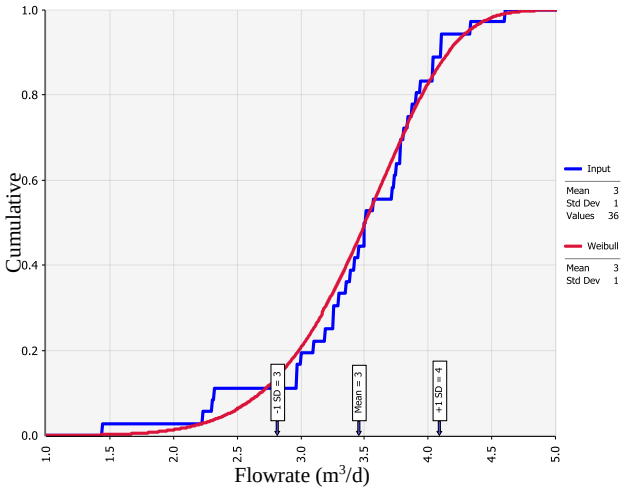

Figure C.33 PDF for daily average flows for Budget Soap, for the top ranking distribution (Weibull)

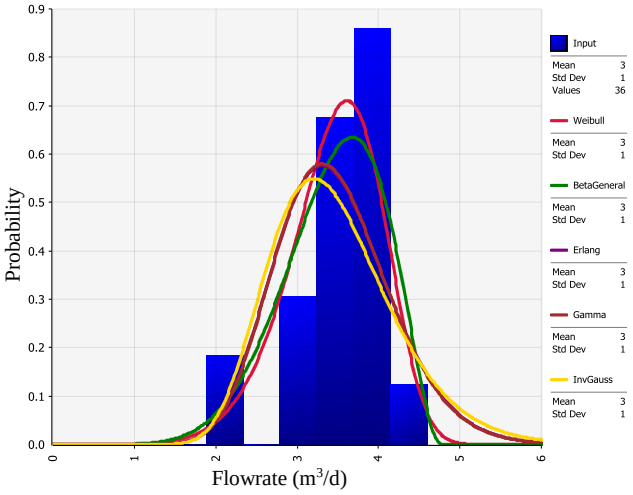

Figure C.34 Fit comparisons of PDFs for daily average flows for Budget Soap, for top 5 distributions

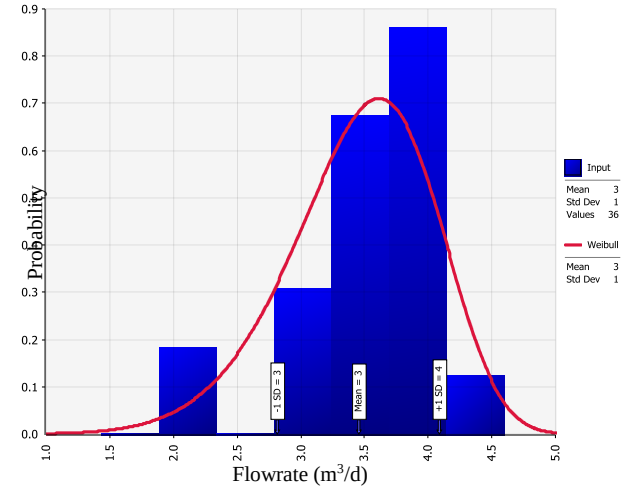

Figure C.35 PDF for daily average flows for Budget Soap, for the top ranking distribution (Weibull)

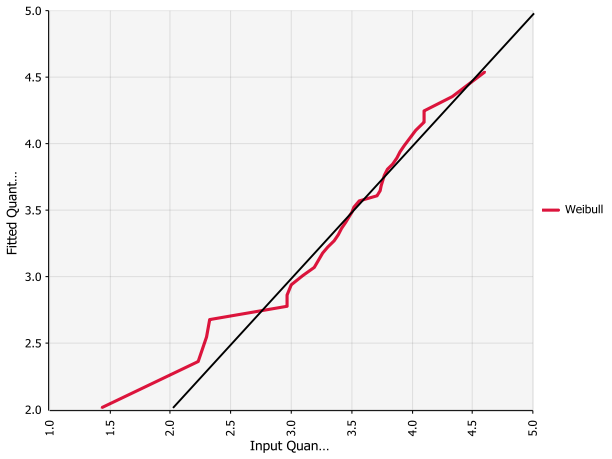

Figure C.36 Q-Q plot for Weibull distribution

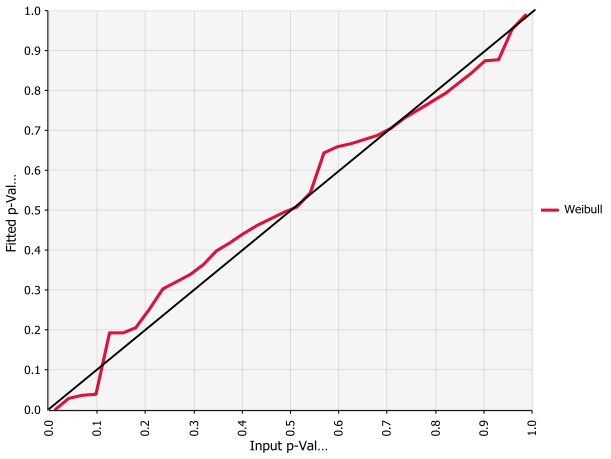

Figure C.37 P-P plot Weibull distribution

Comparison of measured and simulated monthly trade effluent volumes for Nampak

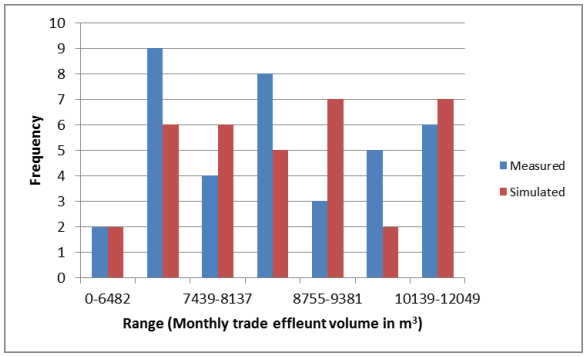

Figure C.38 Distributions of measured and simulated monthly trade effluent volumes-Nampak

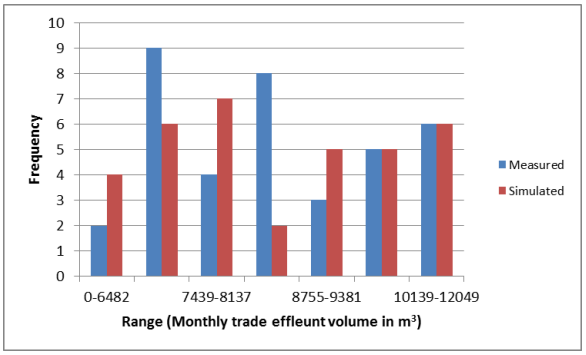

Figure C.39 Distributions of measured and simulated monthly trade effluent volumes-Nampak

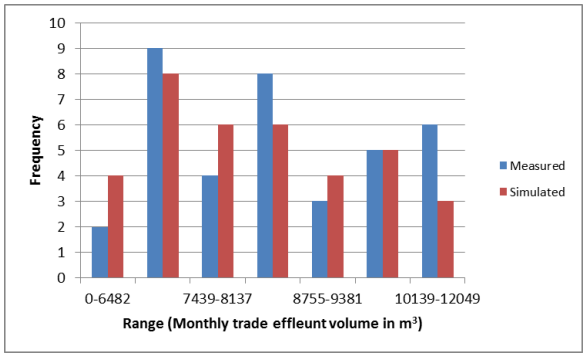

Figure C.40 Distributions of measured and simulated monthly trade effluent volumes-Nampak

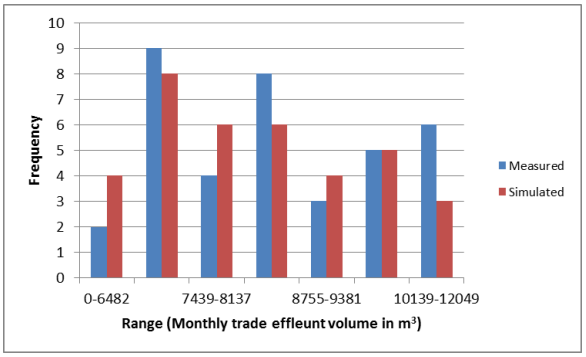

Figure C.41 Distributions of measured and simulated monthly trade effluent volumes-Nampak

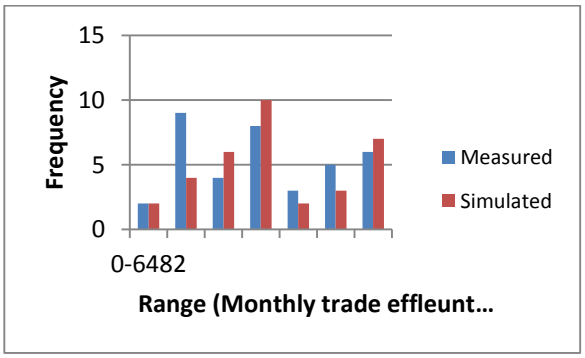

Figure C.42 Distributions of measured and simulated monthly trade effluent volumes-Nampak

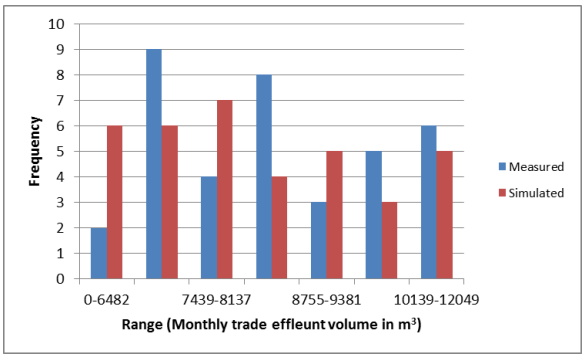

Figure C.43 Distributions of measured and simulated monthly trade effluent volumes-Nampak

Comparison of measured and simulated monthly trade effluent volumes for Frimax Foods

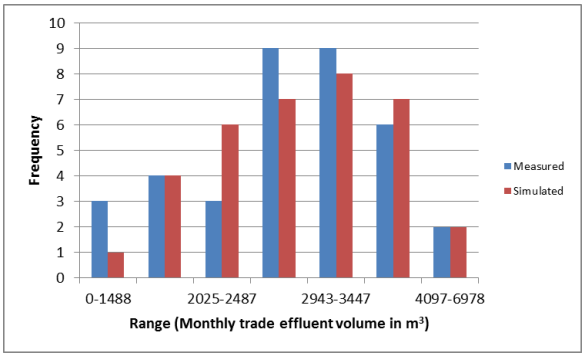

Figure C.44 Distributions of measured and simulated monthly trade effluent volumes-Frimax Foods

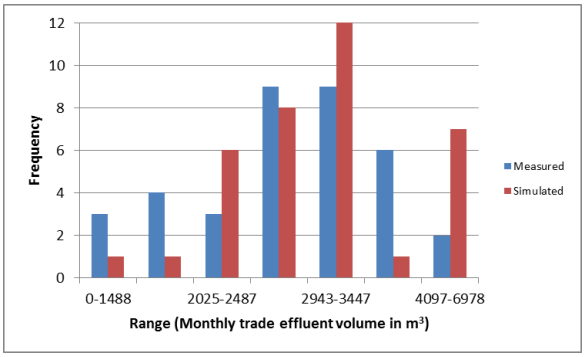

Figure C.45 Distributions of measured and simulated monthly trade effluent volumes- Frimax Foods

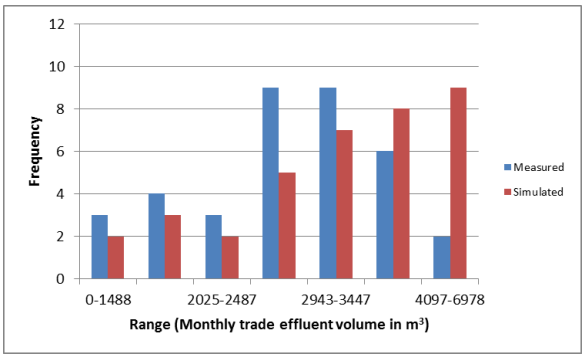

Figure C.46 Distributions of measured and simulated monthly trade effluent volumes- Frimax Foods

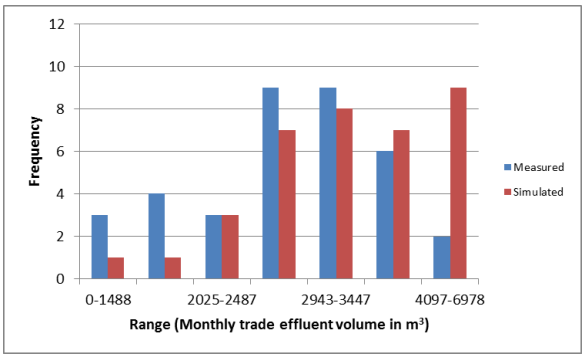

Figure C.47 Distributions of measured and simulated monthly trade effluent volumes- Frimax Foods

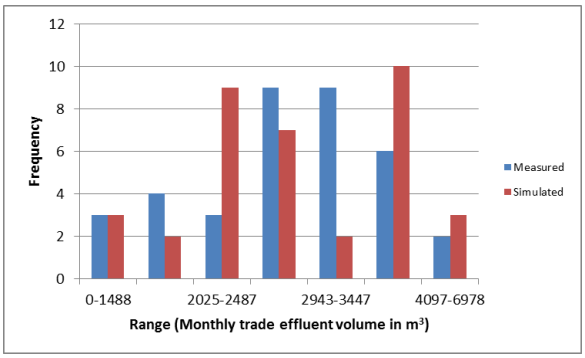

Figure C.48 Distributions of measured and simulated monthly trade effluent volumes- Frimax Foods

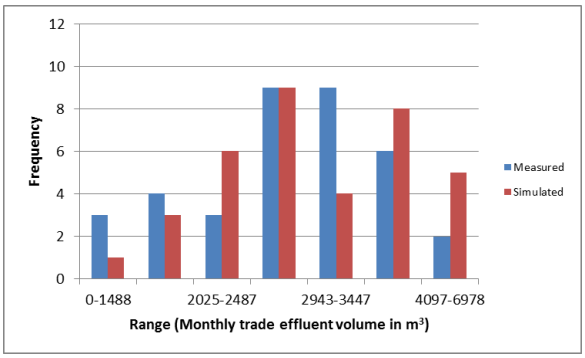

Figure C.49 Distributions of measured and simulated monthly trade effluent volumes- Frimax Foods

Comparison of measured and simulated monthly trade effluent volumes for Packo

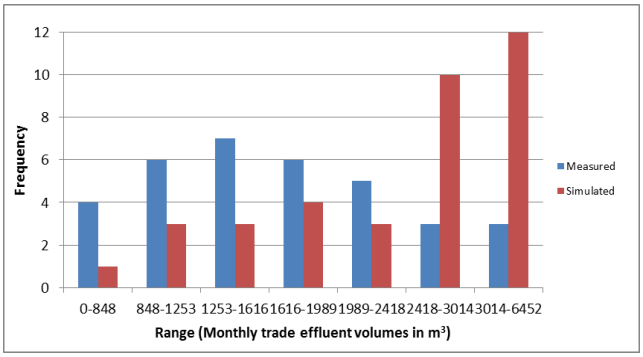

Figure C.50 Distributions of measured and simulated monthly trade effluent volumes- Packo

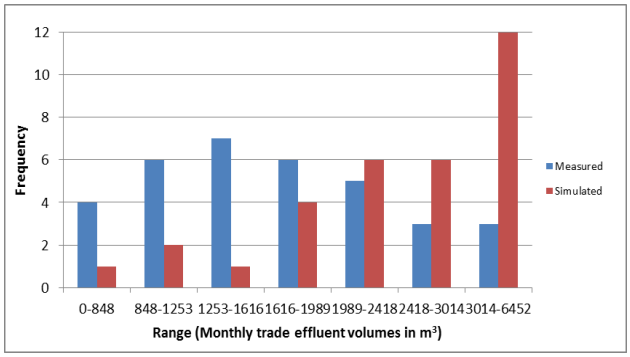

Figure C.51 Distributions of measured and simulated monthly trade effluent volumes- Packo

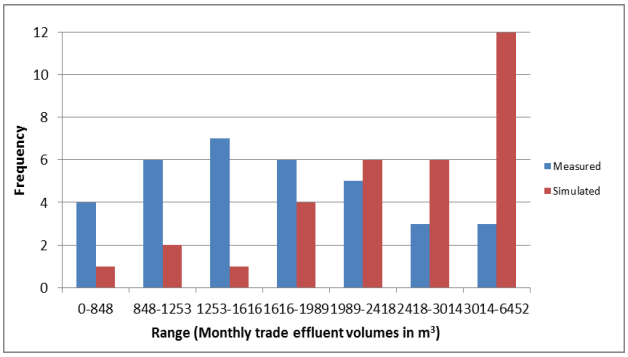

Figure C.52 Distributions of measured and simulated monthly trade effluent volumes- Packo

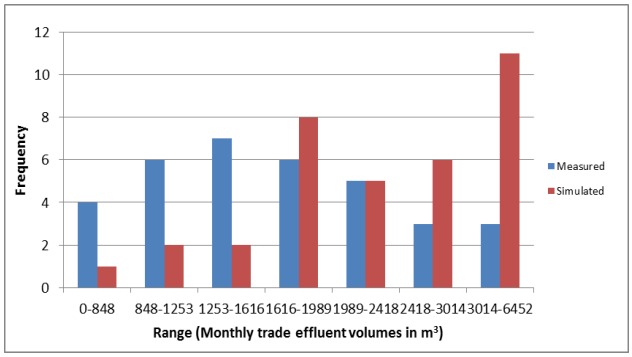

Figure C.53 Distributions of measured and simulated monthly trade effluent volumes- Packo

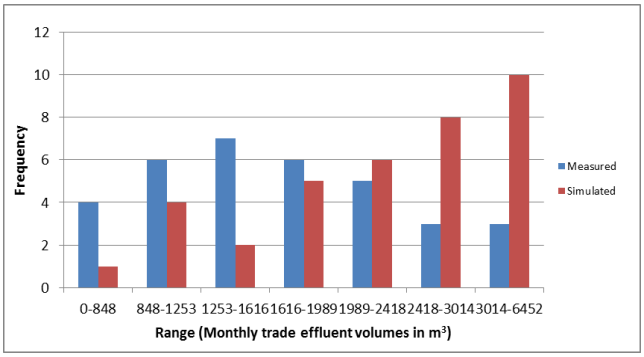

Figure C.54 Distributions of measured and simulated monthly trade effluent volumes- Packo

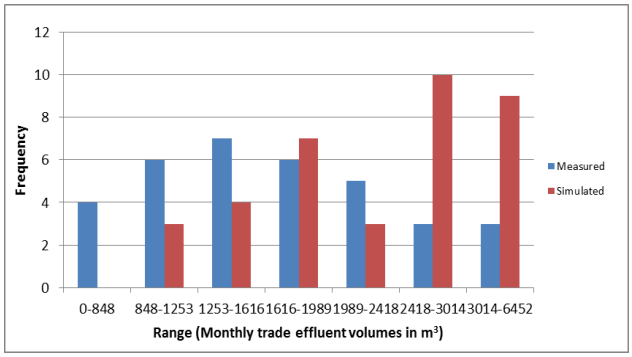

Figure C.55 Distributions of measured and simulated monthly trade effluent volumes- Packo

Comparison of measured and simulated monthly trade effluent volumes for Colgate Palmolive

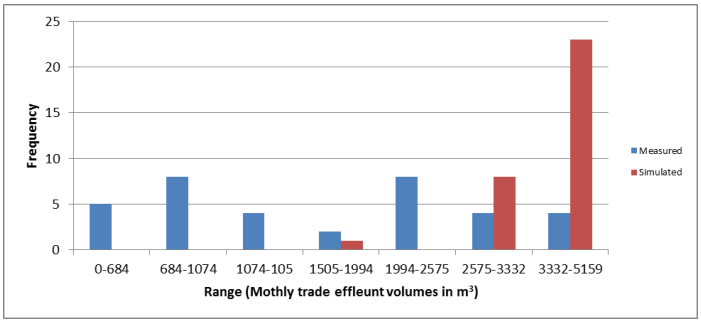

Figure C.56 Distributions of measured and simulated monthly trade effluent volumes- Colgate Palmolive

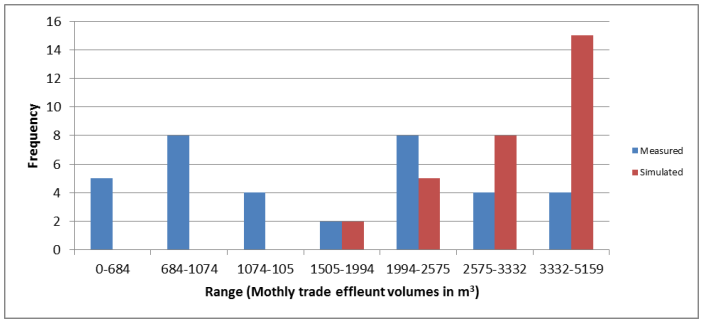

Figure C.57 Distributions of measured and simulated monthly trade effluent volumes- Colgate Palmolive

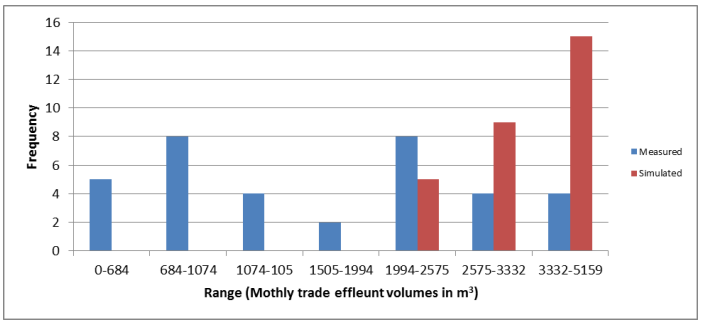

Figure C.58 Distributions of measured and simulated monthly trade effluent volumes- Colgate Palmolive

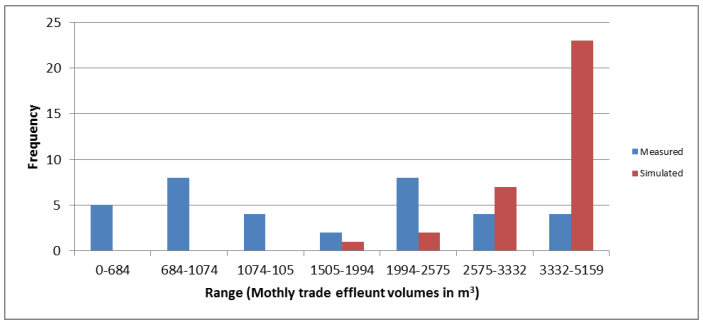

Figure C.59 Distributions of measured and simulated monthly trade effluent volumes- Colgate Palmolive

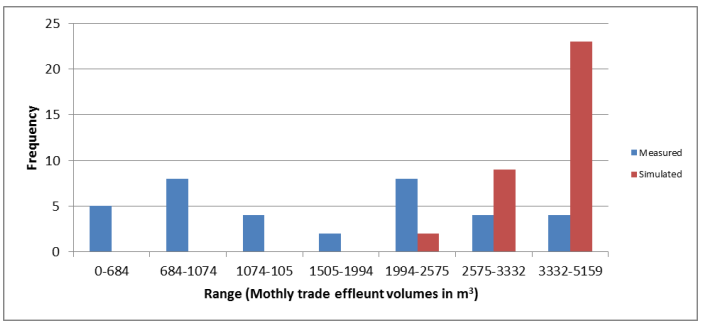

Figure C.60 Distributions of measured and simulated monthly trade effluent volumes- Colgate Palmolive

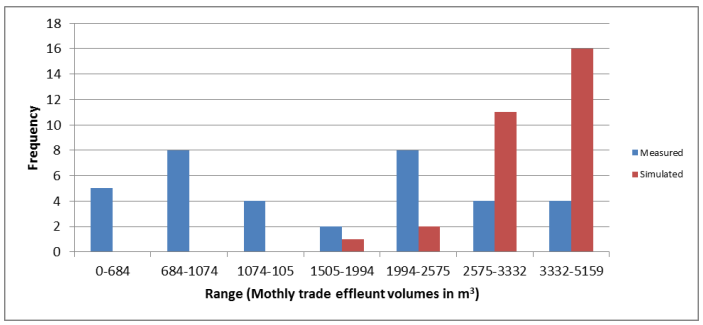

Figure C.61 Distributions of measured and simulated monthly trade effluent volumes Colgate Palmolive

Comparison of measured and simulated monthly trade effluent volumes for Budget Soap

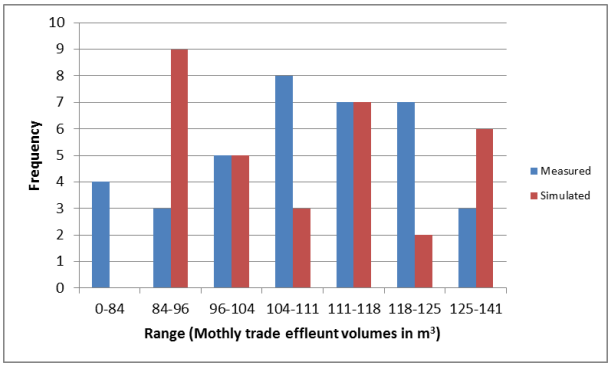

Figure C.62 Distributions of measured and simulated monthly trade effluent volumes- Budget Soap

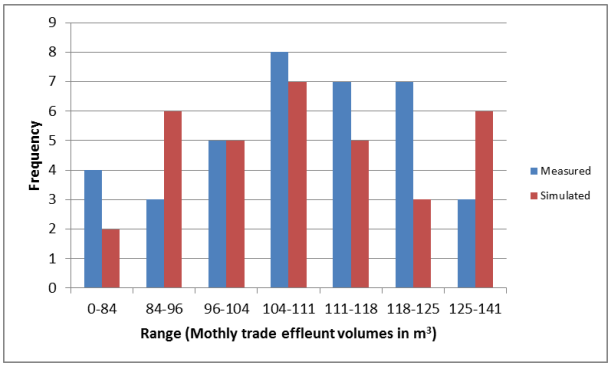

Figure C.63 Distributions of measured and simulated monthly trade effluent volumes- Budget Soap

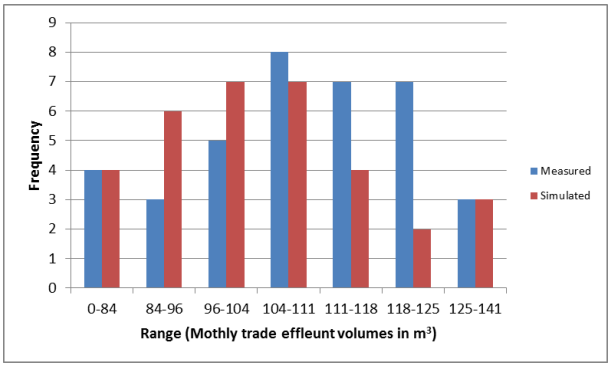

Figure C.64 Distributions of measured and simulated monthly trade effluent volumes- Budget Soap

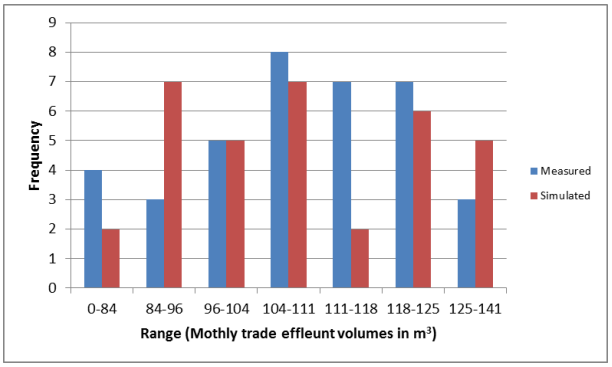

Figure C.65 Distributions of measured and simulated monthly trade effluent volumes- Budget Soap

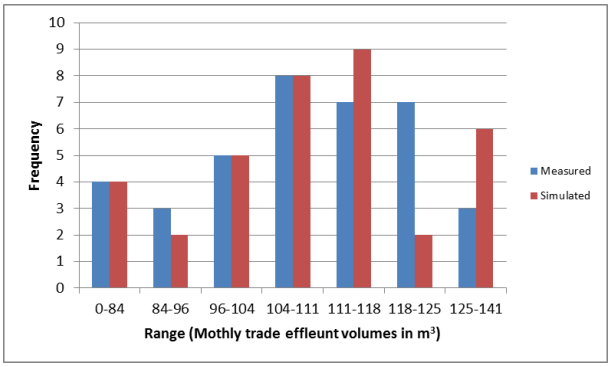

Figure C.66 Distributions of measured and simulated monthly trade effluent volumes- Budget Soap

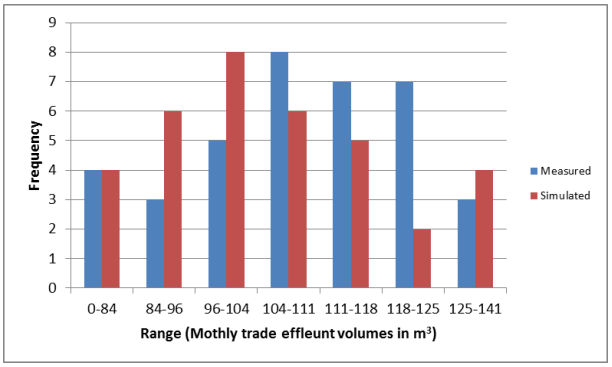

Figure C.67 Distributions of measured and simulated monthly trade effluent volumes Budget Soap

Appendix C.1 Results of distribution fitting on wastewater-COD data for factories in Verulam WWTP catchment

Table C.7 Ranking of probability distributions fitted to daily average trade effluent volumes for JMV Textiles

Rank	Distribution	K-S statistic
1	Weibull	0.1435
2	LogLogistic	0.1548
3	Gamma	0.16
4	Triangular	0.1983
5	Rayleigh	0.2118

Table C.8 Ranking of probability distributions fitted to daily average trade effluent volumes for Nampak

Rank	Distribution	K-S statistic
1	Triangular	0.2651
2	Weibull	0.3565
3	Rayleigh	0.3535
4	Gamma	0.3854
5	Erlang	0.3871

Table C.9 Ranking of probability distributions fitted to daily average trade effluent volumes for Frimax Foods

Rank	Distribution	K-S statistic
1	Pearson6	0.1520
2	LogLogistic	0.1597
3	Erlang	0.1750
4	Exponential**	0.1750
5	Pareto2	0.1750

Table C.10 Ranking of probability distributions fitted to daily average trade effluent volumes for Packo

Rank	Distribution	K-S statistic
1	Rayleigh	0.2248
2	Erlang	0.2355
3	Gamma	0.2361
4	Pearson6	0.2380
5	LogLogistic	0.2389

Table C.11 Ranking of probability distributions fitted to daily average trade effluent volumes for Colgate Palmolive

Rank	Distribution	K-S statistic
1	BetaGeneral	0.1170
2	Weibull	0.1448
3	Exponential	0.1479
4	Pareto2	0.1479
5	LogLogistic	0.1595

Table C.12 Ranking of probability distributions fitted to daily average trade effluent volumes for Budget Soap

Rank	Distribution	K-S statistic
1	Gamma	0.1765
2	LogLogistic	0.1811
3	Exponential	0.1860
4	Weibull	0.1867
5	Triangular	0.1915

Distribution fitting results for daily COD from JMV Textiles

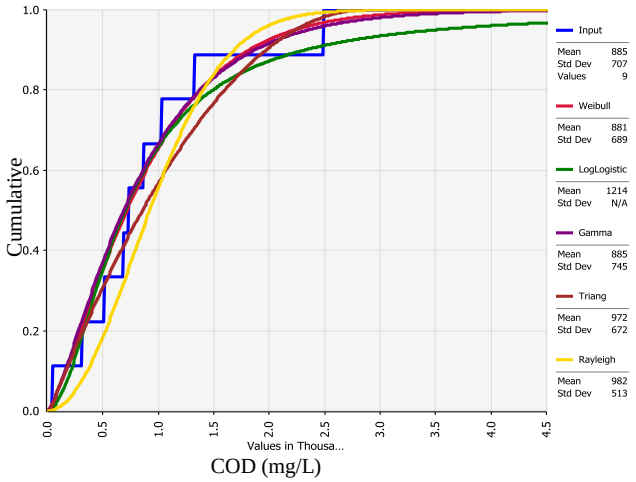

Figure C.68 Fit comparison of CDFs for daily COD concentrations for JMV Textiles, for top 5 distributions

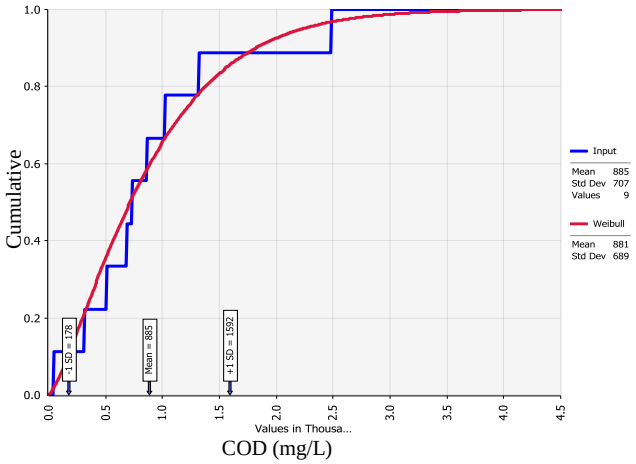

Figure C.69 CDF for daily COD concentrations for JMV Textiles, for top ranking distribution (Weibull)

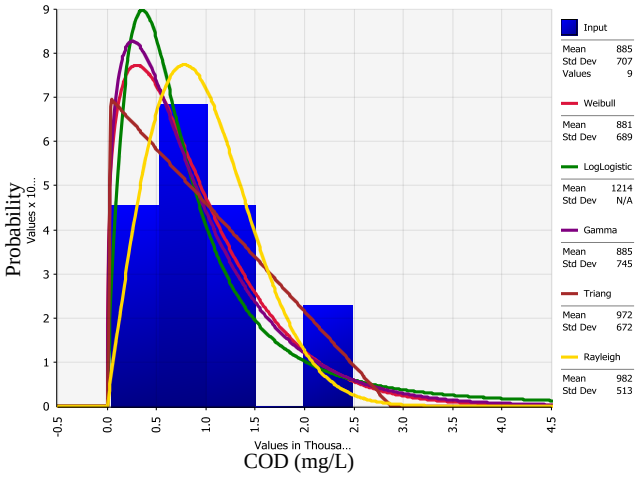

Figure C.70 Fit comparison of PDFs for daily COD concentrations for JMV Textiles, for top 5 distributions

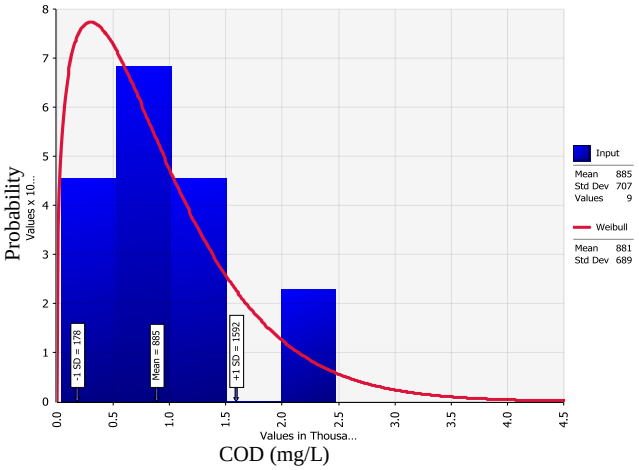

Figure C.71 PDF for daily COD concentrations for JMV Textiles, for top ranking distribution (Weibull)

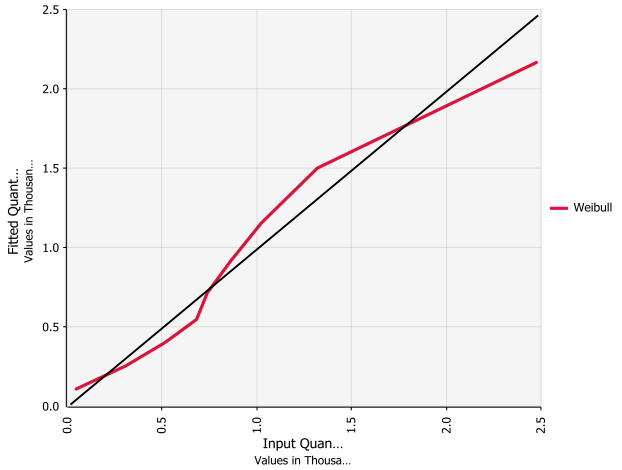

Figure C. 72 Q-Q plot for Weibull distribution

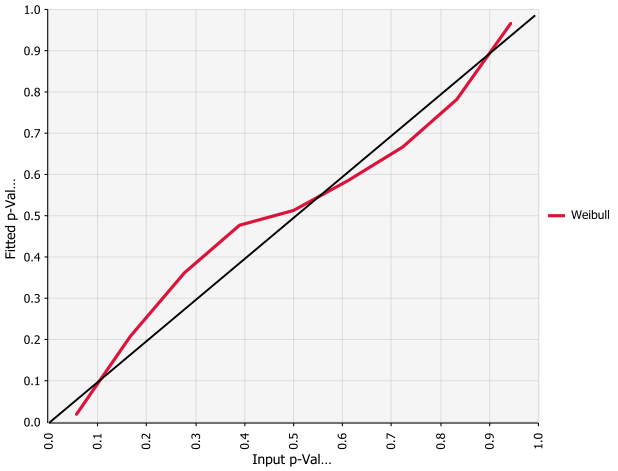

Figure C. 73 P-P plot Weibull distribution

Distribution fitting results for daily COD from Nampak

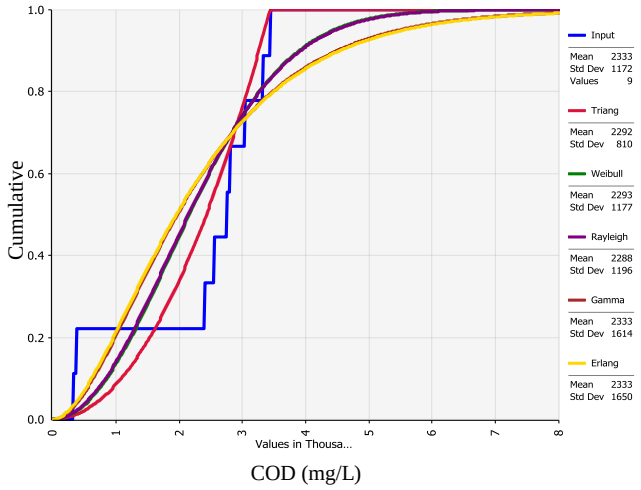

Figure C.74 Fit comparison of CDFs for daily COD concentrations for Nampak, for top 5 distributions

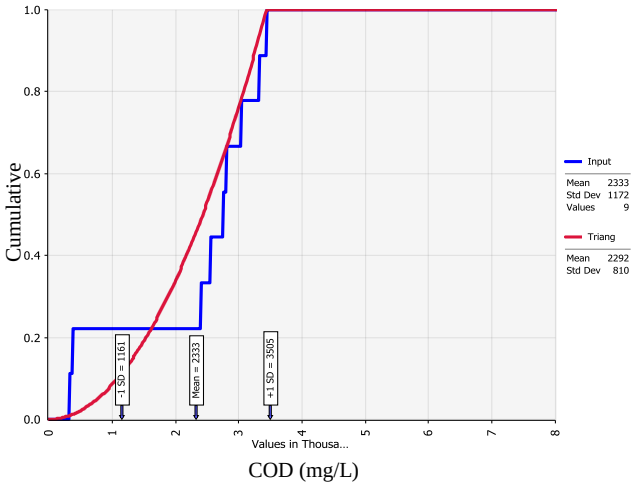

Figure C.75 CDF for daily COD concentrations for Nampak, for top ranking distribution (Triangular)

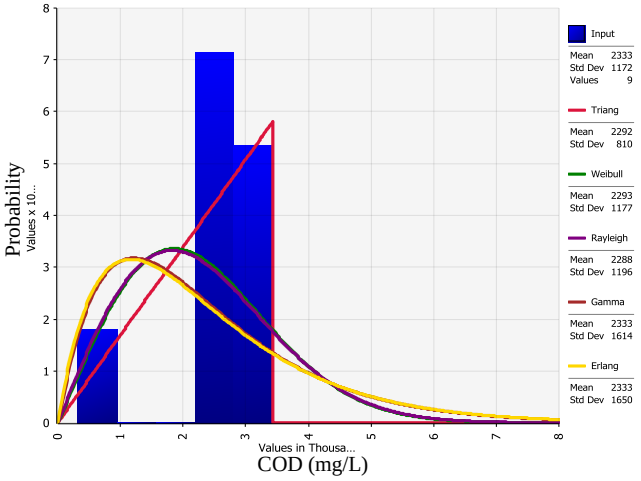

Figure C.76 Fit comparison of PDFs for daily COD concentrations for Nampak, for top 5 distributions

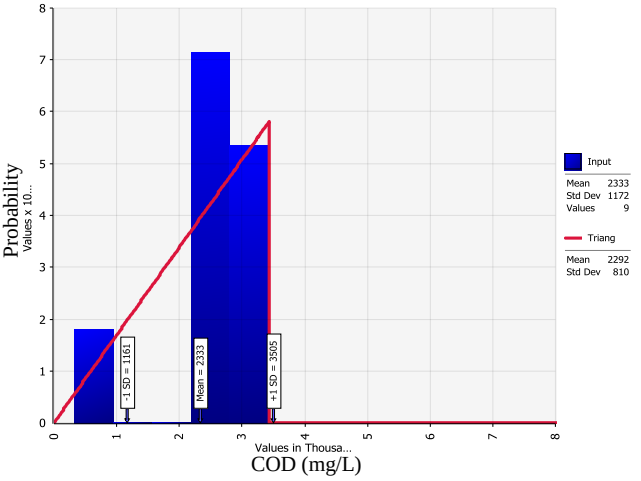

Figure C.77 PDF for daily COD concentrations for Nampak, for top ranking distribution (Triangular)

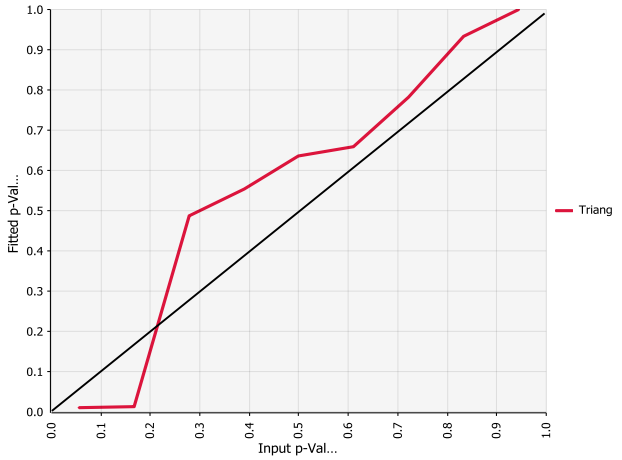

Figure C.78 Q-Q plot for Triangular distribution

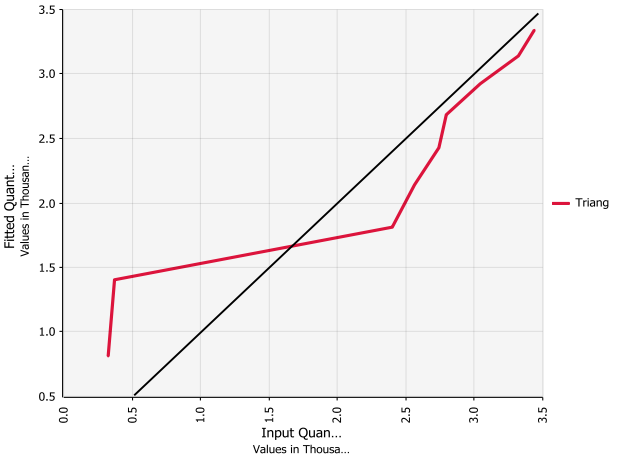

Figure C.79 P-P plot Triangular distribution

Distribution fitting results for daily COD from Frimax Foods

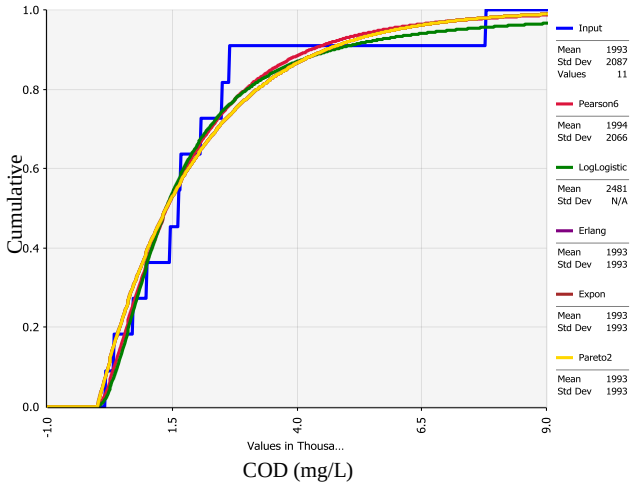

Figure C.80 Fit comparison of CDFs for daily COD concentrations for Frimax Foods, for top 5 distributions

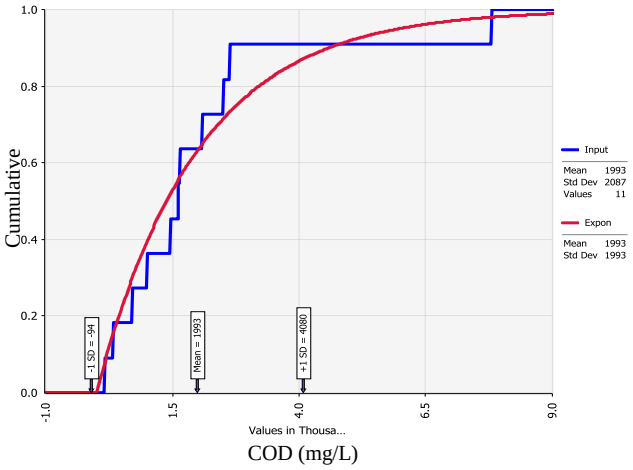

Figure C.81 CDF for daily COD concentrations for Frimax Foods, for top ranking distribution (Exponential)

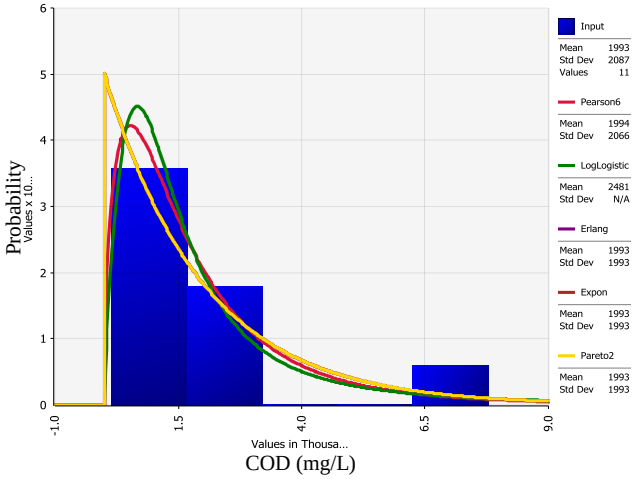

Figure C.82 Fit comparison of PDFs for daily COD concentrations for Frimax Foods, for top 5 distributions

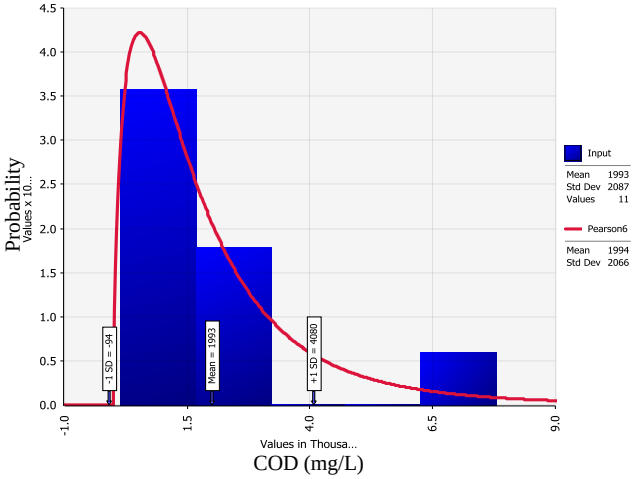

Figure C.83 PDF for daily COD concentrations for Frimax Foods, for top ranking distribution (Pearson6)

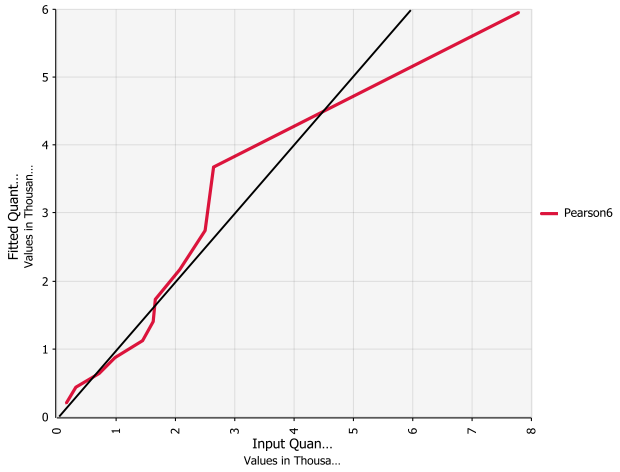

Figure C.84 Q-Q plot for Pearson6 distribution

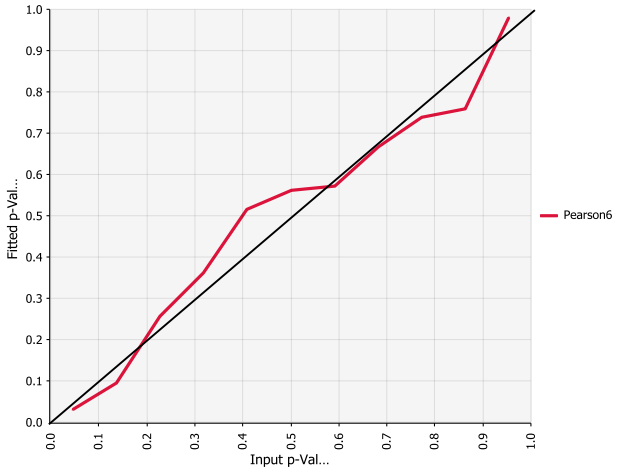

Figure C.85 P-P plot Pearson6 distribution

Distribution fitting results for daily COD from Packo

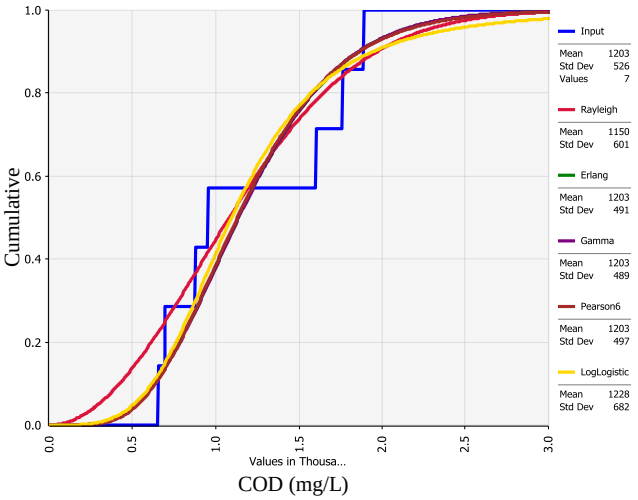

Figure C.86 Fit comparison of CDFs for daily COD concentrations for Packo, for top 5 distributions

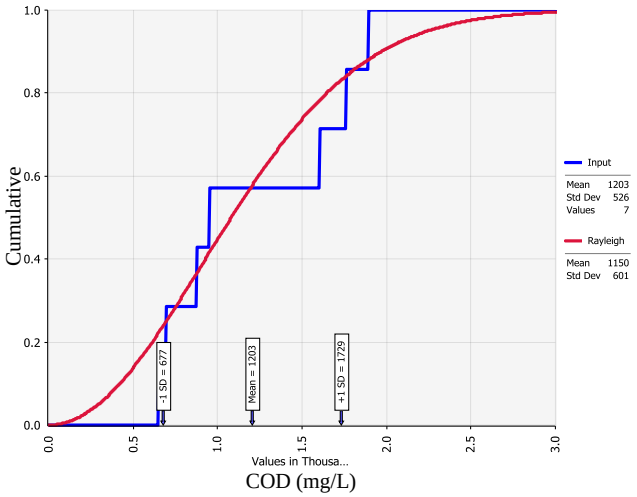

Figure C.87 CDF for daily COD concentrations for Packo, for top ranking distribution (Rayleigh)

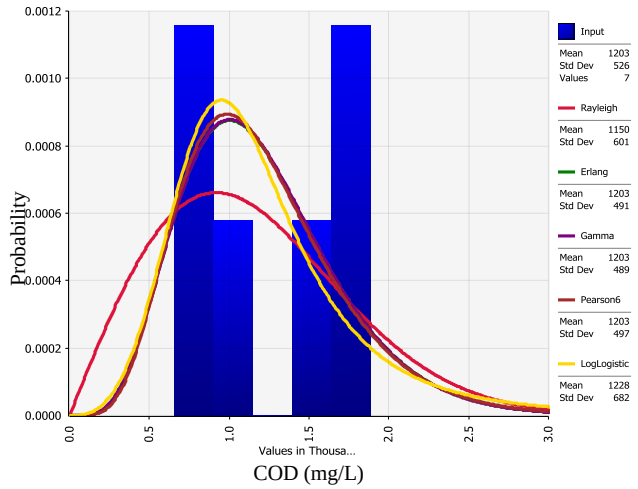

Figure C.88 Fit comparison of PDFs for daily COD concentrations for Packo, for top 5 distributions

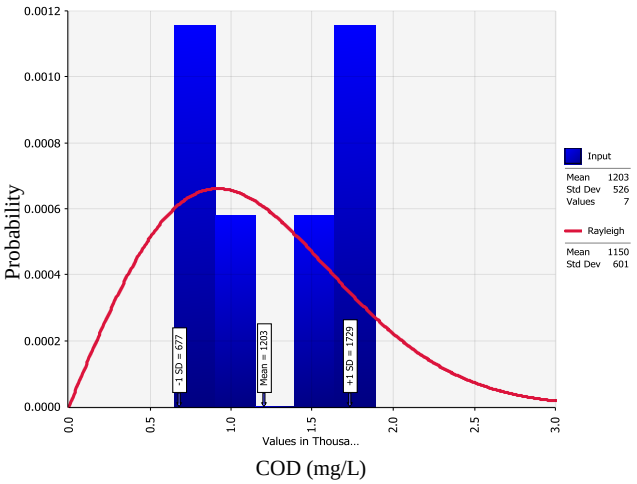

Figure C.89 PDF for daily COD concentrations for Packo, for top ranking distribution (Rayleigh)

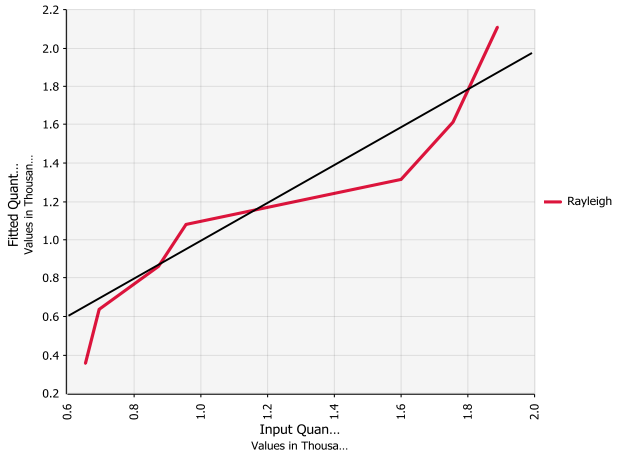

Figure C.90 Q-Q plot for Rayleigh distribution

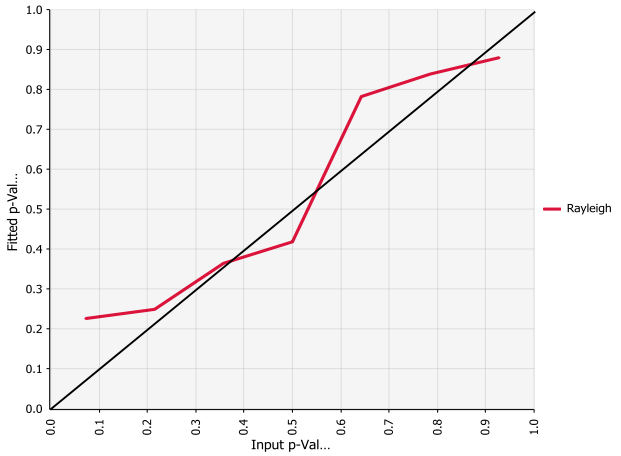

Figure C.91 P-P plot Rayleigh distribution

Distribution fitting results for daily COD from Colgate Palmolive

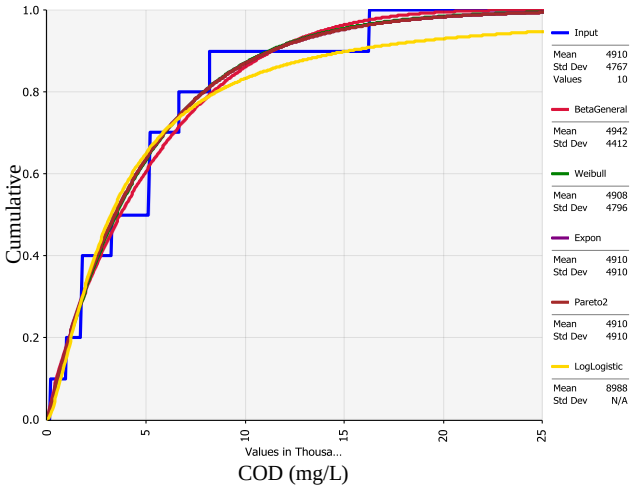

Figure C.92 Fit comparison of CDFs for daily COD concentrations for Colgate Palmolive, for top 5 distributions

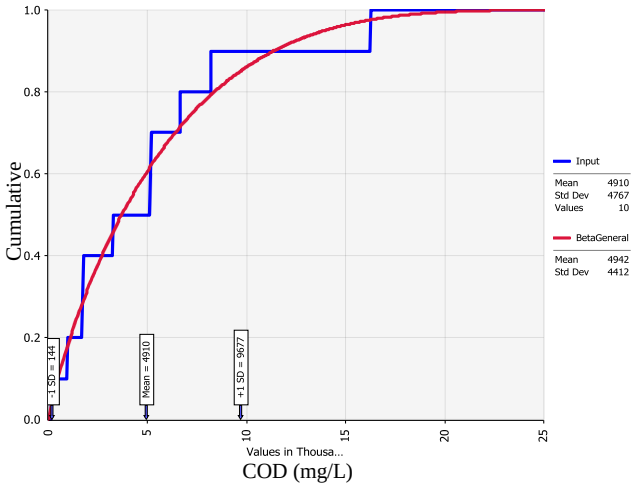

Figure C.93 CDF for daily COD concentrations for Colgate Palmolive, for top ranking distribution (BetaGeneral)

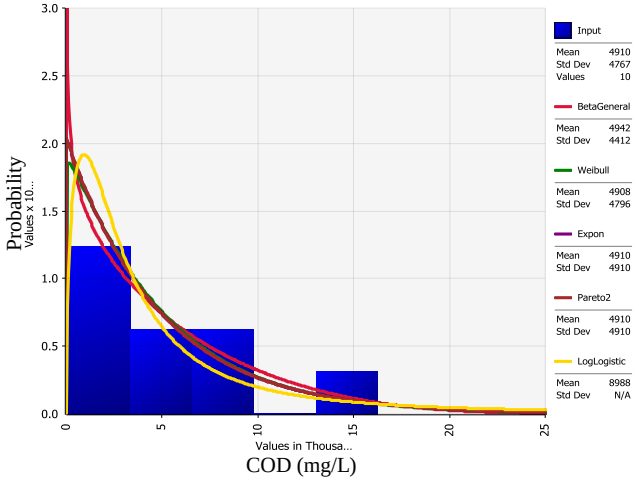

Figure C.94 Fit comparison of PDFs for daily COD concentrations for Colgate Palmolive, for top 5 distributions

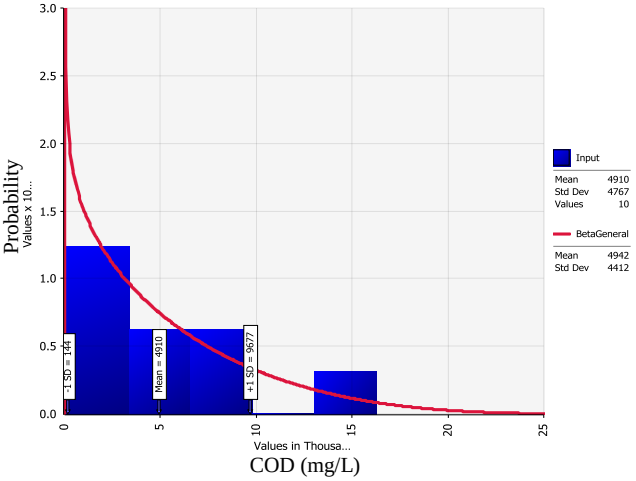

Figure C.95 PDF for daily COD concentrations for Colgate Palmolive, for top ranking distribution (BetaGeneral)

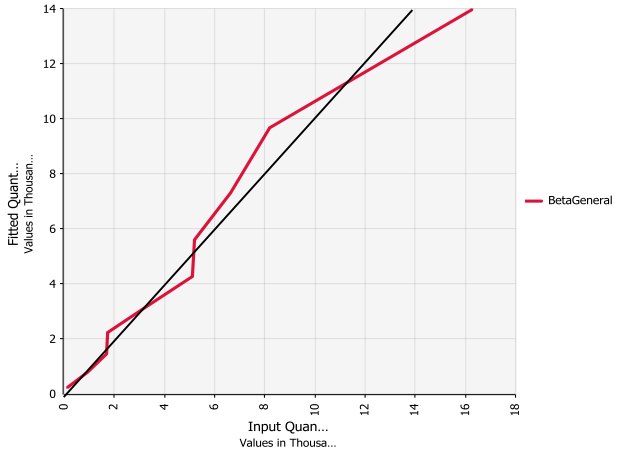

Figure C.96 Q-Q plot for BetaGeneral distribution

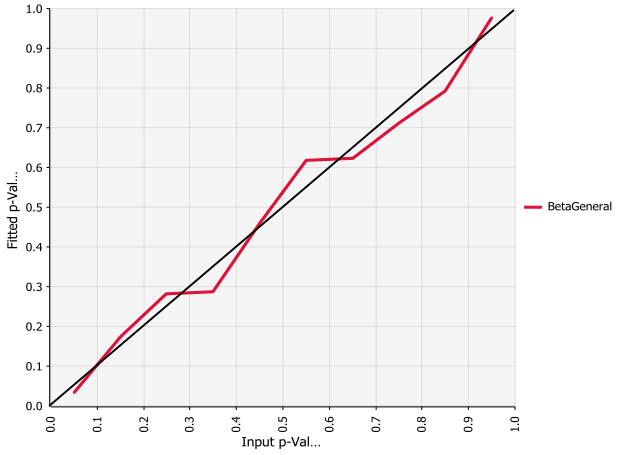

Figure C.97 P-P plot BetaGeneral distribution

Distribution fitting results for daily COD from Budget Soap

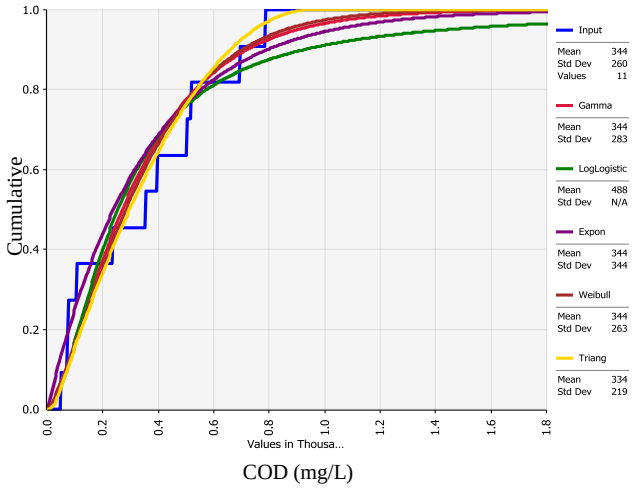

Figure C.98 Fit comparison of CDFs for daily COD concentrations for Budget Soap, for top 5 distributions

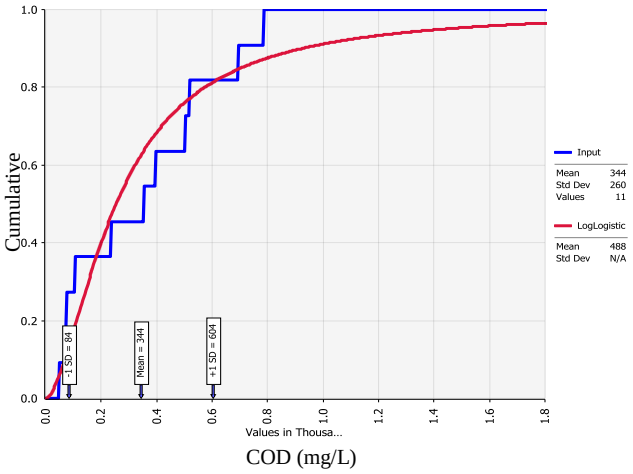

Figure C.99 CDF for daily COD concentrations for Budget Soap, for top ranking distribution (LogLogistic)

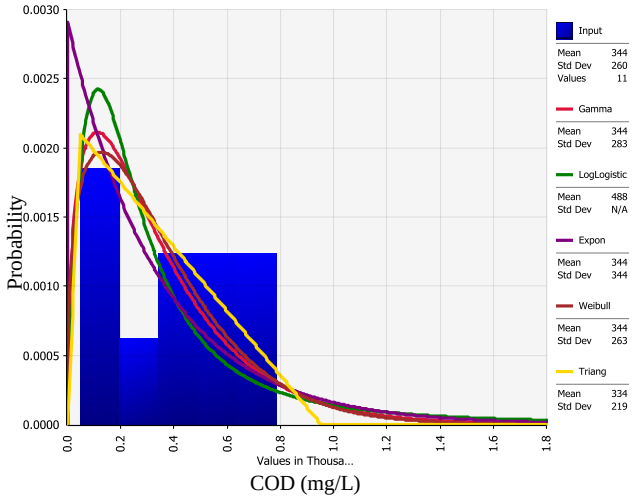

Figure C.100 Fit comparison of PDFs for daily COD concentrations for Budget Soap, for top 5 distributions

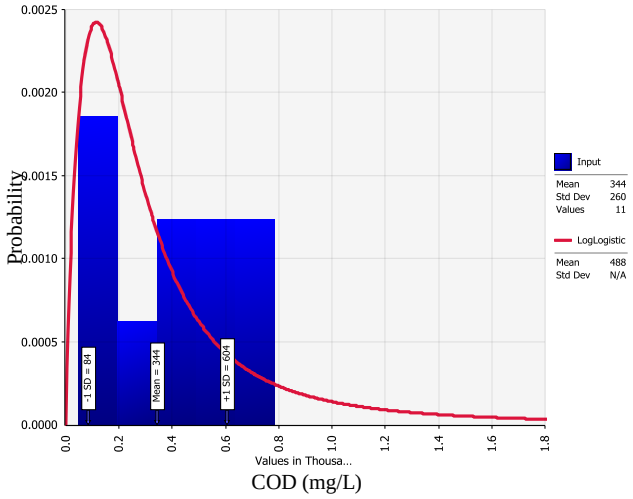

Figure C.101 PDF for daily COD concentrations for Budget Soap, for top ranking distribution (LogLogistic)

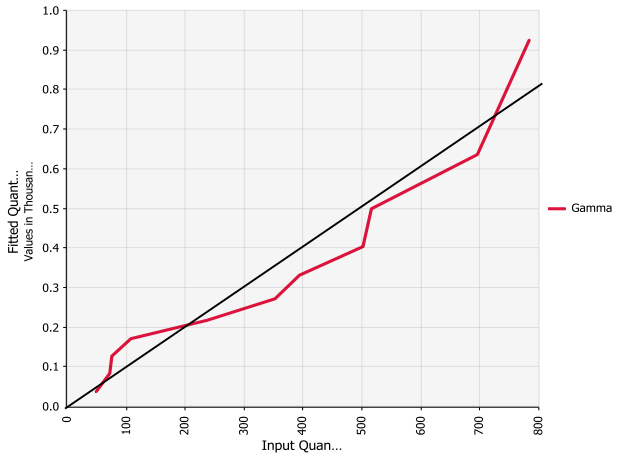

Figure C.102 Q-Q plot for Gamma distribution

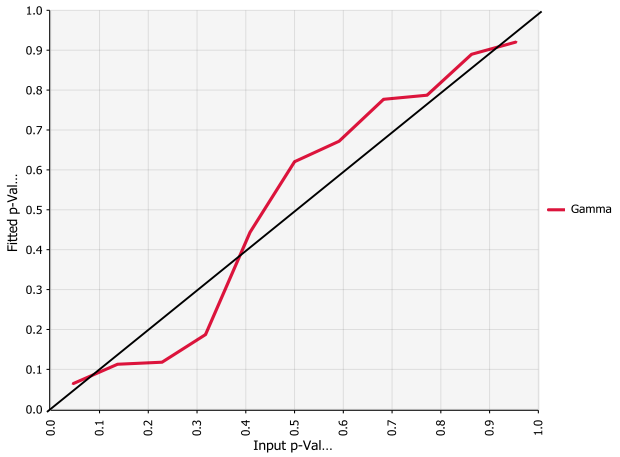

Figure C.103 P-P plot Gamma distribution

Appendix D Concepts of modelling and Monte Carlo simulations

Concepts of modelling

A model can be defined as a purposeful representation or description of a system of interest (Wentzel and Ekama, 1997). The model is not a perfect match of reality but rather a simplification of reality related to human rationalisation of the behavioural patterns of processes conceived to be of interest. The facets of time and scale are important in modelling (Henze, 2008).

From the time perspective, processes can be separated into three groups; the frozen state, dynamic state and steady state. In the dynamic state variations occur as a function of time, while the frozen state means that the process will change in time, but not in the time interval that one is interested in. In the steady state the speed of change exceeds by far the dynamics that one is interested in. When one considers this time in modelling, it is recommended that one thinks through the relevant time constants and select the processes whose dynamics are in the order of the time constants of interest. When modelling WWTPs, this usually means hours or daily dynamics and in some cases yearly dynamics (Wentzel and Ekama, 1997).

The aspect of space in modelling involves choosing the correct space resolution for the model. This involves identifying the space on which to focus the modelling. The choice of the appropriate scale depends on the purpose of the model. In wastewater treatment modelling, reactor sizes are in the order of tens of metres. A scale of a few metres is required to describe the concentration gradient of oxygen, one of the most sensitive components in the activated sludge unit; hence this scale is suitable for the rest of the components in the activated sludge process (Wentzel and Ekama, 1997).

In addition to selecting the correct time and space scale in modelling WWTPs, the modelling of biological processes requires careful choice of the appropriate level of detail of the microbial model. In the past, wastewater treatment designs were based on the 'black box' approach which focused on the wastewater treatment plant influent and effluent characteristics, while nothing or very little was known about what occurs inside the wastewater treatment plant. Over the years the black box approach has been refined to grey-box models as in the cases of the ASM1, (Henze et al., 1987), ASM2, (Henze et al., 1995) and ASM2d (Henze et al., 1999). In the grey box models the sludge was split into fractions such as inert organic matter, nitrifying bacteria, heterotrophic bacteria, denitrifying bacteria and phosphate removing bacteria (Henze, 2008). Furthermore different functional aspects of the sludge have been specified for a population based model where selected microbial communities are defined inside the activated sludge and as such incorporated in the model. The metabolism of the organisms and the metabolic routes inside the organism can also be described in these models (Wentzel and Ekama, 1997).

As the amount of detail and information considered for models increases, the approach becomes close to 'glass-box' modelling such as ASM3, (Gujer et al., 1999) and Technical University Delft Phosphorus (TUDP) model, (Van Veldhuizen et al., 1999). At this point the models become bigger and more complex. The choice between black, grey or glass-box modelling depends on the purpose and application of the model (Wentzel and Ekama, 1997).

Models can be broadly classified as physical, conceptual or mathematical models (Wentzel and Ekama, 1997). Physical models are spatial scaled representations of the system of interest while conceptual models provide qualitative description of the system. Mathematical models give a quantitative description of the system. Mathematical models are powerful tools in modelling wastewater treatment plants. Mathematical models transform a certain input *(u)* into an output *(y)* by some defined relationship. The outputs are the variables that are of interest to the user and the inputs are the disturbances and manipulations that affect the outputs. In a WWTP system, untreated wastewater coming from the sewer system enters the plant and is processed in different physical and biological steps to produce treated effluent. The input for a model of such a system would be the composition and quantity of the incoming wastewater while one of the outputs of the model could be the quality of the treated effluent flowing out of the treatment plant. The biochemical model used in this study can be classified as nonlinear and dynamic. The basic model structure is given by Equation D.1.

$$\frac{dx}{dy} = f(x,\theta,u,t) \quad , \quad x(t_0) = x_0 \qquad y = (x,\theta,u,t) \qquad \text{[D.1]}$$

In this equation x is a vector of state variables, θ a vector of parameters, u a vector of inputs, y a vector of outputs, and t the independent variable.

The dynamic nature of this model is reflected in the fact that it is formulated as a differential equation indicating the change of state variables x with respect to the independent variable t. In order to solve these equations, initial values of x at time = 0 have to be given: x_0.

Mathematical models can also be classified as empirical or mechanistic models. Empirical models are based on the recognition of the parameters that seem to describe the behavioural pattern of interest, and linking them by empirical relationships established by observation (Henze, 2008). In empirical models, the processes operating in the system are not known or are ignored (Wentzel and Ekama, 1997). On the other hand, mechanistic models are based on a conceptual idea or model of the biological or physical mechanisms operating in the system of interest. The complexity of mechanistic models depends on the degree of understanding of the processes taking place in the system. Since mechanistic models have some conceptual basis, they are often more reliable than the empirical models hence they receive more attention and application in WWTPs (Wentzel and Ekama, 1997).

Key steps to modelling wastewater treatment plants

Key steps of approaching a modelling project that were identified from all the protocols and proposed for the unified protocol are as follows:

- Project definition
- Data collection and reconciliation
- Plant model set-up
- Calibration and validation
- Simulation and results interpretation

The first step in a modelling project is to determine the purpose of the model. The purpose of the model will determine the complexity and the level of model calibration required. This in turn affects the data requirements for the modelling exercise (Langergraber et al., 2004; Sin et al., 2005; Pena-Tijerina et al, 2007). An appropriately defined purpose of a modelling project sets clear expectations from the beginning of the project and opens clear communication between all stake holders involved in the modelling project. The elements that are included in the definition of the project include the problem statements and objectives (WEF, 2014). Once the purpose of the model has been established, data collection of relevant data is carried out.

The responses to the questionnaire sent by the first GMP task group (Hauduc et al.,2009) showed that data collection and reconciliation is one of the steps requiring the most effort (greater than one third of the overall effort) of a modelling project. Historical plant data and other plant information are gathered using different means that include planned sampling programmes. A planned sampling programme is usually set up to collect stream and process information which would not be part of the available historical data and is not gathered during daily monitoring of the plant performance such a TSS, VSS, COD TKN, TP and soluble P components of all streams (Pena-Tijerina et al, 2007).

The collected data were screened and analysed by carrying out mass balances and other related calculations. Early data screening is critical in modelling since it avoids use of unreliable data that may lead to unreliable modelling results. High quality data and careful reconciliation of the data saves time in the subsequent steps of the modelling project. The amount of data that must be collected depends on a number of factors such as plant stability and data reliability (Pena-Tijerina et al, 2007). Typical general data requirements for modelling an activated sludge system are shown in Table D.1.

Table D.1 Overview of the general data requirements for a modelling project adapted from Rieger, (2012)

Data type	Requirements	Use in modelling project/remark
Input data	Influent and other input flows	For influent streams (raw wastewater, settled wastewater, side-stream, depending on the model boundaries)
	Influent organics and suspended solids (COD, TSS, VSS,)	Sludge production
	Influent nutrients (TKN, ammonium nitrogen, P, PO_4-P)	N removal P removal, mass balancing
	Influent COD, N and P fractions	Wastewater characterisation
	Alkalinity of influent wastewater	Critical for nitrification
Physical data	Tank volumes, depths and layouts, flow connections and hydraulic behaviour, equipment (aerators, mixers, pumps), P and I-Diagram Main characteristics of the sludge treatment train	
Operating settings	DO control strategy and set points, pumping set-points/ flow splits, other control strategies	
Performance data	Effluent flowrate	Flow balance
	Effluent organics: (COD, BOD_5, TSS)	Calibration of organics removal
	Effluent nutrients: TKN, ammonium nitrogen, nitrate and nitrite, P, PO_4-P	Calibration of nutrient removal
	Alkalinity of effluent	
	Mixed liquor MLSS, MLVSS	Sludge production, Mass balancing
	Total P of mixed liquor	DO control, aerobic sludge age
	DO in tank concentration	
	Temperature	
	Flow of waste activated sludge (WAS)	Sludge production
	MLSS of WAS	
	Total P of WAS	Mass balancing

The above data are typically required in most modelling projects.

Setting up the full plant model involves selecting sub-models to simulate the process units in the WWTP. In this step, operational values such as volumes of units, flows, controller set points and others are set. Average influent wastewater characteristics may be used during the first implementation of the plant model in the simulator. Once this has been done, initial simulation runs can be done to test for functionality, check mass balances and to better define boundaries and critical conditions (WEF, 2014). Once the model has been set up, a more involved task of calibrating the model follows.

Calibration consists of adjusting the predictions of the model until they match the performance of the actual WWTP. This is achieved by adjusting the model parameters accordingly using different calibration strategies. During model calibration, the objective is to mimic the performance of the WWTP with a sufficient degree of accuracy so that the model can be applied with an appropriate degree of confidence (Dold et al., 2003). During the calibration process should the model must be set up using reliable information and operational settings before any model parameters such as bio-kinetic parameters are changed. In cases where there appears to be an immediate need to change bio-kinetic model parameters during calibration, one should investigate the data before changing the model parameters since such a situation points out that erroneous data or wrong transport models have been used. However for atypical conditions such as the presence of a significant portion of industrial wastewater in a WWTP it may be necessary to adjust bio-model parameters and new values maybe assigned to specific parameters (WEF, 2014). Engineering knowledge and judgement must be used to identify the parameters that require adjustment (Hauduc et al., 2011). Since the activated sludge models are considered over-parameterised, automatic algorithms can be used to estimate model parameters during model calibration. It is highly recommended to define the calibration strategy upfront and to keep track of all parameter changes. Once model calibration has been done, the resulting set of parameters are validated using a data set, which is independent of the calibration data, but is still reflects the behaviour of the plant being modelled. The calibrated and validated plant model can be used to run simulations and the output results are interpreted against the objectives of the project. Scenarios can be set up and simulations representing the scenarios are run and the results used.

The BIOMATH Calibration protocol

The BIOMATH calibration protocol was developed in Belgium by Vanrolleghem and co-workers (Sin et al., 2005). A summary of the calibration protocol is illustrated in Figure D.1.

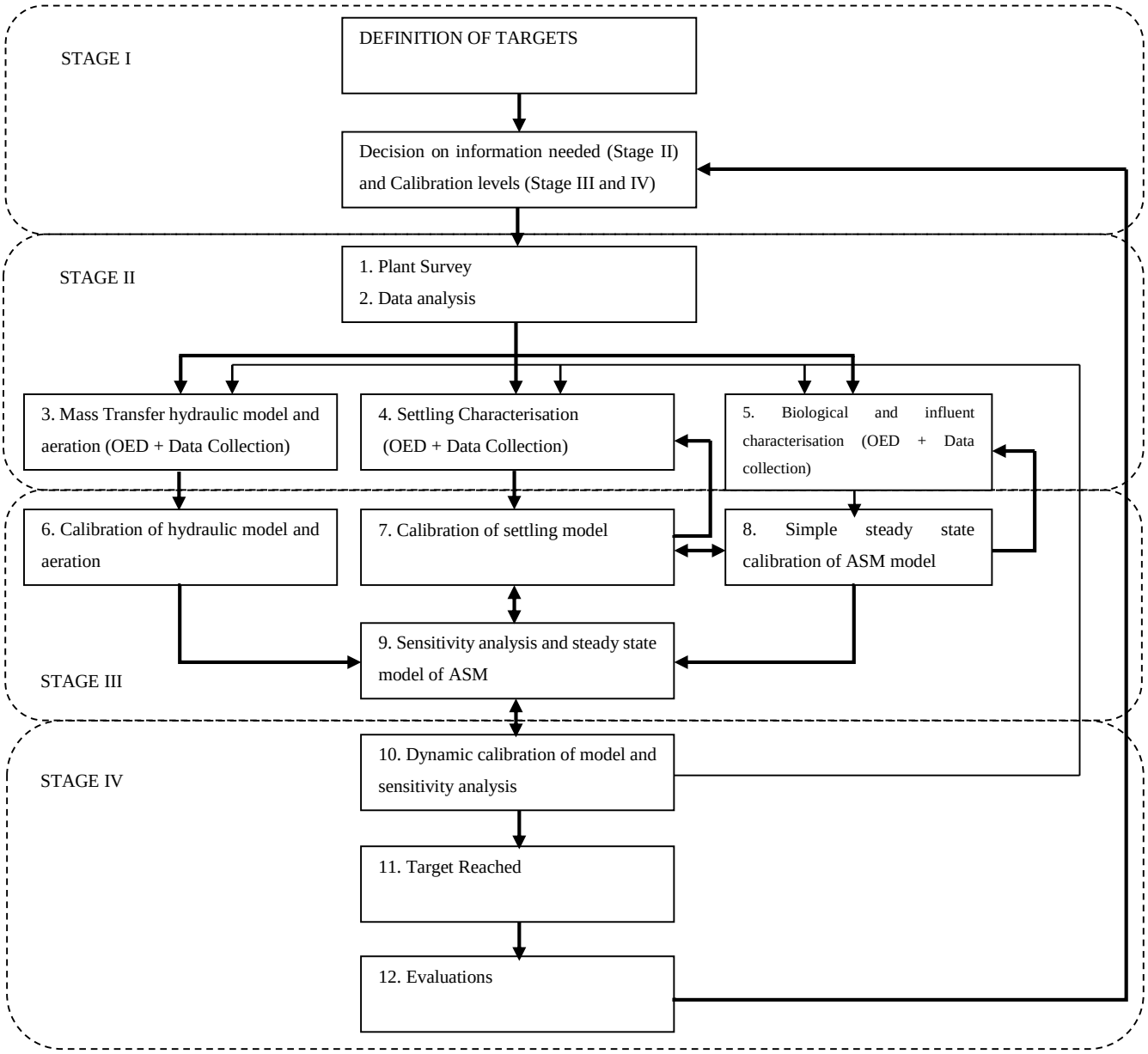

Figure D.1 Overview of BIOMATH calibration protocol (Vanrolleghem et al., 2003)

The BIOMATH protocol is composed of four main stages. The first step of the protocol is to define the goal of the model calibration. The stages that follow can be summarised as follows:

1) Plant survey and characterisation: This stage consists of a comprehensive survey of the WWTP in order to obtain information such as the layout of the WWTP, configuration, operational parameters, input and output characteristics and plant performance. After analyzing and verifying the collected information is used to select the different sub-models for hydraulic, settling and biological processes of the WWTP which make up the full-scale WWTP. The 3 sub-models are calibrated separately using the influent data collected in the first stage.

Following the separate sub-model calibrations, the sub-models are combined to form the full scale model and steady-state calibration of the full scale model is done.

2) The aim of the steady-state calibration is to obtain good prediction of the average sludge production and oxygen consumption in the WWTP. A sensitivity analysis is used to identify the parameters that need to be adjusted during model calibration. The model parameters that are known to affect sludge production include in the long-term operation of the WWTP include X_I, b_H, Y_H, and f_{XI} (Sin et al., 2005). If high accuracy is required in the calibration, more data can be collected for each sub-model. The optimal experimental design (OED) methodology (Dochain and Vanrolleghem, 2001) is recommended.
3) The steady-state calibration is followed by the dynamic calibration where the influent data obtained from sampling and a dynamic measurement campaign are used as input to the WWTP model. Sensitivity analysis is used to identify the most sensitive parameters affecting the variable of concern in the model. The variables considered during calibration are usually selected based on the goal of the modelling project. More information on the most sensitive parameters may be collected during the calibration process if necessary. OED can be used to design the most appropriate experiments that provide the required information at acceptable costs.
4) After dynamic calibration, the model is validated. If the model predictions are not acceptable, recalibration of the model is recommended.

It should be noted that, during the calibration process, not all the steps need to be followed in all cases of model calibration, only the relevant steps are carried out.

The STOWA calibration protocol

The STOWA calibration protocol was developed in the Netherlands. The protocol is based on the calibration of more than 100 WWTPs (Hulsbeek et al., 2002). A summary of the protocol is illustrated in Figure D.2. The calibration protocol starts with formulation of the calibration objectives followed by definition of the relevant processes in the model. Relevant plant data is then collected and verified. The collected data includes composition and flow rates of streams flowing to different process units. The volumes of the process units are also defined at this stage of the calibration process. Carrying out mass balances is recommended as a means of checking data consistency before proceeding with model calibration. The model structure of the WWTP is defined in the fourth step of the protocol. This involves selecting of the sub-models for the description of hydraulics, aeration, settlers and controllers of the WWTP. Once this has been done, information concerning the different flows in the WWTP such as influent, effluent, recycle, waste and internal recirculation flows is collected and transferred into the model.

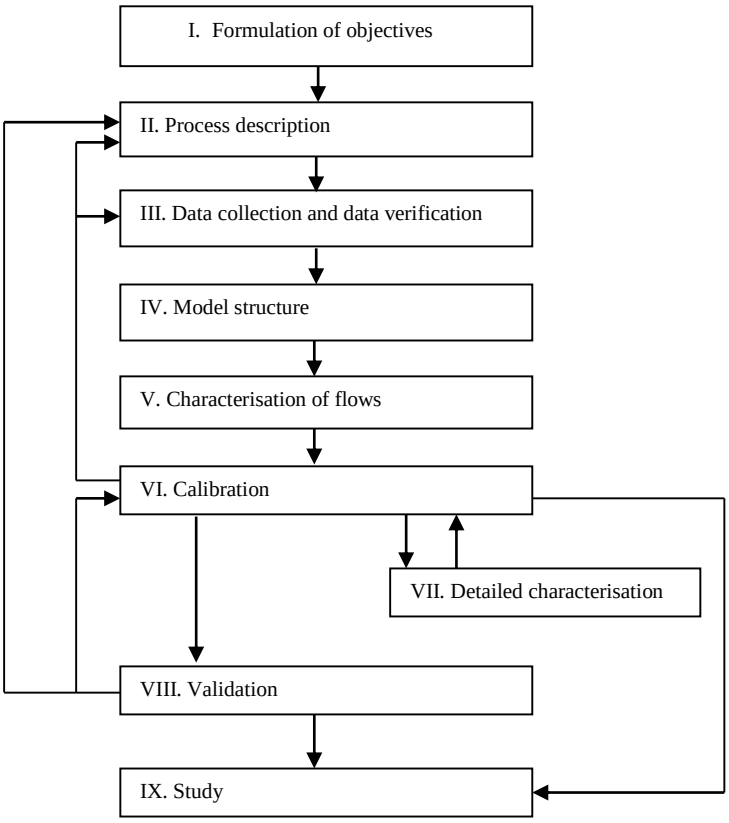

Figure D.2 Overview of STOWA protocol

At this point the model can be calibrated. The STOWA protocol recommends that an initial calibration be done by transferring the information obtained from the data gathering stage into the model, running simulations and evaluating the results (Hulsbeek et al., 2002). If considerable discrepancy is observed between the model predictions and the plant measurements, the protocol recommends checking the data quality again by carrying out more measurements and checking the mass balances again. Detailed calibration of the model can then be done after the aforementioned check. The STOWA protocol recommends a manual calibration procedure in which model parameters of the different bio-chemical processes are adjusted one at a time until the model's predictions match the measured plant data. The protocol provides guidance on which different model parameters of the ASM model and in what order they should be calibrated with respect to different model variables. Validation of the model is the last stage before the model can be used for its ultimate purpose.

The Hochschulgruppe guidelines

The Hochschulgruppe (HSG) protocol was developed by several academic institutes working with ASM models from Germany, Austria and Switzerland (Langergraber et al., 2004). The structure of the HSG protocol is illustrated in Figure D.3.

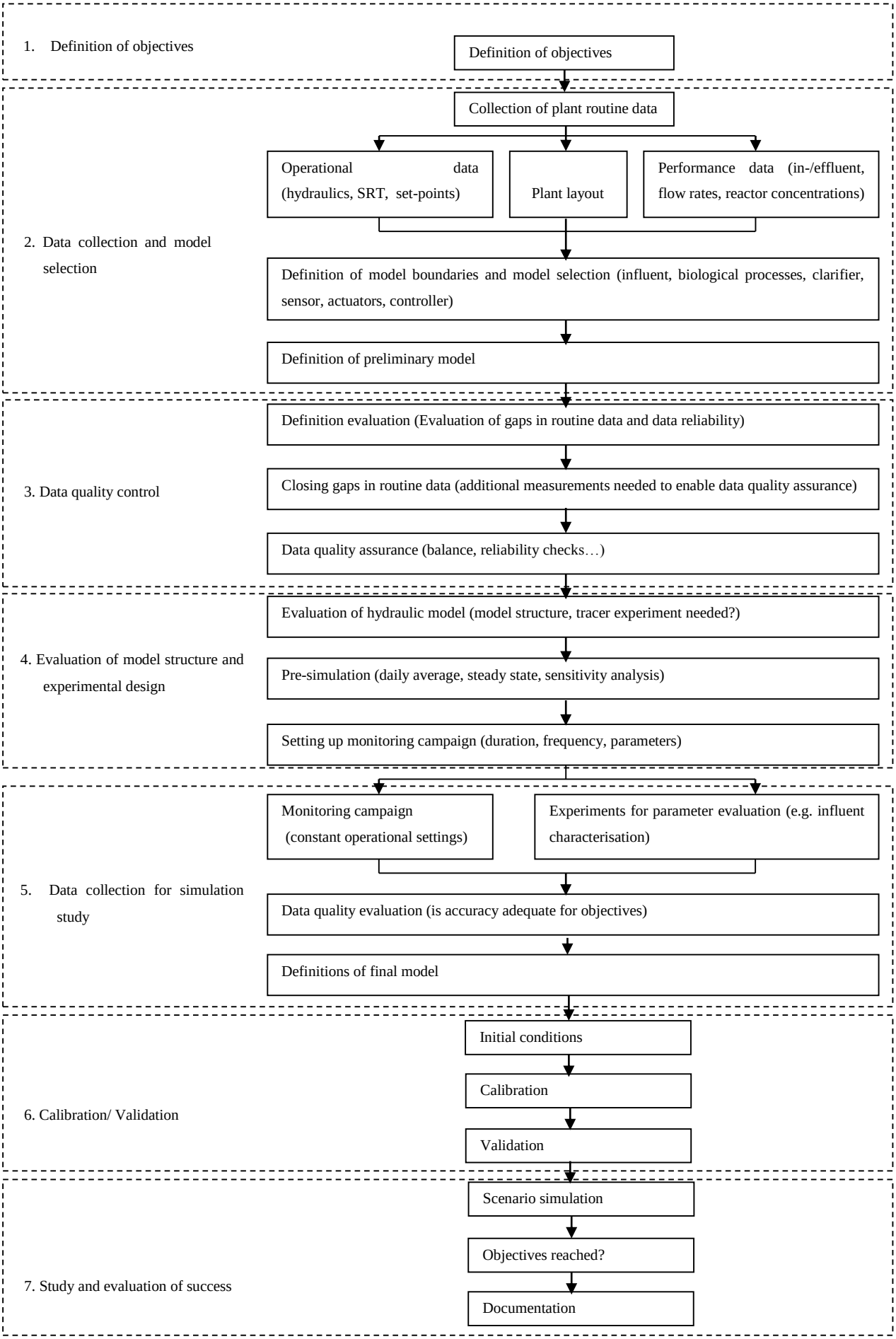
1. Definition of objectives
Definition of objectives
2. Data collection and model selection
Collection of plant routine data
Operational data (hydraulics, SRT, set-points)
Plant layout
Performance data (in-/effluent, flow rates, reactor concentrations)
Definition of model boundaries and model selection (influent, biological processes, clarifier, sensor, actuators, controller)
Definition of preliminary model
3. Data quality control
Definition evaluation (Evaluation of gaps in routine data and data reliability)
Closing gaps in routine data (additional measurements needed to enable data quality assurance)
Data quality assurance (balance, reliability checks…)
4. Evaluation of model structure and experimental design
Evaluation of hydraulic model (model structure, tracer experiment needed?)
Pre-simulation (daily average, steady state, sensitivity analysis)
Setting up monitoring campaign (duration, frequency, parameters)
5. Data collection for simulation study
Monitoring campaign (constant operational settings)
Experiments for parameter evaluation (e.g. influent characterisation)
Data quality evaluation (is accuracy adequate for objectives)
Definitions of final model
6. Calibration/ Validation
Initial conditions
Calibration
Validation
7. Study and evaluation of success
Scenario simulation
Objectives reached?
Documentation

Figure D.3 Flow chart of simulation study according to the HSG guideline (Langergraber et al., 2004)

The first step in this protocol is to define the objection of the calibration study, just like in the other protocols. This is followed by collection of information of the WWTP layout, operation and performance. The preliminary model for the WWTP is then selected based on the collected information. This model is made up of sub-models for hydraulics, settler, controllers and biological process units. The third step of the protocol involves checking and verifying the collected plant data using mass balances.

The fourth stage of the calibration protocol involves calibration of the hydraulic sub-model. The protocol recommends use of tracer experiments or computational fluid dynamics to determine the number of tanks in series that will be required to model the mixing conditions in the aeration tank. After calibrating the hydraulic model a steady-state simulation of the model is done and the simulation results compared with measured plant data. Sensitivity analysis is used to identify model parameters which have the most effect on selected variables in the model.

In the fifth stage data describing the dynamics of the WWTP is collected. The frequency, location and type of measurements carried out are determined by evaluation of the model in preceding steps. The protocol recommends 10 days for the dynamic measuring campaign and the 10 day period must include one weekend to ensure that performance of the plant during weekends is captured. The collected data is checked for quality and consistency. After this stage, the dynamic calibration of the model is done in stage six.

To start the dynamic calibration, model variables should be initialised. This involves modelling the behaviour of the WWTP over several weeks depending on the solids retention time (SRT) of the WWTP. This is followed by calibrating the model parameters in a similar way as in the STOWA protocol. After calibration the model is validated before the final step of evaluating the model by simulating different scenarios related to the objectives of the study.

The WERF protocol

The WERF calibration protocol is based on the experience of consultants and researchers working with ASM models in the United States of America and Canada (Melcer et al., 2003). No illustration of the structure of the protocol was available from the sources that were reviewed for information on the WERF protocol. However in summary, the calibration protocol begins by setting up the plant configuration in the simulator after the collection of physical plant data, influent loading data and plant performance data. In the second step more plant data are collected.

The data collected in this step includes historical data, measurements carried out on the full-scale WWTP and from laboratory experiments. After collecting this information the plant model is calibrated and then validated before use. The difference in the WERF protocol from other protocols is that the WERF protocol performs the calibration step in several different calibration levels. The model calibration starts from a simple level and advances to a more complicated level. The more complicated the calibration level, the more accurate the calibration is.

Calibration level 1 uses default values and assumption for the full-scale model. This calibration level is applicable when designing a new WWTP where information about the wastewater treatment process and influent wastewater is not available. Calibration level 2 only uses historical data for the calibration of the WWTP. The raw historical data are processed, cleaned, corrected where possible and filtered using statistical methods. The data are also checked using mass balances and expert engineering knowledge is applied in this data reconciliation step. Several model parameters can be determined from the historical data at this point.

Calibration level 3 focuses on collecting high frequency data about the dynamics of the plant and influent characteristics. This data is collected by setting up a dynamic monitoring or measuring campaign at the WWTP. Hydraulic characteristics of the aeration tanks in the WWTP can also be determined at this calibration level by using tracer tests. Calibration level 4 includes direct parameters measurements such as detailed influent wastewater characterisation and detailed estimation of kinetic or stoichiometric parameters. Calibration level 4 is recommended in case calibration level 3 does not yield a successful calibration result. The source of the required information for the calibration level 4 can be laboratory-scale experiments and a recommended tool is a sequencing batch reactor (SBR)-based experimental procedure that will allow the estimation of the required model parameters.

SWOT analysis of the systematic calibration protocols

A SWOT analysis is a structured method used to evaluate the strengths, weaknesses, opportunities and threats involve in a project. The four calibration protocols have similarities and significant differences in how some of the steps in the protocols are carried out. Similarities include how each protocol is initiated. All the protocols define the objective of the calibration exercise at the beginning, and emphasise quality checks and verification of the data collected for model calibration. Once calibration of the model has been done, all protocols recommend verification of the model. Key differences in the protocols include the recommended experiments for estimating model parameters such as kinetic or stoichiometric parameters and influent wastewater characteristics.The BIOMATH, STOWA and WERF recommend different experimental methods on this aspect. Significant differences can also be seen in the design of measuring campaigns used to collect data describing the dynamic behaviour of the WWTP and how certain model parameters are calibrated.

A holistic comparison of the four calibration protocols is presented in the SWOT analysis done by Sin et al., (2005). A summary of the SWOT analysis prepared by Sin et al., (2005) is presented in Table D.2.

Table D.2 **Strengths, weaknesses, opportunities and threats (SWOT) of the different calibration protocols (Sin et al., 2005)**

Protocol	Strengths	Weaknesses	Opportunities	Threats
BIOMATH	• Detailed settling, hydraulic and biological characterisation • Detailed influent characterisation • Biomass characterisation • Sensitivity analysis/parameter selection • OED for measurement campaign design • Structured overview of protocol • Feedback loops	• Respirometric influent characterisation requires model-based interpretation • OED has not been applied yet in practice but research is ongoing • OED software and specialist required • No detailed methodology for data quality check • No practical procedure for parameter calibration	• Generally applicable • Works efficiently once implemented in a simulator Dynamic measurement campaigns can be designed and compared based on OED	• Not all modelling and simulation software have OED/Sensitivity analysis (SA) • High degree of specialisation is required for the application
STOWA	• Detailed settling and biological characterisation • Process control • Time estimate for different calibration steps • Detailed data quality check • Step-wise calibration of biological process parameters • Structured overview of protocol • Feedback loops	• No detailed hydraulic characterisation BOD test gives problems (f_p) • No biomass characterisation • No guidance for measurement campaign design • No detailed info on sensitivity analysis • Fixed parameter subsets for calibration of biological processes	• Easy to use • Practical experimental methods No specialist required • Good for consultants and new modellers	• No mathematical/statistical approach for parameter selection for calibration • May not be applicable for different systems since parameter subset for calibration may change for different WWTPs
HSG	• CFD for hydraulic characterisation • Biological characterisation • Design of measurement campaign • A standard format for documentation • Data quality check • Structured overview of protocol	• No feedback loops in overview diagram • Provides only general guidelines • No detailed settling characterisation • No particular methods for influent characterisation or parameter estimation • No detailed sensitivity analysis/parameter selection	• Generally applicable • A standard format for thorough documentation/reporting of calibration studies	• Not detailed/practical enough for new practitioners • The free choice of experimental methodologies for influent/kinetic characterisation may jeopardise standardization of calibration studies
WERF	• Detailed influent characterisation • Detailed μ_A and b_A determination • Biomass characterisation • Sensitivity analysis/parameter selection • Detailed data quality check • A *tiered approach* for calibration • Several examples of case studies	• No feedback loops • Settling process less emphasized • Almost no emphasis on other kinetic parameters than nitrification • No structured overview of protocol	• Based on practical experience • A tiered approach for calibration provides different calibration levels for different goals and accuracy of calibration • Good for consultants and new modellers	• Focus on μ_A determination and influent characterization • Ignoring the significance of the other compartments of the full-scale model • Laborious methods

Conclusion –Calibration protocols

The main purpose of the calibration protocols discussed above is to address the complex problem of calibrating ASM models. While the protocols have made a significant positive impact in the way ASM models are calibrated, the protocols still face several challenges that are inspiring further research. The challenges include the following (Sin et al., 2005):

- Range of applicability of the protocols
- Technical limitations of tools or sensors for data collection
- Limitations in transferring laboratory scale data to full-scale models
- Design data collection (measuring campaigns)
- Complexity of model calibration: limited data versus complex model structure.

The range of applicability of the calibration protocols is limited to certain modelling projects. The development of most calibration protocols was based on municipal WWTPs designed for COD, nitrogen and to a lesser extent, phosphorus removal (Sin et al., 2005). Hence the calibration protocols are more likely to support the municipal WWTPs performing the aforementioned processes. When the calibration protocols are applied to atypical cases such as non-municipal WWTPs or WWTPs with significant proportions of industrial wastewater, deficiencies in the protocol are observed. An example where the recommended approach of the calibration protocols falls short is influent wastewater characterisation and estimation of model parameters where industrial wastewater is being treated. This challenge has been confirmed by this study. The unsuccessful COD fractionation (based on respirometric experiments and flocculation-filtration) of the influent wastewater (containing industrial effluent) at Verulam WWTP highlighted the need for a different characterisation approach for wastewater containing industrial effluent. Thus the existing calibration protocols have room for extension to enable their application to wider range of different WWTP systems.

Technical limitations of tools or sensors used to collected data for calibration poses another challenge for the effective implementation of calibration protocols. The quantity and quality of data used during the calibration of a model determines the quality of the calibration results. If less data are available for calibration or if the data are of poor quality, poor calibration results will be obtained. In many modelling projects collecting the right amount of quality data is a challenge. In this context the availability of robust and reliable sensors at the WWTP for collecting data and well-designed experiment for estimating kinetic and stoichiometric parameters are required for improved calibration accuracy. Researchers (Larsen et al., 2000; Sin and Vanrolleghem, 2004; Sin, 2004 and others) have been working on improving experimental methods to meet the data requirements for improved model calibration accuracy. The great potential of online automatic wastewater fractionation has also been mentioned as an important tool for data collection for model calibration (Vanrolleghem et al., 1996).

The design of data collection methods for calibration purposes in many studies has been based on an ad hoc approach guided by expert knowledge or experience (Sin et al., 2005). This has resulted sub-optimal and poor data quality collected for model calibration. A solution to this challenge is to design experiments using mathematical OED. Dochain and Vanrolleghem, (2001) describe OED based on the fisher information matrix. The OED is based on model simulations that can be used to quantify the information that can be obtained from a particular experiment before the experiment can be performed in the laboratory. The virtually simulated experiment allows evaluation of other properties of the experiment, such as the cost and stability of the processes in the experiment under proposed experimental conditions (De Pauw, 2005). Better designed experiments will improve model calibration accuracy.

An ad hoc approach is used to identify and adjusting model parameters during calibration in different stages in the calibration protocols. The disadvantage of this approach is that reproducibility of the calibration procedure is difficult and the approach introduces uncertainty in the model calibration. An alternative to manual model calibration is automatic calibration. However this has not been successfully implemented in the calibration of WWTP models. One of the reasons for this lack of automation in the calibration process is the complexity of the mathematical models being calibrated. The complex interaction of model parameters of different sub-models of the full scale WWTP limits the success of automatic model calibration (Weijers et al., 1996; Weijers and Vanrolleghem, 1997; Brun et al., 2002). This challenge becomes greater if the data available for calibration are of poor quality or inadequate (Beck, 1987; Dochain and Vanrolleghem, 2001). To address this challenge, the use of advance statistical tools is recommended (Sin et al., 2005). An automatic calibration procedure has been applied in the calibration of river quality models and a partially automated calibration for activated sludge models has been proposed in Sin et al. (2005).

Monte Carlo simulations

It appears that there is no consensus on how the Monte Carlo should be defined. A number of definitions exist in different literature sources. Sawilowsky (2003) differentiates between a simulation, a Monte Carlo Method and a Monte Carlo simulation. A simulation is the imitation of a real process or system over time while Monte Carlo Methods are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical results. The aims of Monte Carlo methods are to solve one or both of two mathematical problems which are; to generate samples of data from a given probability distribution or to estimate expectations of functions under the specified distribution. Monte Carlo methods are useful in situations where it is difficult or impossible to obtain a closed-form expression or where it is impossible to apply a deterministic algorithm.

A Monte Carlo simulation is a type of simulation that relies on repeated random sampling and statistical analysis to compute results (Raychaudhuri, 2008). In a Monte Carlo simulation, a statistical distribution that can be used as a source of input parameters to a model is identified and then random samples are drawn from the distribution to represent the values of the input variables. From each set of input parameters, a set of output parameters are obtained from the model as an output scenario. Each particular outcome is considered a simulation run. A number of such simulations are run and the output values are collected and analysed statistically to make a decision.

When performing the Monte Carlo simulation of a physical process, the following steps are typically performed:

- Static model generation involves generating a deterministic model that represents the physical process. The model is made up of mathematical relationships which transform input variables to the required output variables.
- Input distribution identification is often referred to as probability distribution fitting
- Random variable generation involves generating a set of random numbers that can also be referred to as random variates or random samples, from the distributions identified in the input distribution identification step. Each set of generated random numbers is used as input to the model to provide a set of output values.
- Analysis and decision making is done after collecting the output from the simulation runs.
- Statistical analysis is done on the output values before a decision based on the values is done.

In the work presented in this chapter, Monte Carlo methods were used to generate samples of data from specified probability distributions. The specified probability distributions were obtained from fitting several distributions to measured data and selecting the best fitting distribution from the rest. The Monte Carlo approach used is referred to as, running Monte Carlo simulations. When running a Monte Carlo simulation, values are sampled at random from the input probability distributions. Each set of samples is called an iteration or a trial. The resulting outcome from the sample is recorded. The Monte Carlo simulation does this hundreds or even thousands of times, and the result is a probability distribution of possible outcomes. In this way, Monte Carlo simulations provide a much more comprehensive result of what may happen and the likelihood of happening.

Distribution fitting

Probability distributions assign probability to the event that a random variable has a certain discrete value or falls within a specified range of continuous values. The two main types of probability distributions are parametric and nonparametric. Parametric distributions can be defined using a finite set of parameters while nonparametric and empirical distributions provide estimates of probability densityfunctions or cumulative distributions functions based on sample data.

Nonparametric and empirical distributions are used when the data cannot be described accurately by parametric distributions.

The procedure of selecting a statistical distribution that best fits to a data set generated by a random process is referred to as probability distribution fitting. The principle behind the procedure is to find the type of distribution that fits the data and the value of the parameters (such as the mean or variance) of the distribution that gives the highest probability of producing the observed data. The value of the parameters of the distribution chosen to fit the data should match those of the variable being modelled.

Data for distribution fitting

Before a probability distribution is fitted to a set of observed data, the properties of the data need to be analysed to ensure that the most appropriate distribution is chosen. The nature of the variable to be modelled is important. Whether the variable is discrete or continuous has a bearing of the choice of probability distributions. A discrete variable is usually, but not always, best fitted to a discrete distribution. A common exception is applied where the increment between contiguous allowable values is insignificant compared with the range that the variable may take (Vose, 2008). In certain circumstances, discrete distributions can be closely approximated by continuous distributions when the observed data set is large. Data from a continuous variable are always fitted to a continuous distribution and never a discrete distribution.

The theoretical range of the subject variable should be considered when fitting a probability distribution to observed data. The fitted distribution should, within reason, cover the range over which the variable being modelled may theoretically extend. A correctly fitted distribution will usually cover a range that is greater than that displayed by the observed data. This is quite acceptable because data are rarely observed at the theoretical extremes for the variable in question (Vose, 2008).

The observed data usually comes from a variety of sources. The user of the observed data must investigate the data for bias related to the collection method and it must be established whether the observed data are both reliable and as representative as possible (Vose, 2008).

Identifying the input distribution

Several techniques are used for fitting data to parametric, empirical and nonparametric distributions. Techniques used to fit data to empirical and nonparametric distributions have advantages of simplicity, of use, no need to assume a distribution form before fitting and the omission of inappropriate theoretical (parametric or model based) distributions (Vose, 2008).

Techniques for fitting parametric distributions to observed data employ parametric methods such as the method of moments, maximum likelihood method and optimising goodness of fit statistics and plots. This review discusses in detail, the techniques used when fitting parametric distributions to data due to their relevance to the subject of study.

The maximum-likelihood estimation (MLE) is a method in statistics that is used to estimate parameters of a statistical model from a given data set. If this method is applied to a set of data with a specified statistical model, the maximum likelihood estimation searches for a set of parameters that maximizes the likelihood of observing such data (Hayes, 1973). For a random sample size of n, made up of data that is independent and identically distributed, the following steps are used to derive the maximum likelihood estimator.

For a given probability density function (PDF) or probability mass function (PMF) f , Let θ be the parameter vector for f . If the sample is drawn from the distribution is $x_1, x_2, ..., x_n$ and the PDF or PMF is denoted as f_θ , the likelihood of getting the sample from the distribution is given by equation D.2

$$L(\theta) = f_\theta(x_1, x_2, ..., x_n|\theta) \qquad [D.2]$$

The likelihood can be considered as the joint probability density function of the data, given the parameters of the distribution. Assuming that the sample contains independent data points, equation D.2 can be expanded to equation D.3

$$L(\theta) = \prod_{i=1}^{n} f_\theta(x_i|\theta) \qquad [D.3]$$

In MLE, we try to find the value of θ for which the likelihood $L(\theta)$ attains its maximum. Since this is a product of probabilities, the log of this function can be considered for maximization. Thus, the MLE method can considered as a nonlinear unconstrained optimization problem as given in equation D.4

$$\max LL(\theta) = \prod_{i=1}^{n} In\ f_\theta(x_i|\theta), \qquad \theta \in \Theta \qquad [D.4]$$

Θ represents the domain of each of the parameters of the distribution. The optimization problem can be solved analytically or by using differential equations with respect to the parameters and solving the differential equations (Raychaudhuri et al., 2008). The desirable attributes of the MLE are that they are asymptotically the most efficient; meaning that they make maximum use of the information contained in the sample, resulting in the least variable estimation method (Van Zandt, 2000). Furthermore, even though MLE can have substantial bias, they are asymptotically unbiased; meaning that the bias tends to zero as the number of samples increases to infinity (Raychaudhuri et al., 2008).

The method of moments (MoM) is a method of estimating population parameters such as the mean, variance, median and others. In this approach distribution fitting involves matching the moments of the data to the distribution. In this method the first step is to derive equations that relate moments of the population to the parameters of interest. A sample is then drawn and the moments of the population are estimated from the sample. The derived equations are then solved for the parameters of interest, using the moments estimated from the sample. The method of moments was introduced by Pearson in 1894.

The advantages of the method of moments include that it is relatively simple and gives consistent estimators, though the estimators are often biased. The estimates by the methods of moments may be used as first approximations to solutions of the method of maximum likelihood equations. In some cases, such as for bounded distributions, the method of moments has the disadvantage of giving estimates that are inconsistent with data. Inconsistencies may include a distribution fit to the data having data values below the lower bound of above the upper bound of the distribution. In such cases the number of moments that are matched can be reduced and instead effort is made to match the boundaries sum-squared difference from the sample percentiles or minimizing the sum-squared difference from sample moments. More constraints, constructed from the relations between distribution parameters can be added to define the optimization problem. Different algorithms are then used to solve the nonlinear optimization problem (Raychaudhuri et al., 2008). This method is time consuming and less efficient. The parameter values obtained using this method depend on the algorithm used to solve the optimization problem.

Goodness-of-fit test

Once the data has been fitted to a distribution the goodness-of-fit of the distribution needs to be assessed since it is extremely rare that the fitted distribution equals the true form of the distribution for the observed data. The goodness-of-fit test seeks to establish whether the fitted distribution is acceptable. The bias, variability and accuracy of parameter estimates are taken into consideration. The assessment of the goodness-of-fit of a distribution to a sample is assessed by a statistical test, where the null hypothesis states that the candidate distribution is an acceptable fit to the data and the alternative hypothesis states that the distribution is unacceptable (Altiok, 2010). Two of the most common goodness-of fit tests are the chi-square test and the Kolmogorov-Smirnov test.

The chi-square test (χ^2) essentially compares a histogram of the observed data with the probability distribution (for discrete variables) or probability density (for continuous variables) function. The chi-square test is more appropriate for discrete random variables, since to implement it the range of the data must be divided into discrete classes or bins which can be done more naturally for discrete

data unlike for continuous data where rounding of data into bins may severely discard information (Wilks, 2005). However it can still be used for continuous data. For continuous random variables, the probability density function is integrated over a number of mutually exclusive and collectively exhaustive classes to obtain probabilities for observations in each class. The test statistic involves the counts of data values that fall into each class in relation to the computed probabilities (Wilks, 2005). Equations D.5 and D.6 summarises the chi-square test.

$$\chi^2 = \sum_{classes} \frac{(\#Observed - \#Expected)^2}{\#Expected} \quad [D.5]$$

$$\chi^2 = \sum_{classes} \frac{(\#Observed - n\Pr\{data\ in\ class\})^2}{n\Pr\{data\ in\ class\}} \quad [D.6]$$

The number of data values expected to occur in each class according to the fitted distribution is the product of the probability of occurrence in that class and the sample size *n*. If the fitted distribution is close to the observed data distribution the above equations will yield a small chi-squared value. If the fit is not good, some of the classes will exhibit large discrepancies resulting in a large chi-square value. It is not a requirement to have classes of the same width or equal probability; however classes with small numbers of expected counts must be avoided (Wilks, 2005).

The Kolmogorov-Smirnov (K-S) test is another frequently used goodness-of-fit test. The K-S compares the empirical and fitted cumulative distribution functions (CDFs). In the K-S test the null hypothesis is that the observed data were drawn from the distribution being tested, and a large discrepancy will result in the null hypothesis being rejected. The tests statistic of the K-S test is determined using equation D.7.

$$D_n = \max_x \left| F_n(x) - F(x) \right| \quad [D.7]$$

$$F_n(x_{(i)}) = \frac{i}{n} \quad [D.8]$$

In equation D.7 $F_n(x)$ is the empirical cumulative probability, estimated as $F_n(x_{(i)})$ (equation D.8) for the *i*th smallest data value; and $F(x)$ is the theoretical cumulative distribution function evaluated at *x*. Thus, the K-S test statistic D_n determines the largest difference, in absolute value, between the empirical and fitted cumulative functions. There will always be a non-zero value of D_n even if the theoretical distribution fits well since any real and finite batch of data will exhibit sampling fluctuations. The null hypothesis is rejected if D_n is large. How large is large enough depends on factors such as sample size, the form of the distribution being fitted, the level of the test and whether or not the distribution parameters have been fitted using test data.

Random variable generation

After identifying the underlying distribution for the input parameters of a simulation model, random numbers need to be generated from these distributions. The generated random numbers represent specific values of the variable of concern. There are a number of methods that can be used for generating random variates (RV's) from discrete and continuous distributions. These methods include the inverse transformation method, the alias method, the composition method and the acceptance-rejection method (Rubinstein, 2011). In-depth description of these methods has been omitted in this dissertation. More detailed description and application of these methods can be found in Rubinstein, 2011; Law and Kelton 2000 and Fishman, 1995.

Monte Carlo Simulation output analysis

The output of each trial in the Monte Carlo simulation of a model may be stored and analysed individually or as a group of similar trials. Finding the average of trial values will give an expected value of the output variables. Grouping the output values by size and plotting a frequency histogram gives an approximate shape of the probability density function of the output variables. A range of statistics can be determined from the output results of the Monte Carlo simulations. These include determining percentiles, fitting the output values to a probability distribution or even developing confidence bands. The precision of the expected value of the variable and the shape of the distribution approximately improve as the number of simulation trial increase (Raychaudhuri, 2008).

Uncertainties modelling WWTPs

The confidence that one has in a model's prediction may only be determined after assessing the uncertainties associated with the different steps in the modelling project. The broad modelling project steps may be summarised as:

- Project definition
- Data collection and reconciliation
- Plant model set-up
- Calibration and validation
- Simulation ned interpretation of results

Within these broad steps there are specific tasks that are associated with different types and levels of uncertainty. Uncertainty can be defined as the degree of lack of knowledge about a system or process or the degree of inability to exactly describe its existing state and or behaviour (Belia et al., 2009). The nature of uncertainty can be described as reducible or irreducible. Uncertainty is describes as reducible if the uncertainty can be reduced by further investigations such as carrying out more experiments, while irreducible uncertainty is as a result of inherent variability of a system that cannot be reduced by further research (Belia et al., 2009).

The levels of uncertainty ranging from full knowledge of all outcomes to complete lack of knowledge can be described as follows:

- *quantifiable uncertainty* can be quantified and described using statistics. Sources of quantifiable uncertainties include sampling errors, and uncertainty in measurements.
- *scenario uncertainty* can be described with qualitative estimations of possible outcomes that may develop in the future. Realistic assumptions about relationships and or driving forces within the model can be established. It is not possible, however, to derive the probabilities of the scenario taking place.
- *recognized ignorance* is the state where a deep level of uncertainty is acknowledged to exist and the scientific basis is sufficient to develop functional relationships, statistics, or scenarios.
- *total ignorance* is defined as the state where a deep level of uncertainty exists. It is unknown what is unknown. (Belia et al., 2009)

After the modelling project has been defined, the required accuracy of the model is decided and this in turn defines the uncertainty items that will be taken into account in the modelling project. The nature, source and level of uncertainty for the most significant items in the modelling projects for WWTP modelling projects are summarized in Table D.3.

Table D.3 Nature, source and level of uncertainty introduced in each step of a typical modelling WWTP modelling project (adapted from Beila et al., 2009)				
Area	**Step**	**Details**	**Nature and source of uncertainty**	**Level of uncertainty**
Data collection and reconciliation	Influent data	Flowrate and concentrations of influent	Irreducible: due to the inherent variability of the real system such as the weather and unexpected factory shut downs Reducible: due to data collection e.g. sampling method, location and frequency of sampling, accuracy of analytical techniques	Quantifiable, scenario, recognised ignorance
	Physical data	Process flow diagrams, active tank volumes, clarifier surface areas, flow splits	Irreducible: due to the unpredictable and dynamic behaviour of structures like splitters to flow changes Reducible: due to e.g. unknown true volume constructed or operational depth of structures	Scenario Quantifiable
	Operational settings	Controller set-points, valve positions, pumped flows	Irreducible: due to the unpredictability of operator decisions Reducible: due to actions different from planned or changes not logged, e.g. a change in set-points, incorrect controller set up e.g. scales different between field and control room	Quantifiable, scenario Recognised ignorance, Quantifiable
	Performance data	Effluent data and reactor concentrations such as MLSS	Irreducible: due to the inherent variability of the real system e.g. response of microbial consortium Reducible: due to data collection issues	Quantifiable, scenario, recognised ignorance Quantifiable

Table D.3**: continued**				
Area	**Step**	**Details**	**Nature and source of uncertainty**	**Level of uncertainty**
Plant model set-up	Influent model	Influent dynamics, characteristics, influent fractions	Reducible: due to simplifications of influent dynamics (applying a generic diurnal pattern to average vs. constructing a dynamic profile of the whole sewer system), due to simplifications of influent characteristics (fixed ratios for influent fractions)	Scenario
	Biological model	Model structure: processes (conversion, separation), calculation of composite variables, type of mathematical expression used to describe processes (Monod vs. enzymatic kinetics)	Irreducible: due to the inherent variability of the real system Reducible: due to simplifications in model structure e.g. processes not included, processes included in simplified form (one step vs. two step nitrification), due to the choice of mathematical description of processes	Recognised ignorance Quantifiable
	Clarifier model	Model structure: separation processes, calculation of composite variables and type of mathematical expression used to describe processes Model parameters: fixed, a priori chosen, calibrated, time varying	Reducible: due to simplifications in model structure e.g. processes not included, processes included in simplified form as well as due to the choice of mathematical description of processes Irreducible: due to inherently varying biomass settling properties Reducible: due to our lack of knowledge of the appropriate value	Quantifiable, scenario Quantifiable, scenario

Error! Reference source not found.**: continued**				
Area	**Step**	**Details**	**Nature and source of uncertainty**	**Level of uncertainty**
Plant model set-up	Influent model	Influent dynamics, characteristics, influent fractions	Reducible: due to simplifications of influent dynamics (applying a generic diurnal pattern to average vs. constructing a dynamic profile of the whole sewer system), due to simplifications of influent characteristics (fixed ratios for influent fractions) Irreducible: due to the inherent variability of the real system	Scenario Recognised ignorance
	Biological model	Model structure: processes (conversion, separation), calculation of composite variables, type of mathematical expression used to describe processes (Monod vs. enzymatic kinetics) Model parameters: fixed, a priori chosen, calibrated, time varying	Irreducible: due to the inherent variability of the real system Reducible: due to simplifications in model structure e.g. processes not included, processes included in simplified form (one step vs. two step nitrification), due to the choice of mathematical description of processes Reducible: due to our lack of knowledge of the appropriate value	Recognised ignorance Quantifiable Quantifiable, scenario
	Clarifier model	Model structure: separation processes, calculation of composite variables and type of mathematical expression used to describe processes Model parameters: fixed, a priori chosen, calibrated, time varying	Reducible: due to simplifications in model structure e.g. processes not included, processes included in simplified form as well as due to the choice of mathematical description of processes Irreducible: due to inherently varying biomass settling properties Reducible: due to our lack of knowledge of the appropriate value	Quantifiable, scenario Quantifiable, scenario

Table D.3 shows the sources of uncertainties associated with different steps in a typical modelling project. The importance of quantifying the identified uncertainties depends on the objective of the modelling project. During the identification and quantifying of uncertainty in a modelling project it is important to define the scope and the frame of the uncertainty analysis. A typical approach of framing uncertainties would split the analysis into sections as follows:

- uncertainty analysis to consider uncertainties associated with influent fractions of the ASM1
- uncertainty analysis to consider uncertainties associated with kinetic parameters in ASM1
- uncertainty analysis to consider uncertainties associated with other sources such as model structure (settlers, hydraulics and other items)

Appendix E Raw data: Composition of industrial wastewater from factories

COD concentration of industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**COD (mg/L)**	**Date**	**COD (mg/L)**	**Date**	**COD (mg/L)**
10/11/2010	863	10/11/2010	2 560	10/11/2010	7 783
08/12/2010	512	08/12/2010	3 040	08/12/2010	2 506
10/02/2011	680	12/01/2011	3 438	12/01/2011	327
10/03/2011	42	10/03/2011	375	10/02/2011	1 661
13/04/2011	1 024	13/04/2011	2 400	10/03/2011	984
05/05/2011	308	05/05/2011	3 320	13/04/2011	2 080
02/06/2011	736	18/07/2011	2 744	05/05/2011	719
18/07/2011	1 319	14/09/2011	328	02/06/2011	153
13/10/2011	2 480	13/10/2011	2 793	18/07/2011	1 619
				14/09/2011	1 451
				13/10/2011	2 640
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**COD (mg/L)**	**Date**	**COD (mg/L)**	**Date**	**COD (mg/L)**
08/12/2010	1 888	10/11/2010	6 616	10/11/2010	696
13/04/2011	872	08/12/2010	5 125	08/12/2010	783
01/06/2011	696	12/01/2011	8 200	12/01/2011	72
02/06/2011	655	10/02/2011	1 731	10/02/2011	352
13/06/2011	954	10/03/2011	925	10/03/2011	108
14/09/2011	1 756	13/04/2011	128	13/04/2011	516
13/10/2011	1 600	05/05/2011	3 249	05/05/2011	502
		02/06/2011	16 250	02/06/2011	75
		14/09/2011	5 200	18/07/2011	238
		13/10/2011	1 680	14/09/2011	394
				13/10/2011	48

Concentration of settleable solids in industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Settleable solids (mL/L)**	**Date**	**Settleable solids (mL/L)**	**Date**	**Settleable solids (mL/L)**
10/11/2010	0.0	10/11/2010	1.0	10/11/2010	15
08/12/2010	0.0	08/12/2010	2.0	08/12/2010	5
10/02/2011	0.0	12/01/2011	0.0	12/01/2011	9
10/03/2011	0.0	10/03/2011	0.0	10/02/2011	0.5
13/04/2011	3.0	13/04/2011	10.0	10/03/2011	42
05/05/2011	0.0	05/05/2011	0.2	13/04/2011	57
02/06/2011	0.0	18/07/2011	1.0	05/05/2011	29
18/07/2011	0.0	14/09/2011	0.0	02/06/2011	42
13/10/2011	0.0	13/10/2011	0.0	18/07/2011	65
				14/09/2011	40
				13/10/2011	20
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Settleable solids (mL/L)**	**Date**	**Settleable solids (mL/L)**	**Date**	**Settleable solids (mL/L)**
08/12/2010	0.0	10/11/2010	0.0	10/11/2010	0
13/04/2011	2.0	08/12/2010	0.0	08/12/2010	2
01/06/2011	0.2	12/01/2011	5.0	12/01/2011	0.1
02/06/2011	0.0	10/02/2011	0.5	10/02/2011	0
13/06/2011	0.0	10/03/2011	1.5	10/03/2011	0.1
14/09/2011	0.4	13/04/2011	9.0	13/04/2011	0.2
13/10/2011	6.0	05/05/2011	0.1	05/05/2011	0
		02/06/2011	0.0	02/06/2011	0
		14/09/2011	1.0	18/07/2011	1.2
		13/10/2011	1.0	14/09/2011	0
				13/10/2011	0.1

pH of industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**pH**	**Date**	**pH**	**Date**	**pH**
10/11/2010	7.87	10/11/2010	8.84	10/11/2010	10.27
08/12/2010	7.56	08/12/2010	7.43	08/12/2010	10.72
10/02/2011	6.85	12/01/2011	7.79	12/01/2011	7.94
10/03/2011	9.35	10/03/2011	9.18	10/02/2011	5.55
13/04/2011	9.01	13/04/2011	6.91	10/03/2011	6.97
05/05/2011	9.65	05/05/2011	6.78	13/04/2011	10.95
02/06/2011	9.88	18/07/2011	9.8	05/05/2011	10.01
18/07/2011	10.92	14/09/2011	7.38	02/06/2011	10.18
13/10/2011	6.69	13/10/2011	7.73	18/07/2011	11.55
				14/09/2011	9.28
				13/10/2011	6.47
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**pH**	**Date**	**pH**	**Date**	**pH**
08/12/2010	8	10/11/2010	9.95	10/11/2010	6.72
13/04/2011	6.8	08/12/2010	7	08/12/2010	6.84
01/06/2011		12/01/2011	7.86	12/01/2011	7.7
02/06/2011	8.32	10/02/2011	8.19	10/02/2011	8.9
13/06/2011		10/03/2011	8.33	10/03/2011	9.35
14/09/2011	9.15	13/04/2011	6.93	13/04/2011	9.37
13/10/2011	6.55	05/05/2011	8.99	05/05/2011	9.44
		02/06/2011	8.61	02/06/2011	9.2
		14/09/2011	7.63	18/07/2011	7.16
		13/10/2011	6.46	14/09/2011	8.62
				13/10/2011	8.43

Sulphide concentration in industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Sulphide (mg/L)**	**Date**	**Sulphide (mg/L)**	**Date**	**Sulphide (mg/L)**
10/11/2010	152	10/11/2010	14	10/11/2010	
08/12/2010	147	08/12/2010	312	08/12/2010	
10/02/2011	413	12/01/2011	275	12/01/2011	
10/03/2011	33	10/03/2011	67	10/02/2011	
13/04/2011	17	13/04/2011	70	10/03/2011	
05/05/2011	114	05/05/2011	273	13/04/2011	
02/06/2011	109	18/07/2011	33	05/05/2011	
18/07/2011	29	14/09/2011	30	02/06/2011	
13/10/2011	672	13/10/2011	93	18/07/2011	
				14/09/2011	
				13/10/2011	
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Sulphide (mg/L)**	**Date**	**Sulphide (mg/L)**	**Date**	**Sulphide (mg/L)**
08/12/2010	3	10/11/2010		10/11/2010	
13/04/2011	9.4	08/12/2010		08/12/2010	
01/06/2011		12/01/2011		12/01/2011	
02/06/2011	2.5	10/02/2011		10/02/2011	
13/06/2011		10/03/2011		10/03/2011	
14/09/2011	9.8	13/04/2011		13/04/2011	
13/10/2011	8.2	05/05/2011		05/05/2011	
		02/06/2011		02/06/2011	
		14/09/2011		18/07/2011	
		13/10/2011		14/09/2011	
				13/10/2011	

Concentration of suspended solids in industrial wastewater form factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Suspended solids (mg/L)**	**Date**	**Suspended solids (mg/L)**	**Date**	**Suspended solids (mg/L)**
10/11/2010		10/11/2010	397	10/11/2010	
08/12/2010		08/12/2010	401	08/12/2010	
10/02/2011		12/01/2011	25	12/01/2011	
10/03/2011		10/03/2011	182	10/02/2011	
13/04/2011		13/04/2011	80	10/03/2011	
05/05/2011		05/05/2011	120	13/04/2011	
02/06/2011		18/07/2011	360	05/05/2011	
18/07/2011		14/09/2011	345	02/06/2011	
13/10/2011		13/10/2011	99	18/07/2011	
				14/09/2011	
				13/10/2011	
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Suspended solids (mg/L)**	**Date**	**Suspended solids (mg/L)**	**Date**	**Suspended solids (mg/L)**
08/12/2010		10/11/2010		10/11/2010	
13/04/2011		08/12/2010		08/12/2010	
01/06/2011		12/01/2011		12/01/2011	
02/06/2011		10/02/2011		10/02/2011	
13/06/2011		10/03/2011		10/03/2011	
14/09/2011		13/04/2011		13/04/2011	
13/10/2011		05/05/2011		05/05/2011	
		02/06/2011		02/06/2011	
		14/09/2011		18/07/2011	
		13/10/2011		14/09/2011	
				13/10/2011	

Conductivity of industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Conductivity (mS/m)**	**Date**	**Conductivity (mS/m)**	**Date**	**Conductivity (mS/m)**
10/11/2010	215	10/11/2010	147	10/11/2010	157
08/12/2010	239	08/12/2010	99	08/12/2010	105
10/02/2011	398	12/01/2011	124	12/01/2011	30
10/03/2011	94	10/03/2011	130	10/02/2011	63
13/04/2011	98	13/04/2011	126	10/03/2011	86
05/05/2011	118	05/05/2011	120	13/04/2011	116
02/06/2011	333	18/07/2011	107	05/05/2011	42
18/07/2011	1985	14/09/2011	128	02/06/2011	123
13/10/2011	646	13/10/2011	120	18/07/2011	153
				14/09/2011	66
				13/10/2011	141
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Conductivity (mS/m)**	**Date**	**Conductivity (mS/m)**	**Date**	**Conductivity (mS/m)**
08/12/2010	221	10/11/2010	836	10/11/2010	361
13/04/2011	311	08/12/2010	410	08/12/2010	400
01/06/2011		12/01/2011	863	12/01/2011	50
02/06/2011	189	10/02/2011	221	10/02/2011	455
13/06/2011		10/03/2011	1367	10/03/2011	222
14/09/2011	158	13/04/2011	518	13/04/2011	1178
13/10/2011	377	05/05/2011	631	05/05/2011	1210
		02/06/2011	927	02/06/2011	108
		14/09/2011	1017	18/07/2011	630
		13/10/2011	1017	14/09/2011	169
				13/10/2011	159

Concentration of sugars in industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Sugar (mg/L)**	**Date**	**Sugar (mg/L)**	**Date**	**Sugar (mg/L)**
10/11/2010		10/11/2010		10/11/2010	2.9
08/12/2010		08/12/2010		08/12/2010	2.2
10/02/2011		12/01/2011		12/01/2011	19
10/03/2011		10/03/2011		10/02/2011	4.5
13/04/2011		13/04/2011		10/03/2011	70
05/05/2011		05/05/2011		13/04/2011	85
02/06/2011		18/07/2011		05/05/2011	6
18/07/2011		14/09/2011		02/06/2011	48
13/10/2011		13/10/2011		18/07/2011	180
				14/09/2011	95
				13/10/2011	104
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Sugar (mg/L)**	**Date**	**Sugar (mg/L)**	**Date**	**Sugar (mg/L)**
08/12/2010	2.1	10/11/2010		10/11/2010	
13/04/2011	88	08/12/2010		08/12/2010	
01/06/2011		12/01/2011		12/01/2011	
02/06/2011	4	10/02/2011		10/02/2011	
13/06/2011		10/03/2011		10/03/2011	
14/09/2011	65	13/04/2011		13/04/2011	
13/10/2011	19	05/05/2011		05/05/2011	
		02/06/2011		02/06/2011	
		14/09/2011		18/07/2011	
		13/10/2011		14/09/2011	
				13/10/2011	

Concentration of sulphate in industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Sulphate (mg/L)**	**Date**	**Sulphate (mg/L)**	**Date**	**Sulphate (mg/L)**
10/11/2010	542	10/11/2010	108	10/11/2010	355
08/12/2010	1002	08/12/2010	31	08/12/2010	34
10/02/2011	724	12/01/2011	22	12/01/2011	2.3
10/03/2011	109	10/03/2011	11	10/02/2011	92
13/04/2011	263	13/04/2011	81	10/03/2011	8.6
05/05/2011	328	05/05/2011	51	13/04/2011	7.2
02/06/2011	508	18/07/2011	27	05/05/2011	22
18/07/2011	3547	14/09/2011	10	02/06/2011	64
13/10/2011	9165	13/10/2011	20	18/07/2011	45
				14/09/2011	16
				13/10/2011	10
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Sulphate (mg/L)**	**Date**	**Sulphate (mg/L)**	**Date**	**Sulphate (mg/L)**
08/12/2010	10	10/11/2010		10/11/2010	
13/04/2011	10	08/12/2010		08/12/2010	
01/06/2011		12/01/2011		12/01/2011	
02/06/2011	17	10/02/2011		10/02/2011	
13/06/2011		10/03/2011		10/03/2011	
14/09/2011	10	13/04/2011		13/04/2011	
13/10/2011	27	05/05/2011		05/05/2011	
		02/06/2011		02/06/2011	
		14/09/2011		18/07/2011	
		13/10/2011		14/09/2011	
				13/10/2011	

Concentration of vegetable oils in industrial wastewater form factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Vegetable oils (mg/L)**	**Date**	**Vegetable oils (mg/L)**	**Date**	**Vegetable oils (mg/L)**
10/11/2010		10/11/2010		10/11/2010	
08/12/2010		08/12/2010		08/12/2010	
10/02/2011		12/01/2011		12/01/2011	
10/03/2011		10/03/2011		10/02/2011	18
13/04/2011		13/04/2011		10/03/2011	20
05/05/2011		05/05/2011		13/04/2011	9.6
02/06/2011		18/07/2011		05/05/2011	9.2
18/07/2011		14/09/2011		02/06/2011	7.6
13/10/2011		13/10/2011		18/07/2011	34
				14/09/2011	5.4
				13/10/2011	776
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Vegetable oils (mg/L)**	**Date**	**Vegetable oils (mg/L)**	**Date**	**Vegetable oils (mg/L)**
08/12/2010		10/11/2010		10/11/2010	
13/04/2011	144	08/12/2010		08/12/2010	
01/06/2011		12/01/2011		12/01/2011	
02/06/2011	58	10/02/2011	77	10/02/2011	11
13/06/2011		10/03/2011	119	10/03/2011	3.2
14/09/2011	185	13/04/2011	78	13/04/2011	3.3
13/10/2011	266	05/05/2011	84	05/05/2011	1
		02/06/2011	35	02/06/2011	8.4
		14/09/2011	15	18/07/2011	3.1
		13/10/2011	49	14/09/2011	4.4
				13/10/2011	22

Colour in industrial wastewater from factories

JMV Textiles		Nampak		Frimax Foods	
Date	**Colour (ADMI)**	**Date**	**Colour (ADMI)**	**Date**	**Colour (ADMI)**
10/11/2010	1280	10/11/2010		10/11/2010	
08/12/2010	490	08/12/2010		08/12/2010	
10/02/2011	625	12/01/2011		12/01/2011	
10/03/2011	640	10/03/2011		10/02/2011	
13/04/2011	1825	13/04/2011		10/03/2011	
05/05/2011	275	05/05/2011		13/04/2011	
02/06/2011	1110	18/07/2011		05/05/2011	
18/07/2011	17700	14/09/2011		02/06/2011	
13/10/2011	5650	13/10/2011		18/07/2011	
				14/09/2011	
				13/10/2011	
Packo		**Colgate Palmolive**		**Budget Soap**	
Date	**Colour (ADMI)**	**Date**	**Colour (ADMI)**	**Date**	**Colour (ADMI)**
08/12/2010		10/11/2010		10/11/2010	
13/04/2011		08/12/2010		08/12/2010	
01/06/2011		12/01/2011		12/01/2011	
02/06/2011		10/02/2011		10/02/2011	
13/06/2011		10/03/2011		10/03/2011	
14/09/2011		13/04/2011		13/04/2011	
13/10/2011		05/05/2011		05/05/2011	
		02/06/2011		02/06/2011	
		14/09/2011		18/07/2011	
		13/10/2011		14/09/2011	
				13/10/2011	