INCLUDING THE FATE OF CHEMICAL PRECIPITANTS AND OTHER PRODUCTS OF WASTE RESOURCE RECOVERY FACILITIES IN THEIR STRATEGIC DESIGN AND OPERATION

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Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

The development of evaluative mathematical models for unit process systems of future water and resource recovery facilities (WRRFs) have a significant role to play in defining operational strategies that shall support resource recovery from waste at minimum cost.

Progress to date, towards modelling the entire WWTP system includes the completion of steady state and three-phase dynamic simulation plantwide model for South Africa (PWM_SA) for nitrification denitrification (ND) activated sludge and anoxic-aerobic (AnAerD) or anaerobic digestion (AD) of primary and waste activated sludge from N removal systems. To simulate the entire WWTP, these models combine biological N and P removal activated sludge, AD of primary sludge and AD or anoxic-aerobic digestion (AAD) of WAS with interlinking non-reactive physical thickening unit operations. Because the UCT steady state models are explicit and more simplified than the more complex dynamic simulation model (PMW_SA), they were progressively developed together with the PWM_SA to allow for model verification through mass balanced steady state calculation checks prior to dynamic simulation. The properties of the current PWMSA model include (i) It defines influent wastewater organics concentrations in the same seven types as in municipal wastewater [volatile fatty acids (VFA), biodegradable soluble (BSO) and particulate (BPO) organics, unbiodegradable soluble (USO) and particulate (UPO) organics, where the particulate organics are subdivided into settleable and non-settleable, in the generic form CxHyOzNaPbSc. Further, it uses the routinely measured parameters COD, VSS, OrgN (which equals total Kjeldahl nitrogen (TKN) – free and saline ammonia (FSA)) and OrgP (which equals Total P (TP) – Ortho P (OP)) to quantify the x, y, z a, b, c values, but because the TOC is not routinely measured, the C composition of the organics is obtained from assumed C/VSS mass ratios (fC). (ii) It is fully element (C, H, O, N, P and S) mass and charge balanced. (iii) It has an external algebraic equation equilibrium speciation sub-routine which separates the slow (biological and physico-chemical) and fast (aqueous) processes, (iv) It includes non-ideal aqueous solution effects (ionic strength correction of dissociation constant (pK) values and ion pairing) to calculate the pH and relevant gas partial pressures, (v) It includes the interaction of mineral precipitation on the pH of the aqueous phase due to the release of phosphates, ammonia and inorganic carbon species in the AD or AnAerD systems. These features of the PWM_SA model are global (plant-wide) and so are also included in its primary sedimentation tank (PST; with the UCTPSU sub-model), activated sludge (AS; with the ASM2-3P sub-model), anoxic-aerobic digestion (AAD; also using ASM2-3P) and anaerobic digestion (AD; using UCT SDM3P) sub-models. The model has currently been calibrated against laboratory scale activated sludge (including systems configured for biological N removal and combined N & P removal), anaerobic digestion (for both primary (PS) and waste activated sludge (WAS)) and AnAerD (for WAS) unit operations.

The overarching aim of this project was to apply mathematical models for investigating the fate of chemical contaminants and useful by-products from the waste treatment plant (i.e. biogas, treated water, recovered nutrients, mineral precipitates and stable organics) and to determine whether the industrial utilization of these recovered resources could impact tactical decision making in design and operation optimisation of waste treatment systems. Towards achieving this goal, the following objectives were accomplished:

- Experimental data was generated to answer questions raised from modelling of phosphorus (P) removal systems towards a completer and more acceptable wastewater treatment model, containing the main biological and physico-chemical processes required to predict organic P fluxes simultaneously in both water and sludge lines in the WWTP under different operational modes. Specifically, the experimental data was used towards (i) Proper calibration of stoichiometry and kinetics for the behaviour of polyphosphate (PP) accumulating organisms (PAOs) in activated sludge and anaerobic digestion unit operations.
- The PWM_SA model described above was currently capable of replicating biological processes for organic and nutrient removal. Because chemical precipitation of phosphorus in activated sludge (AS) is commonly practiced for augmenting P removal, the PWM_SA was extended to also include chemically dosed components (i.e. Ferric sulphate) and the chemical P precipitation processes for =AS systems. This model was calibrated against historical data on chemical P precipitation. The improved model will be able to track P for biological excess P removal (BEPR), chemical P removal and for scenarios where both biological and chemical processes are used, in order to assess the environmental and economic impacts of the various wastewater treatment options.
- Further modifications were implemented on the PWM_SA model towards converting it into a tool for the transformation of WWTPs to WRRFs. This process involved:

  - Reviewing the fate of waste sludge types and other WWTP products (i.e. gases and effluent water) towards discovering how best to utilise the ‘resources’ recovered from waste in industrial applications.
  - Development of wastewater treatment performance indices (PIs) that evaluate the entire system, including the fate of the WRRF products.
- Several case studies were performed on selected full scale South African wastewater treatment works (WWTW) to illustrate the capabilities/potential of applying the developed modelling tools. The case studies in this project involved simulating four full scale WWTPs and using the PIs for comparative evaluation (for both environmental and economic feasibility) of at least two control strategies for each WWTP. Examples of such control strategies included the use of chemical dosing (ferric sulphate) for P removal in the AS system versus biological P removal, (ii) utilisation of fermenters versus dosing of volatile fatty acids (VFAs) to augment biological P removal, (iii) sludge disposal in landfill versus sludge treatment via anaerobic digestion and struvite formation for side stream treatment of dewatering liquors. Utilisation of the developed evaluative tools in the case studies proved to be an effective procedure to evaluate WRRF performance on a system-wide level, because they allowed for troubleshooting of prospective scenarios and suggesting of feasible control options.

Towards achievement of the research objectives, both the explicit steady state UCT model and a dynamic simulation model (PWM_SA) were extended. The main extensions to these models included (i) the addition of anaerobic digestion polyphosphate release stoichiometry (which significantly impacts the predicted mineral precipitation potential, aqueous phase concentrations and system pH, hence AD system health), (ii) the addition of chemical phosphorus (P) removal, and (iii) the addition of a balancing tank unit process that could be useful in making tactical system control decisions for the WRRF.

The completed model required calibration against experimental data prior to utilisation against full scale systems. Hence, an experimental campaign involving the operation and testing of a laboratory scale activated sludge system for biological excess P removal (BEPR) connected to an AD system was implemented. The EBPR system was operated to generate enhanced cultures of PAO biomass. Augmented AD batch tests were then used to comprehensively characterise the PAOs generated in the activated sludge system, including their endogenous mass fraction (i.e. the unbiodegradable material that remains after the death and degradation of PAOs), PAO active biomass elemental composition (i.e. the x, y, z a, b, c values of PAO biomass elemental formula, CxHyOzNaPbSc), polyphosphate breakdown rate and kinetics of PAO breakdown in AD. A new method of inorganic suspended solids (ISS) characterisation was developed to distinguish between the (i) ISS from the influent, (ii) ISS that is in the form of polyphosphate (PP, which is generated biologically and stored internally by PAOs) and (iii) ISS that is in the form of mineral precipitates. Hence a new method was developed that comprises of the modified cold perchloric acid (PCA) fractionation which is augmented to included other measurements for inorganic dissolved ions and solids, and the results analysed via a rigorous data modelling procedure. With complete characterisation of the influent wastewater and waste sludge, hypothesized mass balanced equations for biological and chemical processes were added to the steady state and dynamic (PWM_SA) model for their extension according to the research objectives. The results from utilisation of the extended models were checked against the experimental data as part of the calibration process, to ensure confidence in application of the model to replicate WWTP processes. The calibrated model was then converted into an evaluative tool through the development of framework, used for evaluating strategic options, within the model. This evaluative framework was developed through extension of the International Water Association (IWA) Benchmark Simulation Model No. 2P performance indices at system-wide level to allow for inclusion of products that are generated during waste treatment in the evaluative processes.

The modified PWMSA model when tested against experimental data was found capable of predicting system performance for activated sludge and anaerobic digestion unit operations (with P included) reasonably well.

The comparative evaluation of control strategies for full scale wastewater treatment systems, using the extended BSM2-P performance indices (PI) has proved to be an effective procedure to evaluate WRRF performance. Hence, providing ways to troubleshoot prospective scenarios and suggest feasible design and operation control options, in order to determine the most impactful in future decision making for the given WRRF systems. The completed model together with the extended performance indices framework has currently been implemented, as an evaluative tool, in the simulation of four selected wastewater treatment works.

The developed WRRF model, comprising the extended PWM_SA and the system-wide PI evaluation framework can be used as a tool to virtually replicate the real wastewater treatment system, in order to generate critical data that could be applied in long term planning and management of recoverable resources from waste treatment unit operations. The evaluative framework is adjustable for various regions, because the quality criteria (e.g. sludge and effluent) and cost for the recoverable resources (e.g. struvite, biogas, etc.) together with the local chemical dosing and energy costs have been added as adjustable PWM_SA model parameters. The WRRF recovered products (e.g. mineral precipitates, stable organic sludge, biogas, etc.) can also be translated, using subsequent models to predict the ultimate profitability of utilising certain strategic operational methods (i.e. including costs and complications of post WWTP product processing towards generation of final utilisable products).

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ACRONYMS & ABBREVIATIONS

AAD	anoxic-aerobic digestion
AD	anaerobic digestion
ADP	adenosine di-phosphate
AS	activated sludge
ATP	adenosine tri-phosphate
BNR	biological nutrient removal
C	carbon
Ca	calcium
CH_4	methane
CO_2	carbon dioxide
COD	chemical oxygen demand
e^-	electrons
EBPR	excess biological phosphorus removal
FO_c	flux of oxygen used aerobically
H	hydrogen
H^+	protons
HAc	Undissociated Acetate (CH_3COOH)
ISS	Inorganic Settleable Solids
K	Potassium
KH_2PO_4	di-potassium hydrogen phosphate
Mg	magnesium
MMP	multiple mineral precipitations
N	nitrogen
N_2	nitrogen gas
NAD^+	nicotinamide-adenine dinucleotide
$NADH_2$	reduced form of nicotinamide-adenine dinucleotide
ND	nitrification – denitrification
NDEBPR	nitrification – denitrification excess biological phosphorus removal
O	oxygen
OH^-	hydroxide ions
OHO	ordinary heterotrophic organism
OP	ortho-phosphates
P	phosphorus
PAOs	phosphorus accumulating organisms
pCO_2	carbon dioxide partial pressure
PHB	poly3-hydroxy-butyrate ($C_4H_6O_2$)
PP	polyphosphate ($Mg_cK_dCa_ePO_3$)
PWM_SA	plant wide three phase model developed in South Africa
SRT	solids retention time (or sludge age)
TCA	tricarboxylic acid
TKN	Total Kjeldahl Nitrogen
UCT	University of Cape Town
VFA	volatile fatty acid
WAS	waste activated sludge
WRRF	water and resource recovery facility
WWTP	wastewater treatment plant
$Y_{biomass}$	yield coefficient for PAO converting PHB to new biomass (i.e. for growth) aerobically.
Y_{gl}	the mols of glycogen used per mol of PHB formed anaerobically.
$Y_{glycogen}$	yield coefficient for PAO converting PHB to glycogen aerobically.
Y_{PHA}	yield coefficient for PAO converting PHB to energy used in aerobic PP formation and storage.
Y_{PP}	the mols of phosphorus released from polyphosphate for the formation of one mol of PHB

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

The challenges associated with pollution, declining nutrients and water shortage, resulted in the need for strategies towards cost effective recovery of nutrients from waste types fed to wastewater treatment systems, to forms that are usable and possibly marketable, while ensuring maintenance of good effluent quality from the plant. Hence, there is currently a paradigm shift, involving the transition of wastewater treatment plants (WWTPs) into water resource recovery facilities (WRRFs), for promotion of environmental sustainability and preservation of water resource quality. The proposed research essentially seeks to use developed and calibrated mathematical models to investigate the fate of chemically precipitated sludge and other products from the WWTP (i.e. biogas, treated water, recovered nutrients and stable organics) and to determine whether the industrial utilisation of these recovered resources could impact tactical decision making in design and operation optimisation of WWTP systems.

The removal of excess phosphorus (P) in wastewater is known to be important to avoid eutrophication in receiving water bodies such as rivers and lakes. To accomplish P removal from wastewater, WWTPs are designed to accommodate microorganisms that can take up excess P from the water body, hence mediate the treatment process. These microorganisms are known as phosphorus accumulating organisms (PAOs) and can be found in activated sludge (AS) systems that have alternating anaerobic (without any external terminal electron acceptor) and aerobic (where oxygen is available externally as terminal electron acceptor) environments, that are required for PAO metabolism. The PAOs are known to take up high quantities of P in the aerobic (oxygen rich) environments of the AS system. They store the P in their cells in the form of a metal phosphate complex known as polyphosphate (PP; $Mg_cK_dCa_ePO_3$). To maintain required reactor concentrations and solid retention time, a certain quantity of solids is harvested daily from the aerobic reactor of the AS system – this is referred to as waste activated sludge (WAS). This means that the PP also forms part of the WAS that gets harvested (wasted) daily to maintain the activated sludge (AS) system solids retention time (also referred to as sludge age). The AS system wasted sludge (WAS) could get treated aerobically or anaerobically (using anaerobic digestion (AD) systems). The AD systems contain biomass that work to stabilise organics, generating biogas in the process. However, the AD of WAS that contains PP results is known to result in the breakdown of this PP into its constituents of orthophosphate (OP) and metallic counter ions (Mg^{2+}, K^+ and Ca^{2+}). Because the AD bioprocess does not cater nutrient removal, this often leads to high phosphates (and other nutrients) in the effluent. The OP, together with other nutrients (Mg, K, Ca, NH_4^+, etc.) then form part of the reject water (solubles that remain after thickening of AD effluent sludge) that could be recycled to the AS system. Ideally, the phosphorus in the effluent can be recovered and used as part of fertilizer elsewhere, to resolve excess nutrient problems and associated water quality concerns. This recovery process usually involves the precipitation of struvite ($MgNH_4PO_4$ or $MgKPO_4$ that makes good slow-release fertiliser) from AD effluent reject water (containing Mg, K, Ca, FSA and OP). Other metal precipitates such as magnetite, calcite, magnesium phosphate and amorphous calcium also have the potential to precipitate from this AD reject water.

For unit process systems such as the above-mentioned (i.e. AS, AD, crystallisation units, etc.) to, via operational strategies, effect minimum cost and optimum production targets required the development of evaluative mathematical models. These mathematical models contain sets of equations coded into computer simulation programmes to virtually replicate the real system – hence can be used to generate critical data that could be applied in long term planning and management of WWTPs towards resource recovery. Progressive development of these models includes extensions being made to improve the virtual replications of the WWTP unit operations, as information becomes available. The models are based on strict material elemental mass balanced stoichiometry, hence can be defined as 'clear' models that can directly link waste characteristics to predicted system products, exiting the WWTP (now also known as WRRF) via the solid, liquid and gas streams. This allows for calculations such as nitrogen (N) loads in recycle streams, methane production for energy recovery and greenhouse gas generation. Progress to date, towards modelling the entire WWTP system includes the completion of steady state and three-phase kinetic simulation models for nitrification denitrification (ND) activated sludge and anoxic-aerobic (AnAerD) or anaerobic digestion (AD) of primary and waste activated sludge from N removal systems. The WRRF recovered products (e.g. mineral precipitates, stable organic sludge, biogas, etc.) can be translated, using subsequent models to predict the ultimate profitability of utilising certain strategic operational methods (i.e. including costs and complications of post WWTP product processing towards generation of final utilisable products). This is towards preparation of system-wide models that generate expert advice on design procedures and operational strategies, by incorporating the fate of WWTP products, with recovery of various resources from waste (i.e. by tracking organics and nutrients from pollutant source to final product).

In a recent study (WRC report number 1822/1/14), Ikumi et al. (2015) developed steady state and dynamic simulation models to assist in the ongoing investigations for strategic design and optimised operation of water and resource recovery facilities (WRRFs). The steady state and dynamic models were developed simultaneously because the steady state models were required to determine kinetic rates and sludge compositions for dynamic model input and calibration. This was possible because the steady state and dynamic activated sludge and anaerobic digestion models are based on the same basic principles, mass balanced stoichiometry, just in simplified form for the steady state model, without significant loss of accuracy. The steady state models allow sizing and optimization of individual wastewater treatment plant unit operations, i.e. direct calculation of sludge age, reactor volumes and recycle flows for known wastewater characteristics or wastewater characteristics for existing wastewater treatment plants before performing dynamic simulations and so obviate much of the trial-and-error use of dynamic models. Once the wastewater treatment plant layout is established with steady state models, dynamic models can be applied to its operation to minimize energy consumption and cost while maximizing nutrient recovery and improving effluent quality (Ikumi et al., 2015).

To successfully evaluate the full-scale wastewater treatment systems, towards proposing future WRRF design and process optimisation protocols, significant modifications on the models presented by Ikumi et al. (2015) were required. These modifications mainly include (i) proper calibrated stoichiometry for anaerobic poly-phosphate (PP) release (ii) kinetics of PP release and hydrolysis of waste activated sludge containing phosphorus accumulating organisms (PAOs) (ii) validated characteristics of PAOs (including their endogenous residue fraction and elemental composition) (iv) sub-models associated with chemical dosing operations and (v) the development of an evaluative system-wide framework, which is includes the fate of waste resource recovery facility (WRRF) products. The inclusion and validation of these components, within the previously developed three phase plant-wide model, is a novel aspect of the project.

The updated model is then utilised to simulate full-scale systems in South Africa (i.e. case studies for implementation of the models in defining the potential for future WRRFs). The framework developed in this project, towards evaluation of different design or control strategies for the WWTPs, is an extension of the Benchmark Simulation Model No. 2P (BSM2P), which was developed by the International Water Association (IWA) task group (Jeppsson et al., 2007). This study addressed the complex aspects which were deficient within the current plant wide scenario, utilising performance criteria, previously used by the IWA BSM2P task group, such as effluent quality indices (EQI) and operating cost indices (OCI) to cater for a system wide framework that includes the fate of WRRF products. The updated evaluation framework, together with the updated model is useful as a tool that aids the review of best approaches for future planning, optimal configuration and efficient operation of the WRRF systems. This is with the ultimate objective of ensuring effluent quality and acquiring the best monetary value for plant optimisation, while promoting sustainable systems through the resource recovery.

1.2 PROJECT AIMS

The proposed research essentially seeks to use developed and calibrated mathematical models to investigate the fate of chemical precipitated sludge and other products from the WWTP (i.e. biogas, treated water, recovered nutrients and stable organics) and to determine whether the industrial utilisation of these recovered resources could impact tactical decision making in design and operation optimisation of WWTP systems.

Various research gaps are to be addressed in the proposed project. This mainly involves two aspects:

1. Development of a WRRF mathematical modelling consortium.
2. Generate experimental data that can answer questions raised from modelling of P removal systems towards a completer and more acceptable wastewater treatment model, containing the main biological and physico-chemical processes required to predict organic P fluxes simultaneously in both water and sludge lines in the WWTP under different operational modes. Required further developments in the model include addition of properly calibrated stoichiometry and kinetics for the process of anaerobic PP release.
3. Converting the PWM_SA model of Ikumi et al. (2015) to a realistic tool that can be utilised towards transforming WWTPs to WRRFs. This aim could be broken down into the following sub-objectives:
   i. Review of the fate of waste sludge types and other WWTP products (i.e. gases and effluent water) towards discovering how best to utilise the ‘resources’ recovered from waste in industrial applications.
   ii. Develop wastewater treatment performance indices that evaluate the entire system, including the fate of the WRRF products.
   iii. To illustrate the capabilities/potential of applying the modelling tools together with the proposed system-wide approach, using several case studies performed on selected full scale WWTW in South Africa.

1.3 SCOPE AND LIMITATIONS

The research investigation involved (i) A literature review, (ii) experimental studies, (iii) model implementation and (iv) case studies on full scale systems. The literature review was done to investigate the fate of various products generated in the wastewater treatment process, beyond the fence of the WWTP. It was intended that the environmental and economic impact, due to the pathways taken by the WWTP products, could influence the decision-making process for design and operation of future WRRFs. The information generated from this review was useful in developing the extended evaluative framework for WRRFs. The second part of the study included an experimental campaign that was used to generated data that could be applied to address the research gaps in the currently developed model. Mainly the current plat-wide model (PWM_SA; Ikumi et al., 2015) required some calibration to ensure accurate replication of phosphorus (P) removal systems. This was with regards to (i) the behaviour of PAOs in AD systems and (ii) chemical P precipitation in AS systems. The extension of the model hence included (i) capability to accurately simulate the AD of WAS containing PAOs and their stored PP, (ii) the capability to predict system performance with P removal via chemical precipitation processes (i.e. the addition of ferric sulphate for formation of ferric phosphate) and (iii) the addition of an evaluative framework that can be used in comparing strategic scenarios, towards selection of the best decision for WRRF system design and operation. This involved development of formulated performance indices that include the fate of WRRF products as the evaluative framework (which is an extension of the one developed IWA BSM task group; Jeppsson et al., 2007) used to assess strategies in system design or operation, during application of mathematical models that virtually replicate WRRFs. The performance indices shall be included as evaluative equations in the extended PWM_SA model. The utilisation of the modified PWM_SA model for the simulation of a full scale South African wastewater treatment shall be prepared as a case study that showcases the potential for utilisation of the model as WRRF evaluative tool. Figure 1.1 below provides a mind map depicting and overview of the reported project.

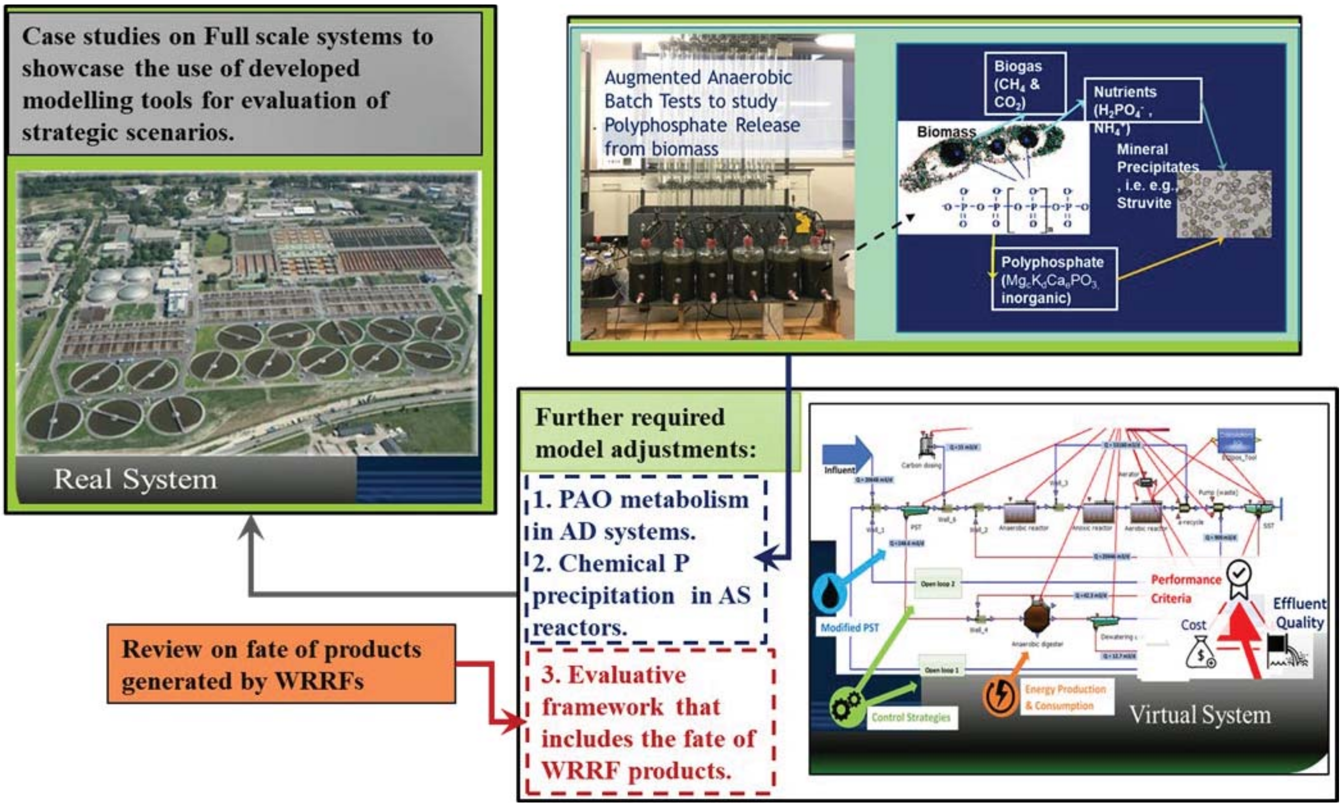

Figure 1.1. Mind map showing an overview of the reported project

CHAPTER 2: REVIEW ON THE FATE OF PRODUCTS GENERATED FROM WRRFS

2.1 INTRODUCTION

As a result of the biological and physical treatment processes, WWTPs generate various products which include gases, sewage sludge and treated effluent. With the view of transitioning towards WRRFs, the need arises to reduce the harm that the traditional pathways of the WWTP products may cause to the environment. In addition to reduction of the polluting effect of those products, it becomes important to consider the potential recovery options, where possible, for the said products for beneficial uses including nutrient recovery. The fate of products generated from WRRFs and their respective potential management options are discussed in this section. Figure 2.1 below provides an overview of the processes that the various WWTP products would commonly take beyond the fence of the WWTP.

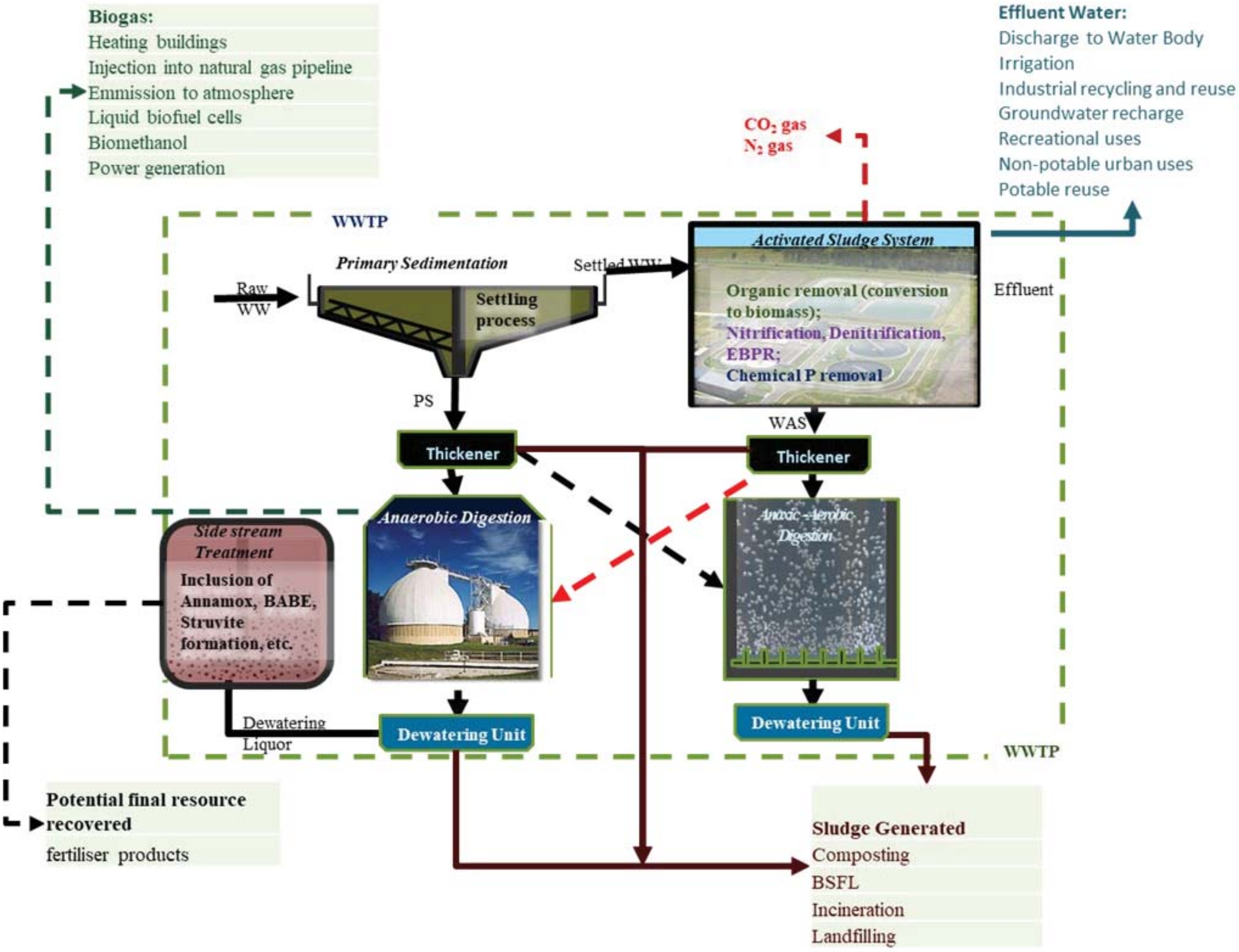

Figure 2.1. Common fates of various products generated by WWTP systems

2.2 GASES

The common gases generated in WWTPs include (i) carbon dioxide (CO_2), which is generated during breakdown of organics in AS and AD systems, (ii) methane (CH_4), which is part of the biogas generated in AD), (iii) nitric oxide (N_2O), which is generated during the nitrification – denitrification (ND) processes in AS systems and (iv) nitrogen (N_2), generated during both ND and AD processes.

In WWTPs, the gas generated via AD (biogas) is commonly recovered as a resource, while that from AS systems is usually allowed to evolve into the atmosphere. Because biogas is a useful resource, there have been numerous studies on its application (Swartz et al. (2013; Musvoto et al., 2018; Zvimba and Musvoto, 2020). Biogas has found various uses, which include (i) gaseous biomethane that could be used to provide combined heat and power in WWTW (for heating buildings and powering other unit operations), injected into a natural gas pipeline or used in manufacture of agricultural fertiliser (Fagerström et al., 2018; Penteado et al., 2017; Poulsen and Adelard, 2017; Hoarau et al., 2018), (ii) converted into liquid biofuel for power generation (Burton et al., 2009; Han et al., 2014 ; Herbes, 2017) and (iii) used in the development of carbon-based nano-materials (Hof et al., 2017; Kamioti et al., 2018). The most common use for biogas is energy recovery via CHP. However, according to Musvoto et al. (2018), the application of biogas to energy is economically viable for large WRRFs, with influent flows above 15 ML/d, and would require long-term investment, with viable returns only possible over a 7-10-year period. Further, 71% of WWTPs in South Africa have the capacity to generate energy, and better opportunities for biogas generation and application are possible via exploring co-digestion of municipal sewage sludge and other biodegradable organics, such as food waste (Nghiem et al., 2017).

However, apart from being a useful resource, the major components of biogas (CO2 and CH_4) are also greenhouse gases, known to be detrimental when released into the environment in large quantities. The potentially adverse effects of this CH_4 on the atmosphere is mitigated by using the biogas to generate energy (Daelman et al., 2012). Other than from the AD process, Daelman et al. (2012) observed that CH_4 formed in sewers enters the WWTP via the influent at a load of approximately 1% of the influent COD load. A negligible amount of the influent CH_4 is stripped at the head of works while a significant amount (80%) is oxidised in the biological reactor. The remaining unoxidized CH_4 is then emitted from the reactor as a minor contributor to the total emission from the WWTP. The main sources of CH_4 emission at WWTPs are the PS thickener, the centrifuge, the exhaust gas of the cogeneration plant, the buffer tank for digested sludge and the storage tank for dewatered sludge (Daelman et al., 2012).

Another well-known greenhouse gas generated at WWTPs is N_2O, which is biologically produced during the denitrification process at WWTPs in areas of high biological oxygen demand and low oxygen concentration such as influent lines, PSTs, SSTs, sludge holding tanks and sludge transfer lines (Czepiel et al., 1995). It was observed by Czepiel et al. (1995) that the N_2O generated is stripped from the liquid as it is agitated by aeration and from turbulent flows in grit tanks for instance. From the study, it was noted that a significant portion of the total N_2O emission at WWTPs emanated from the aerobic tanks. From literature (Campos et al. 2016), three strategies have been identified to reduce greenhouse gas emissions – (1) minimisation, (2) capture and treatment, and (3) prevention which consist of the modification of operational conditions to reduce emissions, the capture and treatment of gases and the prioritisation of anaerobic pathways for organic removal and usage of microalgae or partial nitritation-Anammox for ammonia removal.

Nitrogen gas, which is also generated via the denitrification process in AS and is known to be part of biogas generated during AD is an inert gas that is often released into the atmosphere. However, it can be used as a valuable nutrient in agriculture and can be converted to fertilizer by the Haber-Bosch process, an energy intensive process (van der Hoek et al., 2018).

2.3 SEWAGE SLUDGE

Sewage sludge generated from WWTPs is essentially a mixture of organic matter, water, both dead and alive microorganisms, and organic and inorganic toxic pollutants. Modern sludge management, which revolves around sustainability principles, favours the beneficial use of sewage sludge over the traditional unsustainable options such as use of sewage sludge as landfill. More sustainable management options include (1) utilisation of sludge for its calorific energy value, (2) utilisation of the useful constituents of sewage sludge (carbon and nutrients) and (3) extraction of useful constituents such as phosphorus from sewage sludge (Snyman & Herselman, 2006a).

While the landfill pathway for sludge is a simple and economical management option, there are there are significant downsides to this option. At landfills, the biodegradable organics in the sludge disposed get broken down anaerobically releasing CO_2 and CH_4 greenhouse gases into the atmosphere. The organically bound nutrients are also released as leachate and can potentially contaminate the surrounding environment including groundwater and surface water.

Agricultural use of sewage sludge is deemed to be the one of the preferred sludge management options (Snyman & Herselman, 2006a). With the nutrient content of sewage sludge, its use as fertiliser was shown to be promising as crop yields were found to be similar to yields achieved with chemical fertiliser at equivalent nitrogen rate applied. Additionally, the biological and physical properties of soil has shown improvements with the use of sewage sludge as fertiliser (Suss, 1994). Where the sludge would be used for land applications (i.e. as soil conditioner/ fertiliser), advanced sludge treatment facilities at WWTPs have incorporated the processes of thermal hydrolysis pre-treatment (THP) together with anaerobic digestion (AD). The AD is known to be useful in sludge stabilisation (and generation of biogas in the process). The addition of THP has the effect of (i) changing the sludge viscosity such that a much higher sludge loading capacity to AD is obtained (allows for an effective feed at 9% total solids concertation as compared to the normal feed concentrations of 6% total solids concentration), (ii) generation of lower solid volumes for disposal by improving sludge dewaterability (hence sludge transportation becomes easier) and (iii) the high temperature and pressure from THP units, allow for sludge pasteurization, that improves the quality of sludge for agricultural use.

Depending on the classification of the sludge, it may not be suitable for use in agricultural practices. In this scenario, the remaining two sustainable pathways can be considered as possible option for sludge management (Snyman & Herselman, 2006a). One such alternative pathway is incineration. The advantages of incineration comprise the significant reduction in sludge mass, the complete destruction of pathogens and other harmful substances, and is a means of recovering energy (Đurđević et al., 2019). While the generation of electricity from sewage sludge incineration does contribute to greenhouse gas emissions, Đurđević et al. (2019) noted that the emissions compared to that of combined heat and power (CHP) systems using natural gas and hard coal power plants are 58% and 80% less respectively.

2.4 NUTRIENTS RECOVERED FROM DEWATERING LIQUOR

Stabilisation of sewage sludge (PS and WAS) through aerobic or anaerobic digestion involves the breakdown of biodegradable organic material. As proteins and microorganisms in the sludge are broken down, high concentrations of organically bound nitrogen and phosphorus are released into the bulk liquid in form of ammonia and ortho-phosphates respectively. Should the sludge mixture be aerobically digested, the ammonia released would be oxidised and turned into nitrate (Ikumi & Harding, 2020). Nitrates in turn can be converted to nitrogen gas with intermittent aeration, leaving a sludge liquor rich in ortho-phosphate. On the other hand, if the sludge mixture is anaerobically digested, both ammonia and ortho-phosphates would exist in the sludge dewatering liquor. In addition to the organically bound phosphorus released during the lysis of microorganisms, anaerobic digestion provides the optimal conditions for the release of large amounts of phosphorus due to degradation of polyphosphate chains inside PAOs. (Ikumi & Ekama, 2019)

Due to stringent regulations, many WWTPs recycle the nutrient-rich sludge dewatering liquor to the head of works for further treatment prior to disposal into water bodies. This recycle flow results in an increase in the nutrient load on biological reactor which can potentially have a negative impact on the wastewater treatment process. Side stream treatment of sludge dewatering liquor mitigates the abovementioned negative impacts on the wastewater treatment process as nutrients (N and P) are removed prior to recycling. The common methods of sidestream treatments include: (i) anaerobic ammonium oxidation (ANAMMOX) is a potential side-stream treatment technology that can be used to remove nitrogen from sludge dewatering liquor at WWTPs. This biochemical reaction is mediated by autotrophic ANAMMOX bacteria which have the metabolic ability to oxidise ammonium anaerobically, to produce nitrogen gas, by utilising nitrites as terminal electron acceptors (Kotay et al., 2013), (ii) the BABE (bio-augmentation batch enhanced) process, developed by DHV water (Zilverentant, 1999) – designed to remove ammonia from sludge dewatering liquor and improve nitrification in the activated sludge system through the bio-augmentation of nitrifiers in a side stream reactor and (iii) precipitation of struvite (also known as magnesium ammonium phosphate hexahydrate; $MgNH_4PO_4 \cdot 6H_2O$), which can occur when the Mg^{2+}, NH_4^+ and ortho-phosphates (OP) are at high concentrations (Loewenthal et al., 1994). Magnesium is usually the limiting component and could be dosed in the form of magnesium hydroxide (the hydroxide allows for higher pH for the presence of OP in the least protonated (PO_4^{3-}) form. To improve the quality of struvite formed, various technologies have been developed such as concluded that Ostara Pearl® and Multiform Harvest Sikosana et al. (2016). Struvite has found use as a slow-release fertiliser and can also be used in manufacture of fire retardants.

Apart from struvite precipitation, other methods of nutrient recovery from wastewater include (1) chemical crystallisation, (2) gas stripping and absorption, acidic air scrubbing, (4) membrane separation and (5) biomass production and harvest (Vanrolleghem & Vaneeckhaute, 2014).

2.5 TREATED EFFLUENT

The common practice for treated effluent is its discharge into water bodies. In most countries, less than 10% of the effluent from WWTPs is recycled (Mayer et al., 2016), with the most common form of reuse being through agriculture (Drechsel et al., 2015). With water scarcity becoming a growing concern worldwide, the need for water reclamation becomes important to alleviate the stress on existing potable water sources. There are many potential applications of wastewater effluent reuse that help in decreasing potable water use. These applications, each having their respective water quality standards to be met, include agricultural reuse, industrial reuse, urban reuse, and indirect and direct potable reuse. Current public perception and potential health hazards is a hurdle yet to be overcome when it comes to potable uses of treated effluent. Until there is an improvement in public perception and health hazards are eliminated, the reuse of wastewater effluent will be limited to non-potable applications which exclude its use on crops intended for food production. For successful water reclamation it is also important to ensure the removal of toxic contaminants (from industrial wastewater), heavy metals, pathogens or micropollutants as these could have a detrimental impact on the environment and on human health. In such cases, the WWTP would be connected to a water treatment plants (WTP) facility that is used to process the effluents and often the effluents from the WTP effluent could be used to recharge underground water before its abstraction for potable use.

2.6 CLOSURE

In the context of wastewater treatment, integrated resource recovery involves connecting the wastewater treatment plants to unit operations beyond the fence of the WWTP, such that the source of pollutants to the plant and the fate of the products generated by the plant are included in the management and planning of the entire system for maximum benefit from the recovery of resources. Hence, the decisions made in the design and optimised operation of the WWTP and the connected unit operations (i.e. the entire system) are influenced by the extent of environmental, social and economic progress that the recovered resources would promote. The decision-making processes that would allow for the transformation of wastewater treatment systems to water and resource recovery facilities (WRRFS) that are socially inclusive, cost effective and environmentally sustainable, involves collaboration between a network of stakeholders including consulting engineers, municipal workers, researchers, and public health specialists. Mathematical models could be used as tools in such instances to integrate the ideas that define strategy evaluation for recovery systems (Solon et al., 2019). The extended model used towards evaluating the various strategies proposed for future WRRFS is described in Chapter 4 below. This also includes (i) the extensions made to the unit operation sub-models to ensure accurate prediction of the WRRF unit process performance (Section 4.2) and (ii) the extended evaluative framework used to compare a selected set of strategies (Section 4.3). To ensure that the models are well calibrated for the extensions (to be shown in Section 4.2) for their capability to replicate unit operations for tracking phosphorus (P), various experimental studies were required. The details of these experimental studies and their findings are provided in the following Chapter 3. The review performed in this Chapter 2 was also used to generate the required information that could be used towards formulating the evaluative framework described in Section 4.3 such that it would also cater for the fate of products generated by the WRRF (i.e. beyond the fence of the WWTP). The application of this WRRF model is then showcased in full-scale South African system case study of Chapter 5.

CHAPTER 3: EXPERIMENTAL INVESTIGATIONS

3.1 INTRODUCTION

A major objective of this project was to generate experimental data that can answer questions raised from modelling of P removal systems towards a completer and more acceptable wastewater treatment model, containing the main biological and physico-chemical processes required to predict organic P fluxes simultaneously in both water and sludge lines in the WWTP. To achieve this objective required addressing the following research gaps that were identified by Ikumi et al. (2015) and Ikumi and Ekama (2019):

a. The extent to which PP is released with PHB uptake (resulting in energy generation, alkalinity increase and ρ_{CO2} decrease) rather than PAO death (results in H_2CO_3 alkalinity drop and ρ_{CO2} increase) in the AD and the stoichiometric outcome. It is expected that if this PHB uptake rate can be used also in the AD (since PAOs are again exposed to anaerobic conditions with presence of acetate) to provide reasonable outputs for pH and ρ_{CO2}. This would validate the concept of PP contributing to some 'energy' carry over from AS to AD system (Ikumi and Ekama, 2019).

b. PAO death: In the AS system the PAOs endogenous respiration rate is known to be at about 0.04/d, with the endogenous residue being about 0.25 of the PAO biomass (Wentzel et al., 1990). In the AD system, it is possible that the PAOs die at a faster rate, since the AD biomass is acting on them as a substrate source. However, rather than their death rate, of importance is the rate at which their biodegradable particulate fraction hydrolyses. Ikumi et al. (2014) reports the biodegradability and kinetics of hydrolysis of WAS from NDEBPR AS system. However, this value is obtained from the AD of WAS containing mixed cultures of OHO and PAO biomass.

c. The reason behind the different influent WW $f_{S'up}$ fractions calculated for EBPR systems with the steady state EBPR model (with PAOs) and for ND systems treating the same wastewater with the ND AS model (no PAOs) (Ikumi, Harding and Ekama, 2014). A possible cause for this higher $f_{S'up}$ values may be reviewed by assigning to the PAOs a higher unbiodegradable fraction (f_{EG}) or conversely increasing the PAO biomass concentration (with lower P content) so that more PAO endogenous residue is produced by generating more VFA from hydrolysis of BPO than only the influent readily biodegradable organics (RBCOD). Hence, the f_{EG} value of 0.25 (measured on enhanced PAO culture activated sludge) can be checked by the determination of f_{EG} experimentally through digesting enhanced cultures in batch AD tests.

To address investigations (a) to (c) above, extremely careful and exact experimental work on the augmented bio-methane potential (ABMP) tests of EBPR waste activated sludge (WAS) containing enhanced cultures of PAO biomass was carried out. Figure 3.1 shows a schematic representation of the full experimental layout.

The augmented bio-methane potential (ABMP) tests (described further below) involve incubating wastewater inoculated with anaerobic bacteria for a given number of days. These tests are favoured as they are relatively simple to perform and are repeatable and reliable if performed correctly. A laboratory scale, completely mixed anaerobic digestion steady state system was operated at a solids retention time (SRT) of 20 days to provide seed inoculum for the ABMP tests. These tests were then run for approximately 40 days each. Waste activated sludge (WAS) was used as the substrate for the various ABMP tests. Three different sets of ABMP tests were performed:

(i) Where the WAS was sourced from a full scale NDEBPR AS system that was operated at a long (>30 days) SRT.

(ii) The substrate (WAS containing enhanced PAO cultures) was generated by a laboratory scale University of Cape Town (UCT) configured Membrane (MBR) NDEBPR AS system, operated at steady state at a short 10-day SRT.

(iii) The WAS was generated by a laboratory scale Modified Ludzack Ettinger (MLE) system operated at a short 10-day SRT.

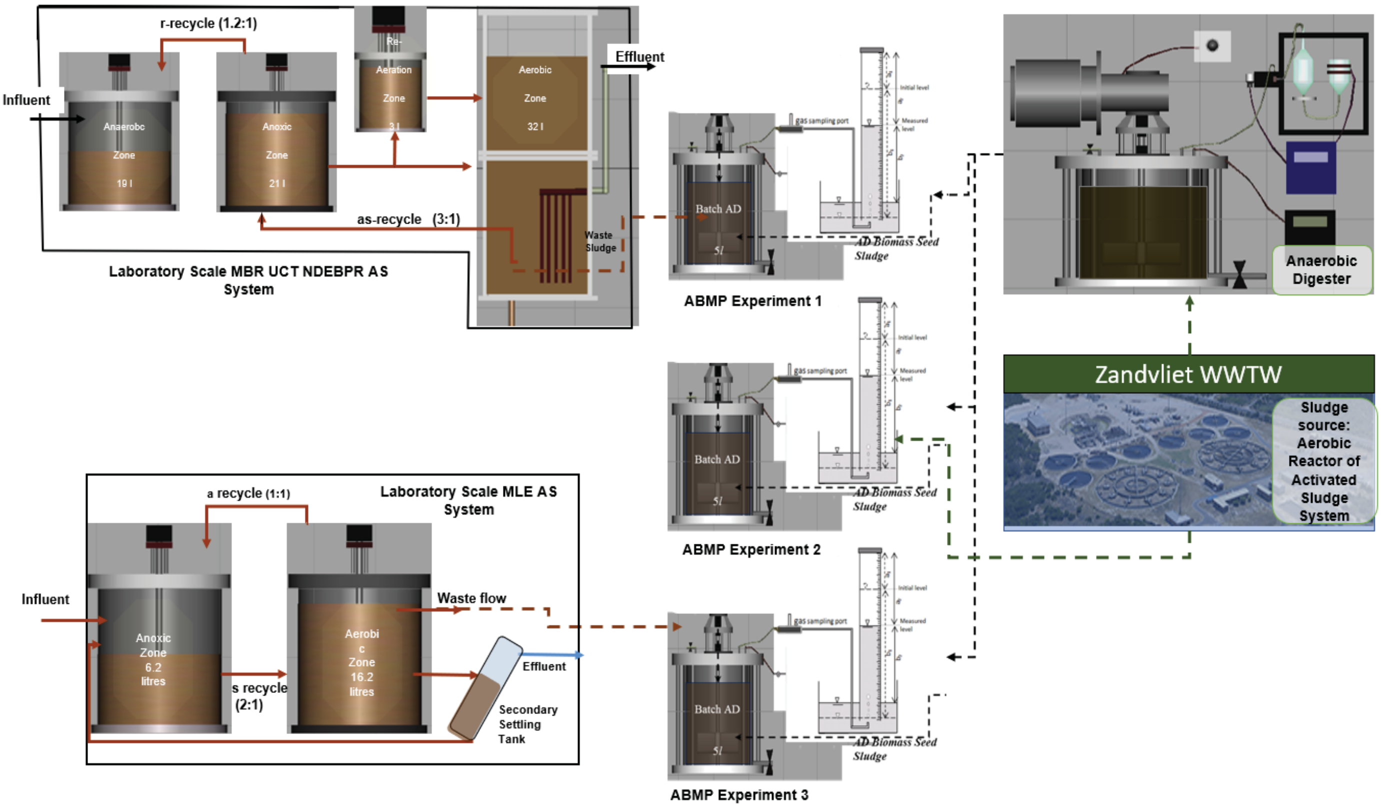

Figure 3.1. Experimental set up used to conduct laboratory investigation

Within the above experimental set up, sampling and testing was planned in consideration of (1) validating PAO biomass elemental composition (including PP components of Mg, K and Ca), (2) determination of the PAO death kinetics in AD and the resultant endogenous mass fraction (3) identifying the stoichiometric pathway and kinetics for the PP release process. This includes determination of the energy budget used by PAOs for PHB uptake and whether this energy is generated prior in the aerobic reactor of the parent AS or in the AD system. As a significant component of this careful experimental work, where conditions of mineral precipitation are likely (i.e. the AD conditions with high concentrations of PAOs) some parameters that are ordinarily not tested required rigorous testing. These included influents (and effluent) pH and alkalinity, ionic conductivity, Mg, K, Ca and for P precipitation, the OP was tested before and after dissolution of precipitates by using perchloric acid (PCA). Further, a novel test method to allow distinguishing between the P in PP, organically bound P and P in precipitates was developed in this project. This novel inorganic solids characterisation procedure is presented in Section 3.5 of this report.

3.2 DETERMINATION OF WAS BIOMASS ELEMENTAL FORMULATION

Parameter estimation (PE) is a process that adjusts the input parameters of a model, by using collected experimental data as an objective for the simulated data. This occurs via the calculation of minimum error towards the identification of the closest match between the simulated model variable components and experimentally measured variables. Therefore, in order to find a substrate (in this case WAS) composition that better fits the observed AD batch experimental data, parameter estimation (PE) was conducted on a virtual AD batch experimental reactor that was simulated using the UCTSDM3P model (Ikumi et al., 2015; Ghoor, 2020). In this case, the parameters that were used as the unknowns were the hydrogen (H), oxygen (O), nitrogen (N) and phosphorus (P) molar fractions of the WAS biodegradable particulate organics (i.e. x, y, z, a and b values of $C_xH_yO_zN_aP_b$; the parameters used to define the elemental composition of the PAO biomass) in the WAS. This procedure is detailed in a previous WRC report (project number K5/2595; Ikumi et al., 2020).

The compositions determined using the parameter estimation procedure, for the biodegradable particulate organics in control sample, the WAS biomass and the unbiodegradable organics are shown in Table 3.1 below.

Table 3.1. Determination of Elemental Composition of WAS

Parameter		Control seed	WAS biomass	WAS unbiodegradable organics
Description in UCTSDM3P model (see below)	.i_$_{\text{C\_Org\_mol\_perC}}$	1.00	1.00	1.00
	.i_$_{\text{H\_Org\_mol\_perC}}$	2.50	1.26	1.40
	.i_$_{\text{O\_Org\_mol\_perC}}$	0.28	0.20	0.40
	.i_$_{\text{N\_Org\_mol\_perC}}$	0.10	0.20	0.20
	.i_$_{\text{P\_Org\_mol\_perC}}$	0.05	0.05	0.02
Resulting component mass fractions	COD/VSS (f_{cv})	2.15	1.73	1.41
	C/VSS (f_c)	0.55	0.58	0.52
	H/VSS (f_h)	0.11	0.06	0.06
	O/VSS (f_o)	0.20	0.15	0.28
	N/VSS (f_n)	0.06	0.13	0.12
	P/VSS (f_p)	0.07	0.07	0.03

Where the i_$_{\text{C\_Org\_mol\_perC}}$, i_$_{\text{H\_Org\_mol\_perC}}$, i_$_{\text{O\_Org\_mol\_perC}}$, i_$_{\text{N\_Org\_mol\_perC}}$, i_$_{\text{P\_Org\_mol\_perC}}$ are the parameter names for the mole ratios of carbon (C) to C, hydrogen (H) to C, oxygen (O) to C, nitrogen (N) to C and phosphorus (P) to C ratios for the biomass organics elemental formula (i.e. the respective x, y, z, a and b values of $C_xH_yO_zN_aP_b$ expressed according to the standard notational framework proposed by Corominas et al. (2010).

The determined elemental compositions for WAS biomass are important input parameters for the WRRF models because they are used to determine the nutrient (N and P) requirement for biomass growth in AS system, hence allow for (i) prediction of possible nutritional deficiency in the feed and also (ii) estimate the quantities of excess nutrients that are available in the bulk liquid following biomass growth. These excess nutrients in AS systems (i.e. excess ammonia and orthophosphates) when exceeding the effluent quality criteria, would require removal via nitrification-denitrification processes and excess biological P removal. Hence, the capacity for nutrient removal can be evaluated for a system, once the biomass quantities have been calculated, in terms of the mass generated form use of sewage organics together with the nutritional requirements for their anabolic (mass-building/ growth) process. Furthermore, for the WAS that is taken through sludge treatment such as AD, the elemental composition needs to be known in order to predict the quantity of nutrients that will be released with the breakdown of biomass during the sludge treatment process. These nutrients when released are known to affect the performance of the AD system. For instance, the release of N organically bound to NH_4^+, results in increased alkalinity, which assists in maintaining the AD pH above 7. Hence if the substrate has a low organically bound N content, there is a chance of system failure due to low system pH, that results in inhibition of the AD methanogenic biomass (Ikumi, 2020).

3.3 DETERMINATION OF THE PAO DEATH KINETICS IN AD AND THE RESULTANT ENDOGENOUS MASS FRACTION

The PAO biomass is known to contain an unbiodegradable portion (known as its endogenous residue) and a biodegradable portion. When the WAS containing PAO biomass is fed to AD systems, its biodegradable portion ultimately gets broken down by the AD biomass into CO_2, methane CH_4 and H_2O. The unbiodegradable endogenous residue will remain unaltered and form part of the AD effluent. The kinetics of death and hydrolysis of PAO biomass can be formulated using saturation kinetics (Ikumi et al., 2014). Saturation kinetics formulation is often used in models to represent the utilization of slowly biodegradable particulate organics (BPO) in activated sludge models (Henze et al., 1995) and hydrolysis of sewage sludge (McCarty, 1974; Ikumi et al., 2014). It includes the growth of acidogenic biomass growth (Z_{AD}; biomass known to exist in AD systems and carry out hydrolysis and fermentation of organics to simpler forms, i.e. fatty acids). Saturation kinetics is based on the quantity of BPO (substrate broken down by Z_{AD}) attached to the organic Z_{AD} active sites, whereby the rate of hydrolysis reaches a maximum at saturation of the active sites of the acidogens. This way saturation kinetics the hydrolysis rate is independent of the bulk liquid residual biodegradable COD concentration (S_{bp}), but rather dependent on the S_{bp} concentration with respect to the acidogenic biomass concentration (Z_{AD}). The saturation kinetic equation used to predict the rate of hydrolysis is given in Equation 3.1 below:

$$r_{HYD} = \left(\frac{k_M \cdot \left(\frac{S_{bp}}{Z_{AD}} \right)}{K_S + \left(\frac{S_{bp}}{Z_{AD}} \right)} \right) \cdot Z_{AD} \qquad [\text{gCOD/ } (l\text{.d})]$$

Where: K_S is the substrate and acidogenic biomass concentration ratio, at which the specific hydrolysis rate is half its upper limit (k_M) at saturation.

[3.1]

The kinetics of hydrolysis for AD of PAO biomass is more important for an AD system fed WAS that will be digested a low sludge age (< 30d). This is because sludge hydrolysis is known to be the rate limiting process in AD of sludge, and hence the COD of sludge hydrolyzed can be directly related to the quantity of biogas that will be generated by the system. This is essential, where the biogas shall be utilized towards energy recovery for the WWTW. For longer sludge ages (>30d), the unbiodegradable fraction of the sludge is more important because most of the biodegradable organics will be utilized by this time.

The determination of the PAO endogenous fraction (i.e. the unbiodegradable portion that remains after PAO death) is important to model both the AS and AD systems. In AD systems, the unbiodegradable portion provides the limit for biomethane potential use of the WAS as substrate. In AS systems, a high endogenous fraction would result in false prediction or reactor volatile solids mass, because the unbiodegradable portion of biomass accumulates in the system with solids retention time. This was one of the main reasons that had initially triggered this investigation; in previous research, it was noted that when the same sewage is fed to two systems (one containing PAO biomass and the other containing no PAOs and only OHOs), the calculated influent unbiodegradable sewage COD fraction ($f_{S'upi}$) was different. To determine the $f_{S'upi}$, a value is entered such that when a comparison is made between the measured and predicted VSS, there is a complete match. Hence for the system that contained PAOs to have a complete match in VSS, but have a wrong $f_{Supi,}$ the model predicted VSS would have to be wrong. According to Ikumi (2011), the uncertainty in the predicted VSS for systems containing PAOs is due to the selected PAO endogenous mass fraction, which initially had not been clearly defined.

The mass balance-based principles, similar to those used by Sötemann et al. (2005) and Ikumi et al. (2015), are adopted here to determine the kinetic constants (k_M and K_S) in the hydrolysis rate equations. The derivation of the Equations used towards determining the KM and Ks values is given in Appendix C.

Table 3.9 shows the saturation kinetic constants for the saturation kinetics hydrolysis constants together with the unbiodegradable COD fraction of the WAS fed to the AD batch tests, for Zandvliet WWTW WAS (i.e. $k_M = 2.51$; $K_S = 4.04$; $f_{SL'up} = 0.51$) and the UCT MBR WAS (i.e. $k_M = 2.64$; $K_S = 9.11$; $f_{SL'up} = 0.28$). Mass components of the UCT MBR WAS, fed to the AD batch tests were calculated in Table 3.2 below and the theoretical the UPO fraction of WAS ($f_{SL'up}$) from determined to be 0.34gCOD/gCOD, using the activated sludge model endogenous fraction values of OHO and PAO ($f_{E\_OHO} = 0.20$; $f_{E\_PAO} = 0.25$ respectively), which is marginally higher than the given 0.28 value. However, according to Table 3.2, the $f_{SL'up}$ of 0.28 would require for the f_{EG} value to be decreased to 0.17gCOD/gCOD.

Table 3.**2**. Estimating the PAO Unbiodegradable fraction in AD systems

	Active OHO	Endogenous OHO	Active PAO	Endogenous PAO	USO	Total
COD concentrations of WAS components	372	163.3	3043.9	278.5	70.1	3927.8
Mass in 2.5 litre WAS fed to AD batch reactor.	930.0	408.3	7609.8	696.3	175.3	9819.5
I UPO mass expected in Effluent at end of AD batch test (Theoretical)	186.0^a	408.3	1902.4^b	696.3	175.3	3192.9
I. Where UPO at end of batch test for Active OHO and PAO are (a) f_{EH} * Active OHO & (b) f_{EG} * Active PAO respectfully. The f_{EH} of 0.2 and f_{EG} of 0.25 from Henze et al. (2008) were applied to get the values of 186gCOD and 1902gCOD respectfully. The endogenous OHO and PAO values were deemed to stay the same without any change due to AD bioprocesses. This results in the UPO mass of 3192.9mgCOD that results in the $f_{SL'up}$ of 0.34gCOD/gCOD.						
II. For a given (measured from the AD batch test) $f_{SL'up}$ value of 0.28 (see Table 3.9) the same procedure as indicated in (I) above (i.e. no change in endogenous mass for OHO and PAO, and maintaining f_{EH} of 0.2) requires for an f_{EH} value of 0.17gCOD/gCOD.						

Figures 3.2 (a), for Zandvliet WWTW WAS, and (b), for UCT MBR WAS, below show a comparison of the experimentally determined and model predicted resulting COD removal plots, for the AD batch reactor at the different time points. The correlation between measured and predicted COD removal would serve as step towards verification of the kinetic constants obtained.

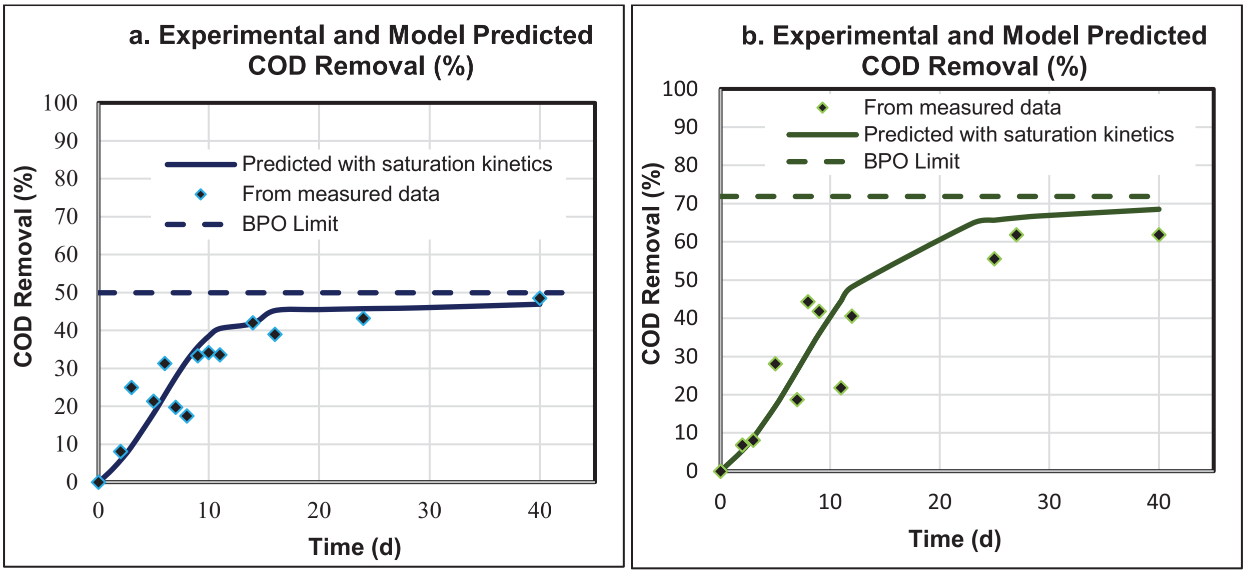

Figure 3.2. Comparison of target COD removal (%; determined from experimental data) with those predicted (calculated from the S_{bp} values predicted using the saturation kinetic hydrolysis constants) for (a) the ZWWTW WAS and (b) the UCT MBR WAS at different solid retention times of the batch AD period.

It can be noted that a reasonably good match is obtained between the experimental and model predicted residual S_{bp} concentrations. Hence, we can adopt these kinetic constants in the AD model used to simulate the AD system fed this same WAS.

3.4 PHOSPHATE RELEASE DURING BATCH- AD OF NDBEPR WAS

Apart from COD removal, the AD batch tests were also useful to observe the rate of AD phosphorus release. For the AD batch tests that was fed the UCT MBR WAS, Ikumi and Ekama (2019) report that there is potential for polyphosphate (PP) breakdown via (i) a similar manner as would have occurred in the anaerobic environment of the parent AS system or (ii) with the ultimate death and breakdown of PAO mass. This PP ($Mg_cK_dCa_ePO_3$) breakdown would result in OP and metals release (Mg^{2+}, K^+ and Ca^{2+}) into the aqueous phase. Consequently, there would be mineral precipitation potential due to the high concentrations of these ions. Mainly, Mg^{2+} and OP would react with NH_4^+ (available from the release of N organically bound in disintegrating WAS biomass) to form struvite ($MgNH_4PO_4.6H_2O$). According to Musvoto et al. (2000), other precipitates that could form include newberryite ($MgHPO_4$), amorphous calcium phosphate ($Ca_3(PO_4)_2$), calcite ($CaCO_3$) and magnesite ($MgCO_3$). A similar method of non-linear regression as was used for the determination of kinetic constants of sludge hydrolysis was used to determine the kinetic constants for polyphosphate release (see Appendix C). Figure 3.3 below shows a comparison of results for PP release from experimentally determined results and those that were model predicted using the derived kinetic constants.

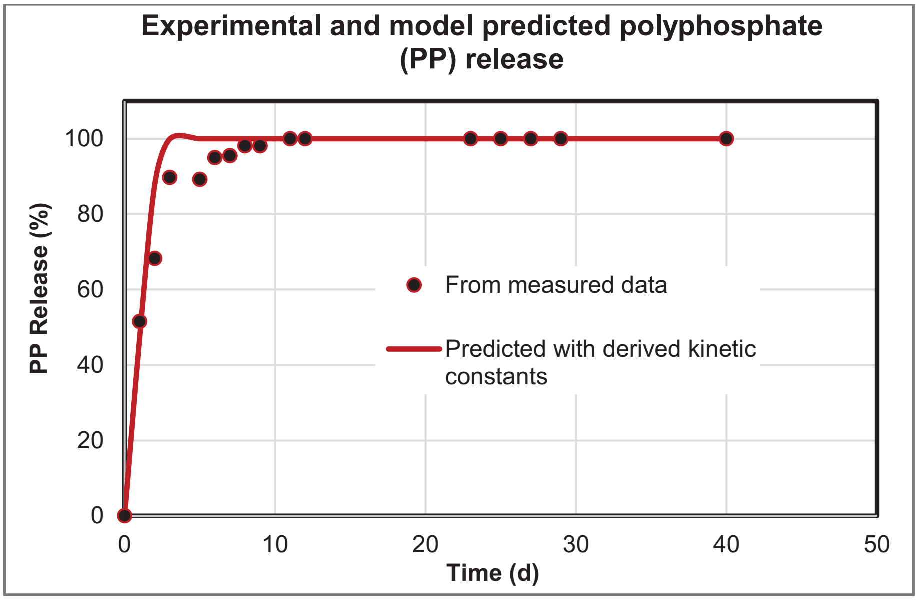

Figure 3.3. Comparison of experimentally determined PP release (%) with those predicted using the derived kinetic constants.

It can be noted that most of the P is released (as ortho-phosphate, OP) within 4 days, after which the P release became more gradual. This conforms to the observation by Jardin and Popel (1994), confirming that stored polyphosphate in PAOs (which forms a large portion of the TP content) is released within seven days. The rapid release of PP in AD environments is usually followed by mineral precipitation. Hence, the PP release kinetic parameters derived here could be useful in dynamic simulation models for EBPR WAS AD as prior parameter values and a more global calibration protocol, that includes the other biological and chemical processes in performed. Harding et al. (2010), when performing a batch test on diluted WAS, containing mixed cultures of OHO and PAO biomass, also confirms that the kinetic model for PP release was able to predict the experimental data when modelled such that most of the PP disintegrates rapidly, with PHA uptake, as would occur in the anaerobic phase of the AS system.

The accurate prediction of PP release is important to determine the concentration of excess metals (Mg^{2+}, K^+ and Ca^{2+}) and OP that would be present in the AD mixed liquor. As noted above, these components would later participate in mineral precipitation and significantly influence the system weak acid/base chemistry, including the predicted pH and associated system health.

3.5 DEVELOPMENT OF A NOVEL INORGANIC SOLIDS CHARACTERISATION PROCEDURE

When modelling WWTP unit operations, there has generally been a greater focus on the organic fraction of sewage or sludge as compared to the inorganic fraction. Consequentially, the development of laboratory tests has been concentrated on the organic portion of the sewage or sludge. Comparatively, there is significantly much less tests developed that yields information about the inorganic fraction of sewage or sludge. Up to now, only the total tests yield information about the lumped mass of the inorganic solids (APHA, 1985; Ekama and Wentzel 2004). When modelling organic or nitrogen removal systems, this lack of information on inorganic solids does not impact on the accuracy of the outputs from the model. This is primarily because the inorganic mass comes mainly from sediments which are inert. On the other hand, in biological phosphorus recovery system such as an excess biological P removal (EBPR) AS reactors followed by AD or AAD, additional forms of inorganic solids such as mineral precipitates or PP phosphate exist. As opposed to sediments, both compounds can affect the processes occurring in the WWTP units. For instance, when modelling AS EBPR, it is assumed that phosphorus removal is due to biomass and PP phosphate (PP) production. However, it is also possible that P is removed via mineral precipitate (especially in membrane reactors) and thus the PP content of PAOs would be incorrect. Further, as proposed by Ikumi and Ekama (2019), underpredicted pH in AD models could be a result of mineral precipitates that are unaccounted for in the AD influent. Thus, in biological nutrient removal systems, it becomes critical to gather more information on the inorganics solids in the sewage or sludge to accurately calibrate the models. With regards to modelling, two parameters are relevant: individual composition (i.e. the empirical formulae of the inorganic compound where relevant) and concentrations of the different inorganic solid components. Although the inorganic suspended solids (ISS) test procedure (APHA, 1985) yields the lumped concentration of the inorganic solids, it does not yield information on the separate composition or concentration of the abovementioned inorganic solids.

Since there is currently no experimental test or procedure that allows for distinguished inorganic’s component composition and concentration, an ancillary aspect of this research project was to attempt the development of such a procedure. The proposed procedure involved the development of a laboratory test method together a with data data-driven modelling approach for analysis of inorganic solids, towards their comprehensive characterisation in sewage or sludge. A sequence of logical steps was followed towards the development of this ISS characterization procedure. This included the application of the a modified cold PCA fractionation procedure (MCPFP) of De Haas et al. (2000) and augmenting it to include other analytical measurements that result in full characterization of inorganic solids into their component concentrations. The results from this augmented MCPFP are rigorously analysed using a data modelling procedure to broadly fractionate EBPR sludge-P content into mineral precipitate-P and polyphosphate-P. The details regarding this augmented MCPFP test and the data modelling procedure are given in Appendix C.

CHAPTER 4: MODEL IMPLEMENTATION

The development and implementation of plantwide models was a key component of this project. The University of Cape Town Water Research Group has opted to develop both steady state and dynamic models in parallel. The steady-state models are useful for design of wastewater treatment plants (WWTPs) because they contain explicit equations that calculate the sizing of reactors, required interconnecting system flows, and other design parameters (e.g. sludge age, reactor mass fractions and oxygen requirement) using the influent characteristics and required system performance criteria (e.g. effluent quality). With the system already sized, dynamic models can be applied refining of design and determination of optimized operation protocol by simulating the system for changing flows and loads. Dynamic models are complex models that use varying flows and loads to evaluate the time-dependent response of the plant due to dynamic loading conditions (Ekama and Wentzel, 2008a).

4.1 OVERVIEW OF THE UCT PLANTWIDE STEADY STATE MODEL

The University of Cape Town-based research group developed a plantwide steady state model that uses mass balanced steady state stoichiometry to track the COD, C, H, O, N masses and charge along the activated sludge (AS) organics degradation, nitrification and denitrification (ND) and anaerobic (AD) and aerobic (AerD) digestion of wastewater sludge of the entire WWTP (Henze et al., 2008; Ekama et al., 2009; Ekama et al., 2011). This was done by assigning a stoichiometric composition (x, y, z, and a in $C_xH_yO_zN_a$) to each of the five main influent wastewater organic fractions, i.e. (i) influent volatile fatty acids (VFA, assumed to be acetic acid), (ii) fermentable readily biodegradable soluble organics (F-BSO), (iii) unbiodegradable soluble organics (USO), (iv) slowly biodegradable particulate organics (BPO) and (v) unbiodegradable particulate organics (UPO), the influent free and saline ammonia (FSA) and the activated sludge (AS) and anaerobic digester (AD) biomass, and determining the products formed from them using the mass balanced stoichiometries. The plantwide steady state model of has been getting refined as new information on the wastewater treatment process modelling becomes available. Further, the plantwide steady state model is being continuously structured into engineering tools that would be applicable by various stakeholder levels for decision making on design and operation of wastewater treatment systems. Contrary to complex dynamic simulation models, simple steady state models assume most of the processes at steady state to have achieved completion. The processes deemed not to have reached completion are then either simplified or retained as rate limiting (when the processes are slowest and dictate the sizing requirements of the system, e.g. sludge hydrolysis in AD and nitrification in AS systems). Although this makes steady state models much simpler than dynamic simulations ones (which contain sets of simultaneous equations that run at different rates), the steady state models have been noted to provide similar results to the complex dynamic models, when simulated at steady state. Steady-state models are therefore known to be complementary to dynamic simulation models for enhancement and reliability of their use through pre-processing the inputs needed for dynamic simulation models. Apart from being simpler than dynamic models, the steady state models can be programmed into spreadsheets which are widely accessible.

4.2 OVERVIEW OF THE PLANTWIDE DYNAMIC MODEL OF SOUTH AFRICA (PWM_SA)

The carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P) and chemical oxygen demand (COD) mass balanced three-phase plant-wide model (PWM_SA, Ikumi et al., 2015) combines biological N and P removal activated sludge based on ASM2d (Henze et al., 1995), AD of primary sludge and AD or anoxic-aerobic digestion (AAD) of WAS with interlinking non-reactive physical thickening unit operations. The properties of the model include: (i) It defines influent wastewater organics concentrations in the same seven types as in municipal wastewater [volatile fatty acids (VFA), biodegradable soluble (BSO) and particulate (BPO) organics, unbiodegradable soluble (USO) and particulate (UPO) organics, where the particulate organics are subdivided into settleable and non-settleable, in the generic form $C_xH_yO_zN_aP_bS_c$. Further, it uses the routinely measured parameters COD, VSS, OrgN (which equals total Kjeldahl nitrogen (TKN) – free and saline ammonia (FSA)) and OrgP (which equals Total P (TP) – Ortho P (OP)) to quantify the x, y, z a, b, c values, but because the TOC is not routinely measured, the C composition of the organics is obtained from assumed C/VSS mass ratios (f_C). (ii) It is full element (C, H, O, N, P and S) mass balanced. (iii) It has an external algebraic equation equilibrium speciation sub-routine which separates the slow (biological and physico-chemical) and fast (aqueous) processes, (iv) It includes non-ideal aqueous solution effects (ionic strength correction of dissociation constant (pK) values and ion pairing) to calculate the pH and relevant gas partial pressures, (v) It includes the interaction of mineral precipitation on the pH of the aqueous phase due to the release of phosphates, ammonia and inorganic carbon species in the AD or AAD systems. These features of the PWM_SA model are global (plant-wide) and so are also included in its primary sedimentation tank (PST; with the UCTPSU submodel of Polorigni et al., 2020), activated sludge (AS; with the ASM2-3P submodel of Ikumi et al., 2020), anoxic-aerobic digestion (AAD; also using UCT ASM2-3P) and anaerobic digestion (AD; using UCT SDM3P of Ikumi et al., 2014) sub-models. A brief overview of the sub models that form PWM_SA model is given below.

- The UCTPSU dynamic model was developed as an extension of a current TSS-based model (Bachis et al., 2015), within PWM_SA. This is a data-driven model that includes the particle settling velocity distribution (PSVD) concept of Maruejouls et al. (2012) and fractionates the settling solids into correct portions of UPO, BPO and ISS (Wentzel et al., 2006; Ikumi et al., 2014). Matesun et al. (2021) provides that detail towards the data driven approach to application of the UCTPSU model.
- A three phase activated sludge dynamic model (ASM2-3P) was developed by adding full element (carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P) and metals (Me)) mass balanced stoichiometry to extending the existing nitrification-denitrification (ND) excess biological P removal (EBPR) activated sludge (AS) model ASM2 (Henze et al., 1995) and ensuring (i) its compatibility with the three-phase anaerobic digestion dynamic model and (ii) its equivalence to the full element mass balanced stoichiometry ASM dynamic model (without P) of Sötemann et al. (2005c). This three-phase activated sludge model with EBPR was applied to plant-wide simulation of NDEBPR activated sludge with anoxic-aerobic digestion of concentrated P-rich waste activated sludge with mineral precipitation to produce dewatering liquor with low nitrogen and phosphorus.
- The dynamic anaerobic digestion model (SDM-3P) was developed by extending the two-phase (aqueous-gas) dynamic anaerobic digestion model for PS and ND activated sludge system WAS by Sötemann et al. (2005b), to include phosphorus from NDEBPR WAS, multiple organic types and three-phase (aqueous-gas-solid) mixed weak acid/base chemistry for multiple mineral precipitation. Ghoor (2020) then adjusted the SDM3P model kinetics to ensure predictive capacity for simulating AD failure, AD start-up conditions and upflow anaerobic sludge bed (UASB) reactors (which have temporary failure conditions at the bottom of the bed). This was accomplished by means of calibrating the AD model to an UASB dataset wherein temporary failure conditions are present in the bottom of the reactor, evident by the presence of the intermediate AD reaction products. The calibrated parameters included the maximum specific growth rates and the half saturation coefficients for the four AD biomass groups. Further, the CO_2 evolution kinetics were adjusted from being always at equilibrium (for steady state scenarios) to rate-controlled (with a better representation of system dynamics).

Due to the significant increase in size and complexity to model wastewater treatment plants, as plant-wide configurations, in three phases, the PWM_SA model was coded in WEST®, which is a program capable of simulating many bioprocesses in various unit operations assembled into a WRRF. As noted above, the various sub models (UCTPSU, ASM2-3P and SDM3P) share the same set of components – i.e. the supermodel approach of Volcke et al., 2006 was adopted. This has the advantage of (i) placing the physico-chemical states globally and linking the biological components between the AS, AAD and AD parts of the model, (ii) including parameterized stoichiometry (the x,y,z,a,b,c values of the influent organics groups and biomass species), for the bioprocesses and share the same ionic speciation, and as a result (iii) the output components of the PST and AS part become directly the input components for the AAD or AD parts without the need for transformation equations. In general, the simulations of the different chemical and biochemical processes in PWM_SA are based on determining the materials present at a particular location and time (mass balancing) and determining the physical state that it will take on at that point (speciation) (Brouckaert et al., 2010, 2016).

To ensure that the extended model goes through rigorous evaluation process, the BIOMATH protocol of Vanrolleghem et al. (2003), was applied by Ikumi (2020) for the current PWM_SA model.

4.2.1 Extension of AD Model to Include PAO and Polyphosphate (PP) Breakdown

During AD treatment of waste sludge (containing PAOs) from the aerobic reactor of the AS system the question arises: are the PAOs capable of carrying out the same P-release mechanisms in the AD as in the anaerobic reactor of the NDEBPR AS system? Essentially, microorganisms are assumed incapable of planning their actions based on a WWTP system configuration and are expected to act according to the capabilities afforded to them by their surrounding environmental conditions. Thus, PAOs containing polyphosphate (PP) sent into an anaerobic digester with volatile fatty acids (VFAs) present, would utilize their PP reserves as they would in the anaerobic zone of an AS process. In the anaerobic zone, the PAOs would break down their internally stored PP chains in a process of generating energy to carry out the conversion of readily biodegradable organics to poly-hydroxy-butyrate (PHB; energy rich organic compounds that are internally stored by PAOs). This suggests that there is some potential for energy transfer from the AS to the AD via PP when WAS containing PAOs is treated in AD systems. However, the quantity of PP used as an energy source is known to vary according to the balance between energy generation and consumption in the cell (Smolders et al., 1995; Mino et al., 1994), a mechanism that is linked to the system pH – Smolders et al. (1995) observed changing P/acetate ratio (0.25 to 0.75) for varying pH ranges (5.5 to 8.5) (Ikumi and Ekama, 2019).

After anaerobic P release (with breakdown of PP) and PHB uptake, the PAOs require a terminal electron acceptor (oxygen, usually supplied in the aerobic reactor of AS system) to utilise this PHB for growth and energy generation metabolism. However, oxygen is not available in AD and, in this case, the PAOs continue to release over time all remaining stored PP and PHB. From anaerobic batch tests on the NDEBPR WAS, Harding et al. (2010) noted that it took 5 to 8 days to release practically all the PP under anaerobic conditions. Whether this is faster than the death rate of the PAOs in the AD is uncertain, but it is significantly faster than AS biomass hydrolysis rate in the AD. Therefore, in the AD, both the PP release with PHB formation (as in the anaerobic reactor of the NDEBPR system) and PP release with the eventual death of PAOs takes place. A generalised a generalised stoichiometry to model the release of PP, with the uptake of acetate (HAc), in the AD system, together with the final PP release with the death of PAOs was added as an extension to the UCT plantwide steady state model and dynamic model (i.e. PWM_SA). The kinetics of these processes for PAO death and PP were calibrated against the experimentally generated data (see Sections 3.3 and 3.4).

4.2.2 The Inclusion of a Chemical Phosphorus Removal Model

As an extension of this ASM2-3P, the model sludge (ISS) production and P removal [$(FeOH)_3$ and $FePO_4$] model of Solon (2017) was included using WEST®. The model was essentially the same as for Solon (2017), with appropriate unit conversions (from molar to mass) in the stoichiometry as was done by Ikumi (2011) in order to ensure its compatibility with the PWM_SA model. Water and protons (H^+) were also included in the stoichiometry to allow for checking the mass balances of hydrogen (H) and oxygen (O) together with that of iron (Fe) and phosphorus (P). This extended ASM2-3P model was calibrated against De Haas (1990) full-scale observations.

4.2.3 The Inclusion of a Chemical Phosphorus Removal Model

As a further extension to the UCT plantwide model, a complete dynamic simulation model for balancing tanks was developed to ensure optimal equalisation of influent flow into wastewater treatment plants (WWTPs) regardless of volume size. As was done with other systemwide model components, this model was developed using two platforms (the simpler one in Ms Excel (Visual basics), VBA and the complex version in WEST® by DHI). Dold (1982) was be used as the main source of background knowledge for the development of this model. The developed model was made compatible with the University of Cape Town (UCT) plant wide model, to ensure that the UCT plant wide model has a model of a complete wastewater treatment system.

From the work of Dold (1982) it can be observed that research into equalization tanks has slowed down due to the poor assessment of their impact on the performance of different processes in WWTPs. It can equally be noted that in South Africa, the implementation of in-plant control cannot yield adequate results, as it requires highly skilled operators and a consistence maintenance of monitoring equipment, due to the variability of daily influent flow and South African operators do not have a great deal of experience, and the technical infrastructure needed to regularly maintain equipment is not available in rural WWTPs and some urban WWTPs. In addition, Dold (1982) points out that even if in-plant control were feasible, it is not as effective as operating the plant under constant inputs.

4.3 THE DEVELOPMENT OF SYSTEM-WIDE PERFORMANCE INDICES FRAMEWORK

Numerous wastewater treatment technologies are available to meet almost any effluent quality regulation. However, the obstacle to meeting the requirements remains the cost of the treatment processes. As effluent quality required become higher, the costs to meet these requirements escalate (Vanrolleghem et al., 1996). Cost-efficiency of WWTPs are generally dependent on the process choices and dimensioning (Benedetti, Bixio & Vanrolleghem, 2006). Studying the various possible process/control choices that can be implemented at WWTPs allows the investigation of their potential financial benefits while mitigating negative environmental impact (De Ketele et al., 2018). Assessment of these control strategies can be done using the evaluative performance indices adopted by the international water association (IWA) benchmark simulation modelling (BSM) task group (Jeppsson et al., 2007). A multi-criteria analysis of the control strategies was implemented in the form of effluent quality and operational cost indices (EQI and OCI) as described by Nopens et al. (2010) and De Ketele et al. (2018). Evaluation criteria is an effective way to assess trade-offs between control strategies to enhance energy recovery efficiencies as well as to potentially reduce effluent limit violation and plant costs. Implementing control strategies are useful to aid decision making processes when evaluating the efficiency of a WWTP, with the aim to define the best plant layout of the future

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The development of performance indices that can be used to evaluate entire systems was done by modifying the existing EQI & OCI adopted by the IWA BSM group (Jeppsson et al., 2007) in line with the concept of WWRFs. The modified performance indices should therefore incorporate the fate of WRRFs products, hence include a broader consideration of environmental impact and resource recovery.

4.3.1 Effluent quality index (EQI)

The EQI is a means of methodically describing the effluent quality at a WRRF. It quantifies the pollution load to a receiving water body into a single term by applying weighting factors (known as the β value) to the pollutants based on their relative environmental impact (Copp, 2002; Jeppsson et al., 2007). De Ketele et al. (2018) modified the EQI formulation such that, the pollutant weighting factor can be determined based on site-specific regulations with regards to effluent emission limits. These weighting factors are calculated using the COD emission limit as a reference point. The weighting factor for COD is thus always equal to 1 while the weighting factor for ortho-phosphates (OP), for instance, is the ratio of the COD emission limit to the OP emission limit. The new weighting factors used by De Ketele et al. (2018) are based on the Water Act No. 54 of 1956 Regulation No. 991 NWA (1984). With the formula set up in this format, when a pollutant is above the emission limit, its component (i.e. β*(Limit – pollutant(t)) in the formula will be negative. In the case where the effluent concentration is within the limit, the component in the formula will be positive. Since each pollutant is independent of each other, there is a possibility that some terms cancel each other out. It is therefore required that the negative terms and positive terms are grouped separately into EQI negative and EQI positive. An EQI negative of zero implies that the regulatory limits have not been exceeded by any of the pollutants (acceptable effluent). Improvement in effluent quality is translated to an increase in the EQI positive value. This is because the better the effluent quality, the lower the pollutant concentration and hence, the larger the difference between the limiting concentration and the actual concentration becomes. Conversely, an EQI positive of zero would imply that the concentration of pollutants in the effluent have all exceeded their respective regulatory limits (EQI negative <0). If EQI positive and EQI negative are both not zero, it means that the regulatory emission limit for at least one pollutant has been exceeded. Analysis of the data can then help identifying the pollutant above the discharge limit. When striving for better effluent quality, the emphasis should be to reduce the value of EQI negative to as close to zero as possible (De Ketele et al. (2018).

4.3.1.1 *Modification of the existing EQI*

Existing EQI used in simulation models only evaluate the impact of treated effluent on water bodies. The new EQI (Equation 4.1) is formulated by modifying the existing one used by De Ketele et al. (2018) through including two additional EQI, evaluating the impact on land and on the atmosphere respectively, were devised.

- First the EQI as used in the BSM2 (Jeppsson et al., 2007) was extended to include all pollutants according to South African effluent discharge limit – i.e. based on the National Water Act (NWA; 1984). Similar to the approach taken by De Ketele et al. (2018), the weighting factors assigned to each pollutant were based on its impact on the environment relative to COD.
- Secondly, an expression for EQI_{gas} specific to the impact of wastewater treatment processes on the atmosphere was formulated. This expression included greenhouse gases that evolve from WWTPs such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The weighting factors assigned to each gas were set equal to their respective global warming potentials – a measure of the amount of heat greenhouse gases trap relative to CO_2 (EPA, 2017).
- Lastly, an expression for EQI_{sludge} specific to the impact of sludge disposal on land was formulated. The pollutant class for South African wastewater sludges (Snyman & Herselman, 2006) were used as a basis for this EQI. Weightings for each pollutant were based on the relative pollutant limits.

Hence the final EQI formulation has three components as shown in Equation 4.1 below:

$$\mathrm{EQI} = \mathrm{EQI}_{\mathrm{water}} + \mathrm{EQI}_{\mathrm{gas}} + \mathrm{EQI}_{\mathrm{sludge}} \tag{4.1}$$

The detailed breakdown for each component of the EQI formulation is provided in the Appendix D.

4.3.2 Operational Cost Index (OCI)

Design and operation cost analysis of WWTPs is performed using OCI, which includes cost factors pertaining to operation and potential savings that could be realised through strategic plant design or control operations. The OCI gives an overview of the variables that have the most substantial impact on the total costs at WWTPs.

Originally, only 3 criteria were used to assess the costs at WWTPs in the BSM1-sludge production, aeration energy and pumping energy (Copp, 2002). However, with the development of the BSM2, more variables were considered when evaluating cost, pertaining to the new unit processes added to the model. To achieve uniformity in the units, De Ketele et al. (2018) modified the formula into 3 categories: energy cost, sludge disposal cost and carbon cost. These costs are naturally country or region dependent. For instance, the unit energy cost will depend on the tariff set by the local authorities.

4.3.2.1 *Modification of existing OCI*

The new OCI is formulated by modifying the existing one used by De Ketele et al. (2018) through inclusion of operating cost factors and potential savings arising from the implementation of WRRF design or control operating strategies (Equation 4.2).

Recovery of resources, for instance struvite or calcium phosphate, are incorporated into the OCI as a benefit in terms of tangible costs. Additionally, any operational cost incurred related to side stream nutrient recovery are now included in the OCI. For instance, precipitation of struvite requires dosing lime to maintain pH and may also require dosing magnesium.

$$OCI = (AE + PE - MP + ME + HE) \cdot Energy\ cost + SP \cdot Sludge\ disposal\ cost + EC \cdot Carbon\ cost + Metals\ dosed \cdot Metal\ cost + Lime\ dosed \cdot Lime\ cost - NR \cdot Market\ price + Fines \quad [4.2]$$

Where:

AE	: Aeration energy (kWh/d)
PE	: Pumping energy (kWh/d)
SP	: Sludge produced (kgTSS/d)
EC	: External carbon addition (kgCOD/d)
ME	: Mixing energy (kWh/d)
MP	: Energy from methane produced (kWh/d)
HE	: Total heat energy required by anaerobic digester for sludge treatment (kWh/d)
NR	: Nutrient recovered; e.g. Struvite (kg/d)

Furthermore, to ensure that effluent quality is not compromised for lower operating costs while aiming to achieve optimal design and operation of WWTP, effluent violation charges are included in the OCI. Once a "unit fine" is decided, the total fines incurred is calculated as the product of the unit fine and the $EQI_{negative}$. The latter, as described by using the approach described by De Ketele et al. (2018), disregards all non-negative terms in Equation 4.3 below. As a result, the only terms left in the formula are pollutants that have exceeded the regulatory effluent limit. Therefore, as the pollutants are all standardised by application of weighting factors, the product of unit fine and EQI negative gives the total fine. This method of calculating fines is similar to the approach used in Flanders (Vanrolleghem et al., 1996).

$$Fines = Unit\ fine \times EQI_{negative} \quad [4.3]$$

4.4 CLOSURE

The updated model is capable to simulate P removal both via the biological processes (EBPR) and chemically (via addition of ferric sulphate). Further, the sludge generated could be virtually tracked in AD systems (where WAS is fed to the AD) to predict the AD system performance (including effluent quality, system pH and biogas generation). These were necessary extensions to the WRRF models to allow for prediction of the products that could potentially be generated by nutrient removal systems, which is later required towards rigorous evaluation of system design or operation strategy. Further, extending the plantwide model, such that it can be used for the control of equalization tank enables significantly less variable input of flows and consequentially load, but also ease operations and reduce operational cost, as the oxygen provided will not fluctuate as much, and if a new WWTP is to be designed, the capital cost will be lower, as the unit processes will not have to be built for peak weather flow conditions. Finally, an evaluation framework that includes the fate of products generated from the WWTP has also been included in the extended model. This will be useful, to allow for evaluative calculations to be performed for every simulation, such that design or operational strategies could be directly compared using the extended model. The application of this model towards a full scale South African wastewater treatment system is showcased in the following Chapter 5.

CHAPTER 5: FULL SCALE CASE STUDY SCENARIO EVALUATION

The PWM_SA model, extended to include the systemwide evaluation framework was used to carry out scenario analyses for full scale system case studies. In this project various such studies were performed on different full-scale systems, including (i) Waterval WWTW (Coothen, 2022), (ii) Cape Flats WWTW (Darries, 2022), (iii) Zeekoegat WWTW (Molefe, 2022) and (iv) Bellville WWTW (Nqayi, 2022). The details of these studies can be found in the thesis for the students that carried out the individual projects. In this chapter we shall showcase the study performed on Bellville WWTW, which is located in Western Cape province, South Africa.

For all case studies, the results obtained from explicit steady state model equations using MS Excel were compared with the dynamic model (PWM_SA) predictions. It was noted that the steady state MS Excel model predictions matched very well with the dynamic plant-wide model in WEST®. Once the confidence was achieved, then the plant wide model together with performance indices (PIs) were used to evaluate the scenarios considered during the full scale WWTW case studies. Simulation and evaluation of proposed operational strategies was done using the performance indices (PI's: operational cost index (OCI) and effluent quality index (EQI)) presented in Section 4.3.

5.1 BELLVILLE WWTW CASE STUDY

The Bellville WWTW, situated in Sacks Circle Bellville South Industrial, first became operational in 1951. It consisted of a conventional biological filtration works with maturation ponds. The WWTP was later modified for the anaerobic treatment of industrial wastewater with the commissioning of the Orbal (oxidation ditches) plant and secondary sedimentation in 1968.

With the development and growth of the Bellville area, an additional diffused aeration (DA) activated sludge plant, consisting of 2 basins and 4 secondary settling tanks (SSTs), was commissioned in 1979. A third basin and 2 SSTs were added to the WWTW in 1989, after which the old biological filtration works was decommissioned. The capacity of the WWTW was further extended in 2014 with the commissioning of a novel membrane bioreactor (MBR) plant, the second largest MBR plant in Africa. The latest changes to the WWTW include the decommissioning of the Orbal plant and subsequent addition of 3 primary settling tanks (PSTs) and 4 Howden blowers for the diffused aeration plant with an MLE bio-reactor, to improve the organic and hydraulic capacity of the existing DA plant as well as aeration challenges. The addition of the PSTs includes the handling of primary sludge. The 3 PSTs and 2 primary sludge dewatering system were commissioned in 2020. The Bellville WWTW receives wastewater from both municipal and industrial sources. The DA plant (including the PSTs) can treat an Average Dry Weather Flow (ADWF) of 60 Ml/d of domestic and industrial wastewater together with leachate from the adjacent Bellville landfill site. The MBR plant is designed to treat 20 Ml/d of domestic wastewater. This brings the total capacity of the Bellville WWTW to 80 Ml/d ADWF. The WWTW is fed by 4 pump stations, i.e. Rietvlei, Sarepta, Nooiensfontein and Hardekraaltjie, as well as gravitational flow. The catchment area comprises: Bellville; Durbanville; Kuils River and Brackenfell. The population served by Bellville WWTW is currently not known with no recent updated data. The treated effluent is used for industrial clients, reuse on site, or matured before UV/chlorine disinfection and discharged into the nearby Kuils River. Figure 5.1 below depicts the process configuration of the Bellville WWTW.

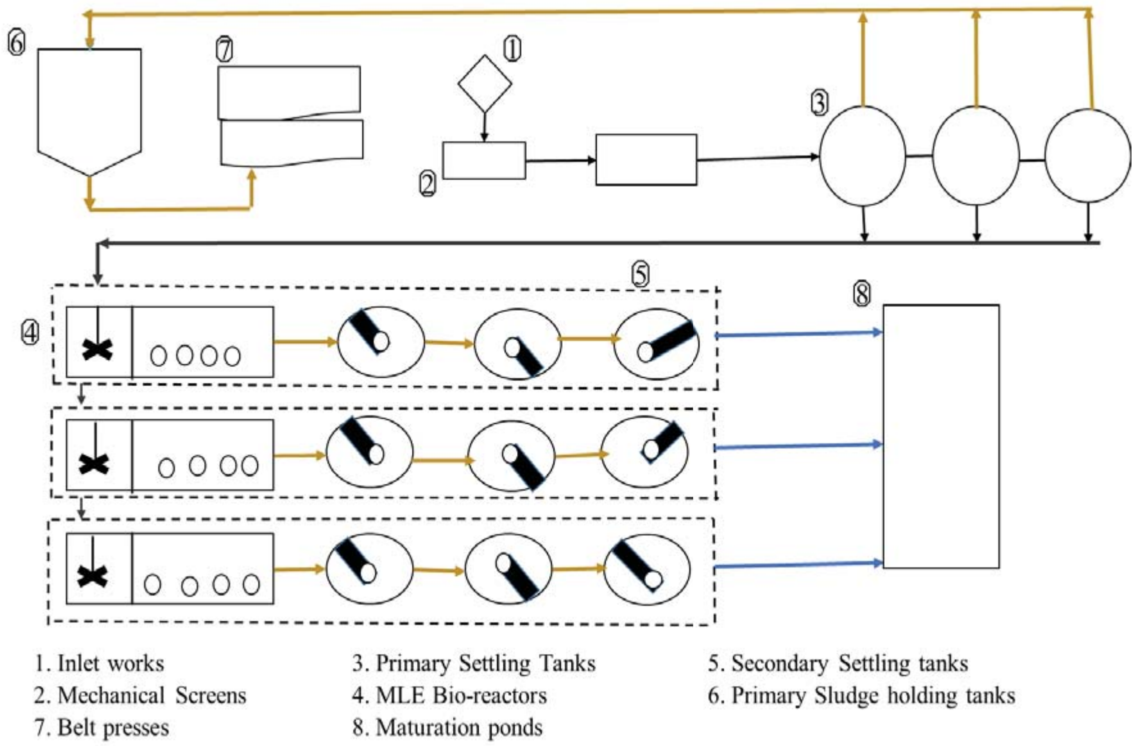

Figure 5.1. Process Configuration for Bellville WWTW

5.2 SCENARIO ANALYSIS FOR PHOSPHORUS REMOVAL AT BELLVILLE WWTW

In Bellville WWTP biological phosphorus (P) removal is a challenge due to the current design of the MLE reactor that does not account for Phosphorus removal. The solids retention time (SRT) is difficult to control as the wasting is done directly from the return activated sludge (RAS). Phase 2 of the upgrade of the plant is changing of the MLE reactor into a UCT reactor to in order achieve biological P-removal. In order for this to be achieved, a modification in the aerobic zone is done to include an anaerobic zone. The sludge wasting line is now changed to maintain the SRT and waste directly from the activated sludge zone of the reactor. The extended PWM_SA model, described in Chapter 4, was tailored to suit the design and operational conditions for one of the DA modules of Bellville WWTW. These initial simulations were used as reference simulations, after which, two identified design and operational strategies used to deal with future upgrades towards P removal in the system were simulated. Hence to showcase the application of the extended PWM_SA model, three configurations were simulated for the Bellville WWTW. These include:

1. Reference Layout (Ref): Modified Ludzack Ettinger (MLE) activated sludge (AS) system. Sludge generated is thickened and disposed. Since all three modules of the DA plant were similar, only one module was simulated.

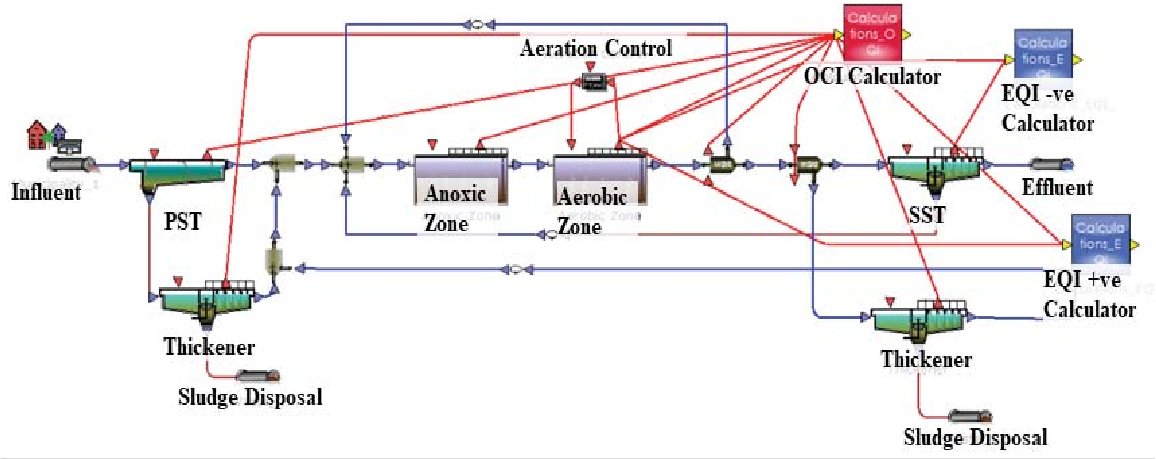

Figure 5.2. Depiction of simulated reference layout (Ref) for Bellville WWTW

2. ***Scenario 1 (Scen_1):*** MLE AS system with ferric sulphate dosing before the SST for Chemical P Removal. Sludge generated is thickened and disposed. 1568.8kg/d of $Fe_2(SO_4)_3$ is dosed before the entrance to the SST.

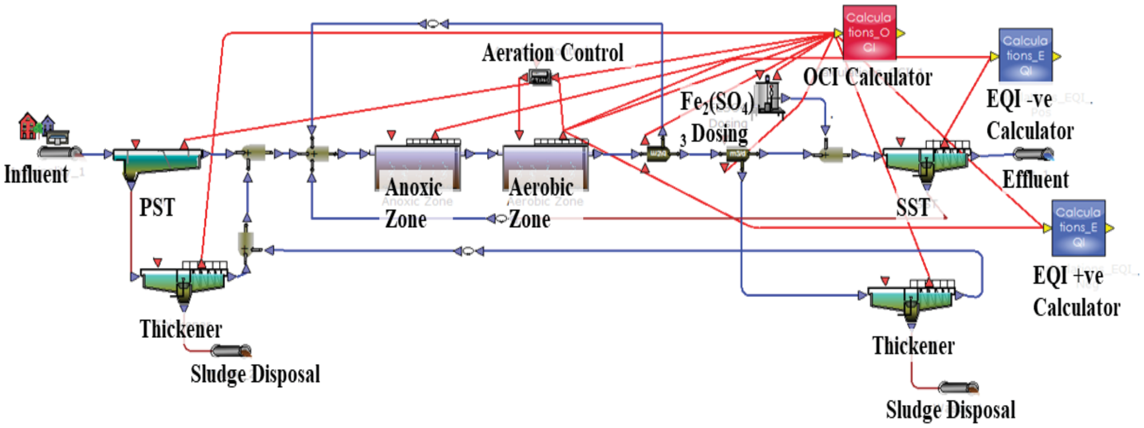

Figure 5.3. Depiction of simulated scenario 1 for P removal in Bellville WWTW

3. ***Scenario 2 (Scen_2):*** University of Cape Town (UCT) configured nitrification-denitrification, excess biological P removal (NDEBPR) AS system. The sludge is treated using AD (1000 m^3 Vol) and 147.4 kg/d Magnesium hydroxide (mg(OH$_2$) is dosed prior to dewatering to encourage struvite ($MgNH_4PO_4$) precipitation. The resulting thickened sludge is given to farmers for use in growing animal fodder.

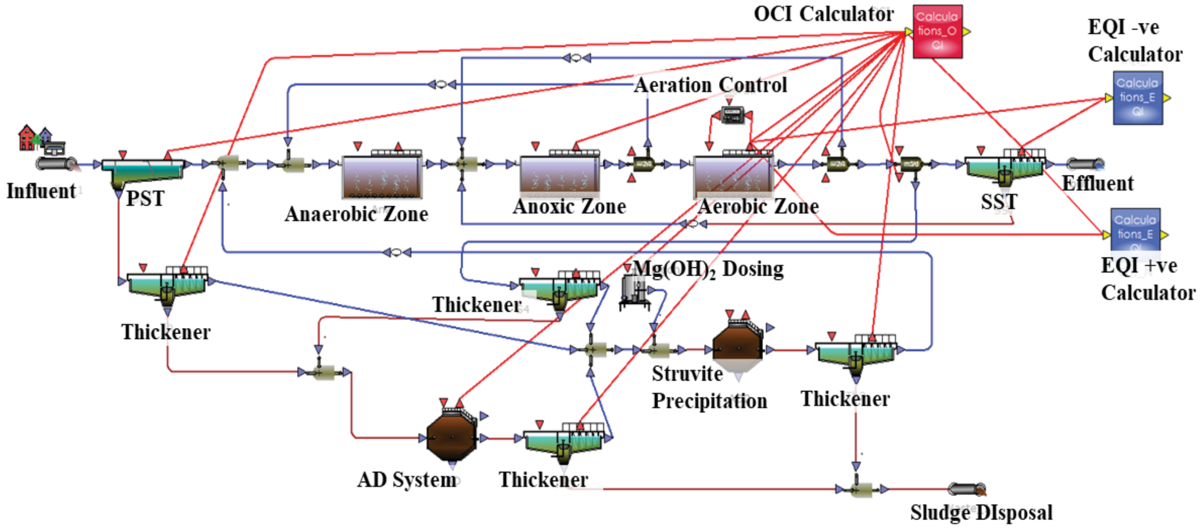

Figure 5.4. Depiction of simulated scenario 2 for P removal in Bellville WWTW

5.2.1 RESULTS AND DISCUSSION

Figure 5.5 (a to e) below show the comparison of AS system results for the three scenarios described above. It can be noted that both scenarios 1 and 2 have higher total solids concentration than that for the reference configuration, with the highest at scenario 2. The extra inorganic solids (ISS) in scenario 1 comprise of chemically precipitated sludge, containing the $FePO_4$, while the extra ISS in scenario 2 comprise the polyphosphate chains of the PAOs (which precipitate as ISS during the drying stage of the ISS test). Hence, in both scenario 1 and 2, the excess P is converted into an inorganic solid phase, resulting in lower effluent P concentrations as shown in Figure 5.5 (f). The volatile suspended solids (VSS) for scenario 1 is the same as that for the reference configuration because the chemical P removal is deemed not to have significant influence on the biomass growth and only impacts the inorganics in the system. However, scenario 2 has a higher VSS than the reference configuration – the component contributors to total VSS can have been shown in Figure 5.5 (b), where the inert organics (X_I) are the same for all three scenarios (because the same system volume and sludge age is maintained), but for scenario 2, the endogenous residue concentration (X_E) is lower, while the PAO (X_{BG}) concentration is much higher and the OHO (X_{BH}) concentration is lower. This is mainly because the X_{BG} is known to have a much lower endogenous death rate than X_{BH} biomass (Henze et al., 2008). The lower endogenous death rate also results in reduced carbonic oxygen demand (FOc). Also, with more N used for biomass nutrition, in scenario 2, there is less N used for nitrification which impacts the population of autotrophic nitrifying organisms (ANOs) in the system and accounts for the slightly lower nitrification oxygen demand (FOn). Further, the PAOs utilising large quantities of influent RBCOD, result in less substrate availability for facultative OHOs, which use the biodegradable organics anoxically as an electron donor (nitrate being the electron acceptor is converted to nitrogen gas; i.e. denitrification) for their catabolism, resulting in the slightly lower oxygen recovery for denitrification (FOd). The nitrates generated and nitrates denitrified results, shown in Figure 5.5 (d), together with the effluent TKN and FSA results, in Figure 5.5 (e), also agree with this.

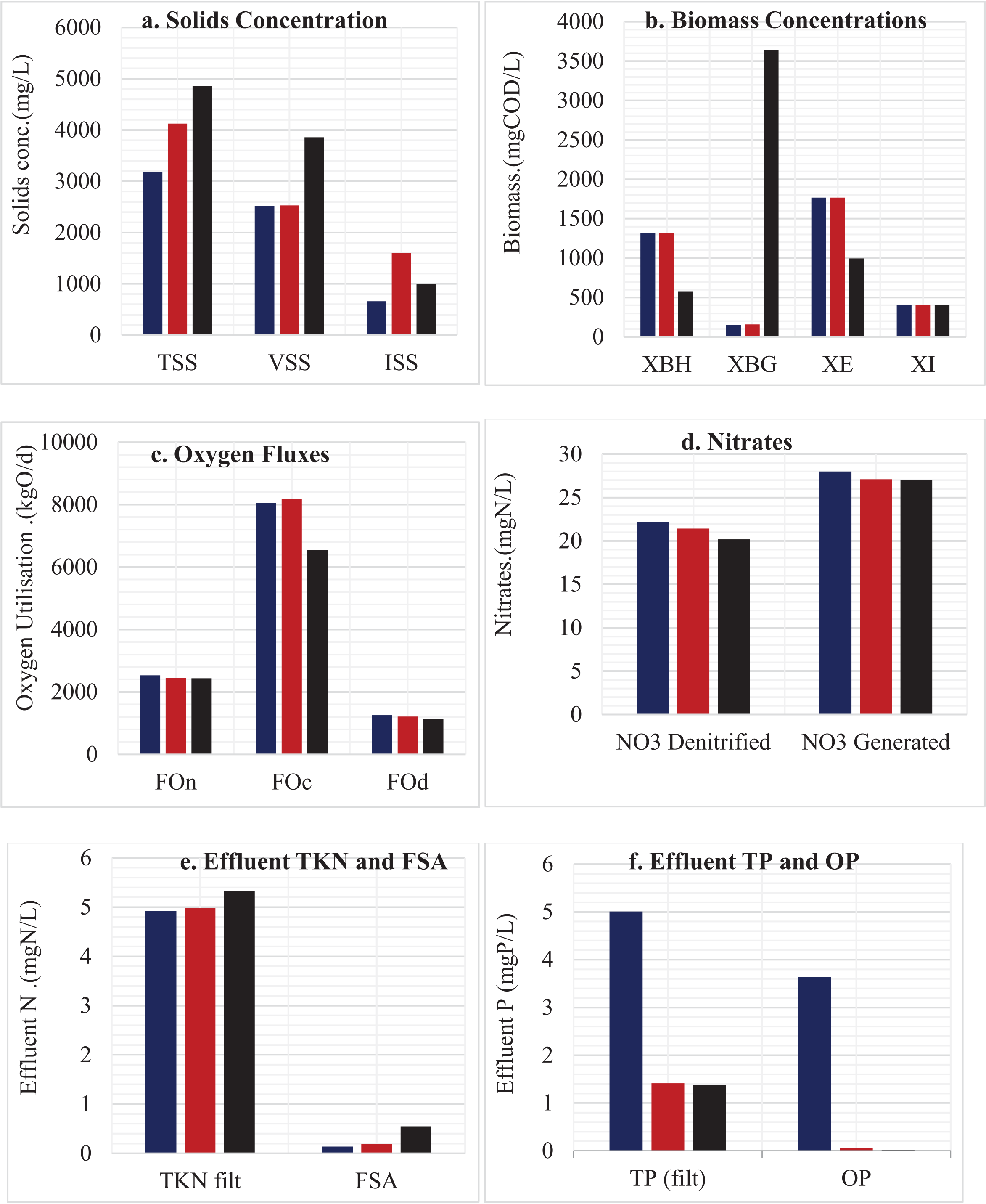

Figure 5.5. Predictions of system performance for the given strategic scenarios, including (a) reactor solids concentrations – i.e. total, volatile and inorganic suspended solids (TSS, VSS and ISS respectively) (b) reactor VSS components (c) Oxygen utilization for organic removal (FOc) and nitrification (FOn) and oxygen recovery via denitrification (FOd), (d) nitrates (NO_3) generated and denitrified and the resulting effluent NO_3, (e) Effluent Total Kjeldahl Nitrogen (TKN) and free and saline ammonia (FSA) and (f) Effluent total phosphate (TP) and orthophosphate (OP)

Table 5.1 and corresponding Figure 5.6 below show the EQI results related to the three scenarios simulated for Bellville WWTW. It can be noted that the EQI-positive is higher for Scenario 1, while the EQI-negative is higher for scenario 2 and highest for the reference layout. Despite both scenario 1 and scenario 2 improvement on effluent P concentration, for Scenario 1, the chemical P dosing results in slightly lower effluent N (i.e. FSA and nitrates) than for scenario 2.

Table 5.1. EQI Results and Effluent concentrations

Scenario	Ref	Scen_1	Scen_2
Total_EQI_Neg	-216.25	-133.84	-156.33
Total_EQI_Pos	55.85	82.85	73.14
Effluent COD (mgCOD/l)	80.26	80.28	80.95
Effluent FSA (mgN/l)	0.14	0.19	0.55
Effluent OP (mg P/l)	3.64	0.05	0.02
Effluent Nitrates (mg N/l)	5.84	5.68	6.77

Effluent limits are: 30mgCOD/l, 1mgN/l, 1mgP/l and 1.5mgN/l for COD, FSA, OP and NO_3 respectively.

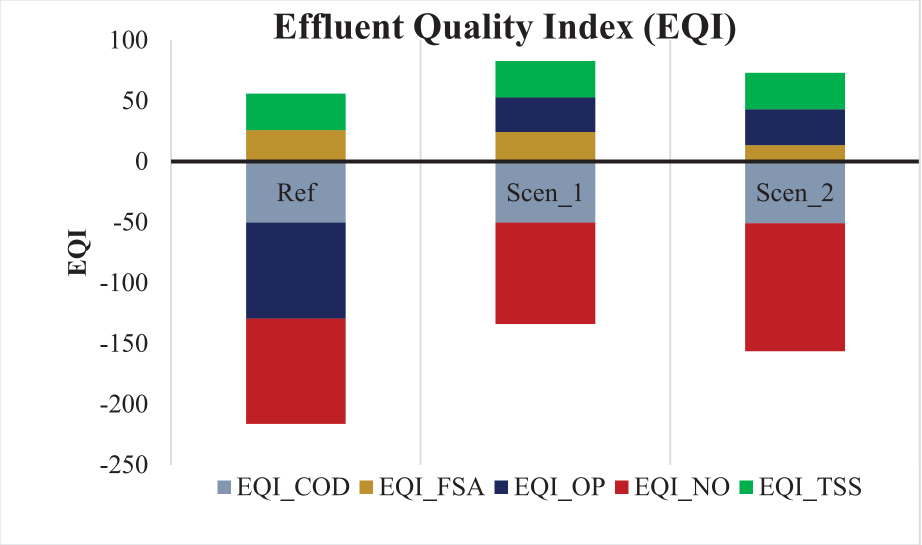

Figure 5.6. Effluent quality index results

The summary of the key drivers of the OCI for the Bellville WWTW simulations is provided in Table 5.2 and Figure 5.7 below provides a breakdown of the operational costs for the simulated strategies. It can be noticed that the operational costs for scenario 1 are highest, mainly due to the chemical dosing required for P removal. In scenario 2, the aeration costs are low, but the mixing and heating costs (due to inclusion of AD) are higher. However, there is significant potential for energy recovery with methane generated by the AD process. Because struvite has a low market in South Africa, the option of precipitating the P as struvite before the sludge thickening allows for the struvite to be added as part of the solids taken to the farmers for free that it may be utilized in growing animal fodder. This way there are some savings from the cost of disposal via landfills. However, the sludge from scenario 1, containing iron phosphates is harder to degrade in the natural environment and can cause leaching out of nutrients from when applied on land, hence it may have to be disposed via landfill deposition, which is currently being avoided in South Africa.

Table 5.2. Summary of key OCI drivers when simulating scenarios for P removal at Bellville WWTW

Component		Ref	Scen_1	Scen_2	Units
Energy Requirements	Aeration Energy	2500869	2511133	1934332	kWh
	Pumping Energy	735521	735756	741807	kWh
	Methane Production	0	0	3155943	kWh
	Heating Energy	598202	733216	931551	kWh
	Mixing Energy	11811	11874	27480	kWh
Chemicals	Magnesium dosed	0	0	87325	g/d
	Fe Iron dosed	0	626483	0	g/d
	Struvite Recovered	0	0	386355	g/d

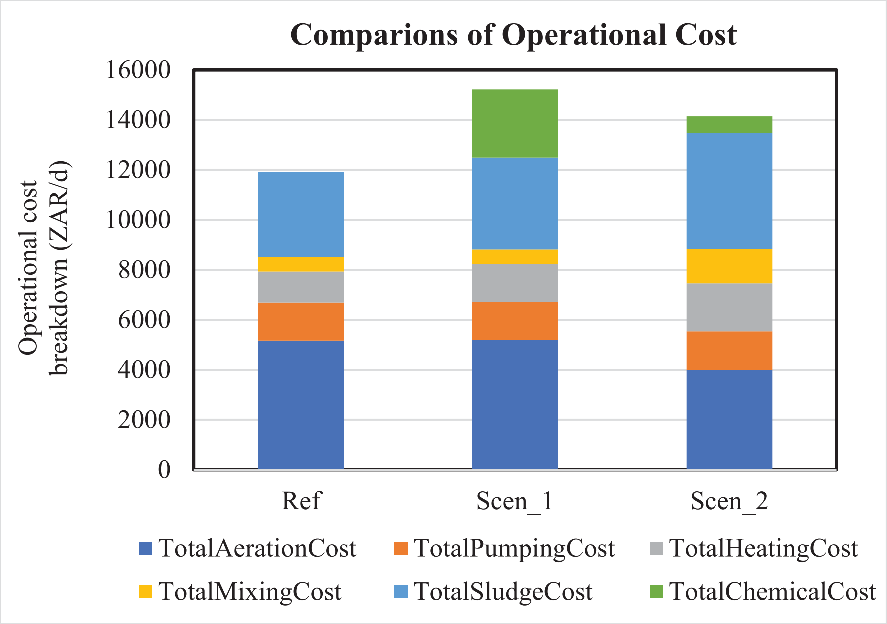

Figure 5.7. Breakdown of predicted operational cost for the simulated strategies of P removal

CHAPTER 6: CONCLUSIONS & RECOMMENDATIONS

6.1 CONCLUSIONS

The main objectives of this research project are to develop a validated model that could be used in decision making towards defining the design and optimised operation of future water and resource recovery facilities (WRRFs). This process involved the construction of both an explicit steady state model in MS Excel (by extending the UCT plantwide steady state model of Ekama (2009)) and a dynamic simulation model (by extending the PWMSA model of Ikumi et al. (2015)). The main extensions to these models included (i) the addition of anaerobic digestion polyphosphate release stoichiometry (which significantly impacts the predicted mineral precipitation potential, aqueous phase concentrations and system pH, hence AD system health), (ii) the addition of chemical phosphorus (P) removal by including the processes of Solon (2019) and (iii) the addition of a balancing tank unit process that could be useful in making tactical system control decisions for the WRRF. The completed model requires calibration against experimental data prior to utilisation against full scale systems.

The project experimental campaign generated useful data that has been rigorously analysed and used towards determining the comprehensive characteristics of phosphorus accumulating organism biomass. This is a crucial step towards determining the correct stoichiometric pathway for phosphorus rich sludge in anaerobic digestion and evaluating the potential for energy transfer from activated sludge to anaerobic digestion systems this way. This is one of the missing pieces of information required towards tracking phosphorus through the wastewater treatment system, using the mathematical models. The completed model (including P and also including the currently developed system-wide evaluative framework) shall then be used to simulate selected full-scale systems as case studies.

In the prospective application of the model for evaluation of design and operational strategies, an evaluation framework has been developed at system-wide level to allow for inclusion of products that are generated during the treatment processes. Such a framework shall be useful in promoting resource recovery by ensuring that the products generated by the WRRF are included in decision making processes for the system design and operation. The completed model together with the evaluation framework was used in full-scale case studies, whereby the model is applied as an evaluative tool in simulating full scale systems of South Africa. Currently four full scale wastewater treatment works have been replicated using both the steady state and complex dynamic (PWM_SA) models. The tailoring of steady state and dynamic models towards virtual replications of these full-scale systems were performed as part of a capacity building exercise for postgraduate students in the UCT Water Engineering programme. Currently a new postgraduate programme in professional Water Engineering shall include a structured research project that can be opted by the future engineering students towards carrying out similar projects to replicate the various treatment systems in South Africa and beyond. This is towards the future generation of region-wide digital twins for water and sanitation systems as identified in future projects below.

The comparative evaluation of control strategies, using performance tools has proved to be an effective procedure to evaluate WRRF performance on a system-wide level. Hence, providing ways to troubleshoot prospective scenarios and suggest feasible control options. The extended performance indices framework is currently being implemented, as an evaluative protocol, in the simulation of all considered strategic scenarios in order to determine the most impactful in future decision making for the given WRRF systems. Under the ERASE (evaluation of resource recovery alternatives in South African water treatment systems) initiative, a project supported by WRC to include Danish research partners, there have been engagements over the year (2020) with various stakeholders on the most suitable strategies that could meet the WRRF needs of the municipalities. To promote further continuous engagements, a water institute of South Africa modelling and data (MAD) division was established, under this project (details in Appendix B)

6.2 RECOMMENDATIONS

It has been noted that wastewater treatment systems are part of the larger water and sanitation systems and for holistic decision making to occur, the mathematical models often have to be extended to beyond the fence of the wastewater treatment plant. This is important to promote the changing paradigms that encourage sustainable infrastructure, such as ensuring the change of wastewater treatment systems to WRRFs and the conversion of water stressed regions to water sensitive zones. In this project, the evaluative framework for models has been extended to include the fate of products generated by waste treatment processes. This is to ensure that decisions on development of future systems considers the products (resources) generated by waste treatment. The evaluative framework is an extension of the IWA BSM version, which uses the effluent quality and operational cost indices (i.e. EQI and OCI). However, it was noted that in order for this evaluative framework to be more effective, the models shall require modifications, such that the predictions made regarding system performance include the variables of significance, related to prioritised criteria for the products generated by the system. For example, the sludge generated as fertiliser would require for the model to predict its quality in terms of the heavy metal content to present the quality for use (which can be connected to environmentally sustainability) and prospective market price (which is linked to economic sustainability). Similarly, the quality of the final effluent could be predicted in terms of the environmental impact and (for countries that promote fines) the cost implications and also, where tertiary treatment for water reclamation is included, the cost benefit of recovering effluent water. Hence it can be noted, for system-wide models, the EQI is linked to the OCI and the manner in which these are weighed against each other (i.e. does it cost more or less to have poor design and operated infrastructure if it does then there may be some modifications needed for policies that govern water and sanitation infrastructure). This way the mathematical models could begin revealing the aspects that need to be addressed for improvement in sustainable wastewater treatment systems, hence providing guidance towards decision making at various levels. For the mathematical models to be trusted, they must be developed from a scientifically sound basis, hence the extension of these models is an ongoing process that requires continuous development and calibration of components that make up the water and sanitation infrastructure. Some of the ongoing and prospective projects that are working towards this objective include: (i) The WRC project (C2021-2023-00488), that involves tracking micropollutants throughout the waste treatment process, which is important if the models are to predict potential for water reclamation and sludge valorisation (the removal of micropollutant is important to ensure the recovery of these resources). (ii) The WRC project (C2021/2023-00628) has included sewer modelling (which will be able to address concerns such as the impact on treatment works of variable influent loads due to rainfall events, sewer and pump station failures and new developments coming online) together with river and integrated urban water system modelling (which would address concerns around the impact of treated wastewater discharge to river bodies).

Besides the attempt to convert complex models to user friendly tools for engineers (and other stakeholders) in the water and sanitation sector, UKZN and UCT are currently collaborating on a WRC project (C2021/2023-00628) that involves training of municipal engineers in WWTP modelling techniques together with provision of a support system for the ongoing training. Further, to promote ongoing engagement between the model developers and users, a specialist Water Institute of Southern Africa (WISA) modelling and data (MAD) division has been formed and a website for sharing models and data for urban wastewater systems is being developed. This is all important to ensure continuous review and uptake of the models for their application in critical decision making for improved design and operation of future systems.

Related to the above, the UCT Water Engineering division, within the department of Civil Engineering has initiated a new postgraduate programme that trains future engineers to evaluate systems beyond the fence of wastewater treatment plants. The virtual replication of various wastewater treatment systems within African regions can now be taken up as possible research topics for prospective students, following similar approach (tailoring of systems, using steady state and dynamic models) as has been showcased in this study. This would be useful in both capacitating future engineers and towards the development of regional system-wide digital twins. There is necessity in development of such digital twins because the most suitable solutions for future water and sanitation infrastructure, could vary from one region to another and depends on multiple factors (e.g. the waste source, industrial activities of the region, climate, social culture, etc.). Hence, in this way the models would be useful towards the potential for including water and sanitation systems in future smart cities that promote efficient ways of waste reduction and use of resources. Some of the advantages that come with future digital transformations of the water and sanitation sector include (i) the possibility for real-time update of connected systems (ii) stakeholders could get required information for increasingly complex systems (this will be useful since the number of stakeholders in the water sector are increasing and so are other advances such as climate change, new system regulations, etc., hence decision making is becoming more complex) (iii) potential utilization of advanced planning tools that allow for integration with other sectors for more optimised infrastructure (Vanrolleghem, 2019).

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APPENDIX A: CAPACITY BUILDING

15 postgraduate students (10 at MSc. level and 5 at MEng Level) were supported under the project. The list of students and the project topics are listed below.

Table A 1. Master of Engineering (MEng.) Student Projects

No.	Name	Year		Research Topic	Progress
		First Reg.	Proj. Grad.		
1	Shanen Jelliman	2018	2021	Determination of the optimal treatment method for treating a nitrogen rich digestate stream from a proposed regional digestion facility at Cape Flats WWTW	Completed
2	Corne Rautenbach	2016	2021	Simulation of PAO enhanced culture bioprocesses in aerobic and anaerobic environments	Finalising thesis write up
3	Hopewell Molefe	2016	2021	Using Mathematical models and system-wide evaluative frameworks to simulate Zeekoegat wastewater treatment plant	Submitted thesis
4	David Modiri	2016	2021	Application of mathematical models to evaluate mineral precipitation Potential at full scale waste treatment system	Finalising thesis write up
5	Ghoewylah Darries	2017	2021	Using Mathematical models and system-wide evaluative frameworks to simulate Cape Flats wastewater treatment plant	Finalising thesis write up

Table A 2. Master of Science (MSc.) Student Projects

No.	Name	Year		Research Topic	Progress
		First Reg.	Proj. Grad.		
1	Eugene Fotso Simo	2018	2020	Modelling optimised utilisation of flow equalisation tanks	Completed
2	Matthieu Quavauvilliers	2018	2020	Calibration of anaerobic stoichiometric pathways for enhanced cultures of Phosphorus accumulating organisms	Completed
3	Johan Du Toit	2016	2021	Anaerobic digestion of waste activated sludge containing mixed cultures of heterotrophic organisms	Completed
4	Vukuthu Maake	2017	2021	The performance of augmented bio-methane potential tests on waste activated sludge containing PAOs	Finalising thesis write up
5	Imraan Paleker	2017	2020	A plant-wide evaluation of the Benchmark Simulation Model No.2 (BSM2) and BSM2P for WRRFs	Finalising thesis write up
6	Edward Maganga	2017	2021	Comparison of biological and chemical phosphorous removal in activated sludge system	Finalising thesis write up
7	Yuva Coothen	2018	2021	Development of a framework for performance indices used in evaluating system wide outputs of WRRFs	Submitted thesis
8	Njabulo Thela	2018	2021	Operation and testing of an activated sludge system that grows enhanced cultures of PAOs	Submitted thesis
9	Adam Oodally	2019	2021	Development of experimental methods to aid tracking of inorganic material in waste treatment processes	Submitted thesis
10	Nosisa Nqayi	2021	2022	Development of Modelling tools for Bellville Wastewater Treatment Works.	Finalising thesis write up.

APPENDIX B: KNOWLEDGE DISSEMINATION

The knowledge dissemination was via publications and via establishment of the WISA modelling and data division for continuous engagements with stakeholders on modelling aspects.

Publications

Currently, 4 journal research articles and 2 conference proceedings have been published. It is expected that 9 more journal articles shall be published as part of the requirement for the 9 other MSc. Students. The consolidated findings from this project shall also be presented in the upcoming WISA (2022) and the IWA WRRmod202 conferences.

Table B 1. Journal Publications

No.	Title
1	Ikumi D.S. and Ekama G.A. (2019). Plant wide modelling – anaerobic digestion of waste sludge from parent nutrient (N & P) removal systems. Water SA 45(3), 305 0-316. https://doi.org/10.17159/wsa/2019.v45.i3.6698.
2	Ikumi D.S. (2020). Sensitivity analysis on a three-phase plant-wide water and resource recovery facility model for identification of significant parameters. Water SA 46 (3).
3	Ikumi D.S., and Harding T.H (2020). Kinetics of biological and chemical processes in anoxic-aerobic digestion of phosphorus rich waste activated sludge. Water Research 170, Doi: https://doi.org/10.1016/j.watres.2019.115333.
4	Maake V and Ikumi D., (2022). Utilizing augmented batch test results to determine comprehensive characteristics of PAOs. (Reviewed by Water SA)

Table B 2.Conference Proceedings

No.	Title
1	Maake V., Ikumi D.S., Ekama G.A. (2018). Modelling Poly phosphate Release during Anaerobic Digestion of Sludge from Nutrient Removal Systems. Proc. WISA 2018, Cape Town, South Africa, June 2018.
2	Paleker I.M., Ikumi D.S., Ekama G.A. (2018). A plant-wide evaluation of the Benchmark Simulation Model No.2P (BSM2P) for wastewater treatment systems – Part 1: Model introduction. . Proc. WISA 2018, Cape Town, South Africa, June 2018.

WISA Modelling and Data Division

This division shall be focused on the development of mathematical models that allow for a better understanding of complex processes and systems associated with the water and sanitation sector and the generation of tools that can be applied, within various stakeholder levels, up to and including decision-makers, in planning and assessment of water and sanitation infrastructure and operations. To ensure that such models are effective, the division is also purposed towards ensuring that more structured, efficient and accurate data acquisition methods are employed to provide useful data that is important for the decision-making processes. The objectives of this division have been outlined below.

Modelling

- To address and promote all aspects of modelling, simulation and the formal methods of applying systems analysis to managing and improving the quality of the aquatic environment. This includes the development and application of mathematical models and modelling tools across all levels of complexity, such as optimisation algorithms, time-series analysis and forecasting, computational procedures for decision analysis and support, and uncertainty analysis.
- To stimulate and promote transfer of knowledge between academia, industry and decision makers across different areas within the water cycle. This is achieved through maintaining a vital support base and an electronic forum for the connection of ideas and discussion of inter-disciplinary issues, that require quantification through scientifically sound principles (i.e. using

the models) within WISA to augment the engineering, social and economic elements of problem-solving with those having human, institutional and cultural dimensions to them.
- The development and promotion of the application of systematic procedures for integrated assessment towards offering holistic and tangible solutions to water and resource recovery.
- To revolutionise the WRRF in Africa, Empowerment and Education of Africans and attracting them towards influencing the future development of WRRFs. To present an invaluable platform for the advocacy. Furthermore, the paradigm shift towards resource recovery promotes the imperative need for the recycling and reuse of valuable finite materials across the water and sanitation sector.
- Promoting the availability of recently developed engineering tools and software applications for utilization by various stakeholders for training purposes, networking and assistance in decision making processes.

Data Acquisition for the Water and Sanitation Sector

- Advancement/improvement of accurate, cost saving and efficient data generation collection techniques/ processes.
- The establishment of a centralised virtual network for water and sanitation data across the various universities and research institutes in selected regions of Southern Africa, and to promote means by which this virtual network would enable all nationwide water and wastewater analysis needs to be met.
- Connecting the enhanced data procurement methods to mathematical models that virtually replicate water and sanitation systems of selected catchment areas to allow for holistic evaluation of various improvement strategies.

APPENDIX C: DETAIL REGARDING THE ANALYSIS OF EXPERIMENTAL RESULTS

The results from the experimental setup presented in Chapter 3 or the report, together with their analysis to determine the required parameters for the mathematical models (i.e. the kinetics of hydrolysis, polyphosphate release rates and composition of the waste activated sludge) are presented in this Appendix.

ACTIVATED SLUDGE (AS) SYSTEM RESULTS

Description of AS System Operation

A laboratory scale nitrification-denitrification excess biological phosphorus removal (NDEBPR) activated sludge (AS) system in a form of a University of Cape Town Membrane system (UCTMBR) (Figure C 1) was setup. This laboratory scale NDEBRP AS setup alternates microorganisms between anaerobic and aerobic reactors and introduces volatile fatty acids (VFAs) in the anaerobic reactor which places PAOs at an advantage over ordinary heterotrophic organisms (OHOs). It also used membranes for solid-liquid separation which meant that relatively high concentrations of biomass can be achieved (Ramphao et al., 2005).

To seed the UCTMBR AS system, the most logical choice was to source the biomass seed from a plant with a NDEBPR configuration and this was indeed the initial approach. After two failed attempts, it was hypothesized that the seed probably contained a relatively large community of glycogen accumulating organisms (GAOs) which may have been responsible for the observed absence of phosphorus removal during start-up of the failed attempts. Consequently, a decision to start-up with a seed from another system, with an MLE configuration was taken because the expectation was that the concentration of GAOs was very low, if at all present. The Mitchell's Plain Wastewater Works (MPWWTW) was selected as the source of wastewater and sludge seed to the UCTMBR systems because the sewage to MPWWTW is mainly domestic, hence was deemed to have a low concentration of toxic elements.

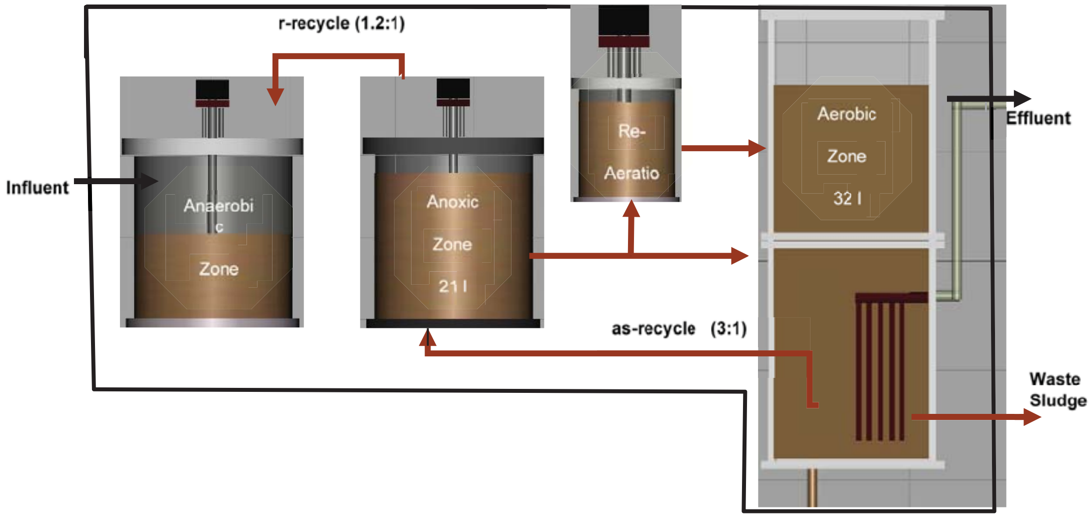


Figure C 1. NDBEPR system used in research project.

The UCTMBR system, as shown in Fig 4, consisted of an anaerobic, anoxic and aerobic reactors. The anaerobic reactor was 29 L, the anoxic 17 L and aerobic 32 L. The aerobic zone comprised two reactors; a 29 L membrane reactor and a 3 L side stream reaeration reactor used for oxygen utilization rate (OUR) measurements. The anaerobic, anoxic and reaeration reactors were all cylindrical Perspex containers that had motorised sirrers to allow for continuous mixing of th ereactor contents. The 29 L aerobic reactor was a Perspec tank that was fitted with KubotaTM A4 size membranes, through which the final effluent was produced. The membrane panels were fitted vertically in the bottom section of the main aerobic tank. Continuous coarse-bubble aeration was supplied at the base of the reactor. The air bubbles were forced to rise between the membrane panels to mix the reactor contents while providing scurr to minimize membrane fouling. To measure the OUR, the reaeration reactor was fitted with a DO/OUR meter. The flow rate from the aerobic reactor to the aerobic/anoxic to the reaeration reactor was set to give the same hydraulic retention time as in the aerobic reactor.

A peristaltic pump with multiple channels was used for all pumping requirements of the system, namely; feed and recycles. Reactor flow connections and recycle lines from the pump to the reactor and vice versa were all connected using silicone tubing.

The mixed liquor recycle-ratios, with respect to the influent flowrate, were set at 1,63 for the flow from anoxic to anaerobic zone and 1,73 for the flow from aerobic to anoxic zone. These recycle-ratios and influent feed flowrate were checked regularly (approximately every three days) using a measuring cylinder and a stopwatch.

Ramphao et al. (2005) details the relationship between mass and volume fractions in terms of recycle ratios. This was used to verify the measured recycle ratios though the measurement of total suspended solids (TSS) in each reactor. In order to maintain a solids retention time (STR) of 10 days, thrugh ensuring that 4,5 *l* was wasted daily from the aerobic reactor.

The required feed for this system comprised of a mixture of settled wastewater from MPWWTW, acetate to supplement the feed COD together with nutrients ad other additives, to encourage PAO activity (see Table 2.1 below). During the experimental period of the tests, the COD load of acetate was 75% of the total COD load fed to the AS system, while the remaining 25% was from MPWWTW settled wastewater. The calculations of required nutrient and additive concentrations was performed as recommended by Wentzel (1988). Table C 1 shows the quantities of nutrients and additives used as part of the feed.

Table C 1. Composition of Influent Feed to UCT MBR AS System

Component	Elemental composition	Quantity	units
Magnesium Chloride Hexahydrate	$MgCl_2.6H_2O$	24	g
Calcium Chloride Dihydrate	$CaCl_2.2H_2O$	6	g
Ammonium Chloride	NH_4Cl	1	g
Sodium Acetate Anyhydrous	$NaC_2H_3O_2.3H_2O$	61	g
Dipotassium hydrogen Phosphate	K_2HPO_4	33	g
Yeast		0.42	g
Iron (III) Sulphate Heptahydrate	$FeSO_4.7H_2O$	0.313571	g
Boric Acid	H_3BO_3	17.86	mg
Copper Sulphate	$CuSO_4.5H_2O$	17.93	mg
Potassium Iodide	KI	4.50	mg
Manganese Chloride	$MnCl_2.4H_2O$	118.86	mg
Sodium Molybdate Dihydrate	$Na_2MoO_4.2H_2O$	8.93	mg
Zinc Sulphide Heptahydrate	$ZnSO_4.7H_2O$	89.71	mg
Cobaltus Chloride Hexahydrate	$CoCl_2.6H_2O$	34.07	mg
MPWWTW settled influent sewage		9	litres
Water		53.00	litres

Description of AS System Results

In operating the AS systems, these important criteria for the investigation were that (i) the EBPR in the UCT system was not affected by nitrate recycle to the anaerobic reactor, (ii) there was evidence that showed presence of a high population of PAO biomass (this was noted from the very high P removal (59.2 mg P/l) observed relative to the reactor VSS mass generated, indicating that there was substantial PP synthesis as expected from the influent RBCOD (about 75% of the 818mgCOD/l influent COD added) and (iii) the active fraction of the WAS was sufficiently high to study the behaviour of the PAOs in AD conditions . These objectives were met in the investigation.

In the interests of concision, only the relevant concentrations are given for the AS system performance (see Table C 2 and Table C 3) – i.e. all the results from the investigation that were used towards achievement of steady state are not included.

Table C 2. NDEBPR AS System Influent and Effluent Results

	Flow	COD	TKN	FSA	Nitrate	TP	OP	Mg	K	Ca
Units	(l/d)	(mgCOD/l)	(mgN/l)	(mgN/l)	(mgN/l)	(mg P/l)	(mg P/l)	(mg/l)	(mg/l)	(mg/l)
Influent	62	818	61.6	33.8	-	98	95.4	42.04	228	27.28
Effluent	57.5	70.1	3.7	1.2	11	38.8	38.8	30.54	186	17.06

Table C 3. NDEBPR AS System Performance Results

Sludge age (d)	COD removal (%)	TKN removal (%)	P removal (mgTP-P/l)	Aerobic reactor TSS (mgTSS/l)	Aerobic reactor VSS (mgVSS/l)	Aerobic reactor ISS (mgISS/l)	Nitrogen nitrified (mgN/ l influent)	Nitrate denitrified (mgN/ l influent)
10.0	91.4	92.4	59.2	5624.0	2916.0	2708.0	28.9	17.9

The mass balanced steady state models presented in Henze et al. (2008) were used to characterize the WAS into VSS components, ISS components (including PP and OHO biomass ISS and accumulated influent ISS) and USO as described by Ikumi (2011) (see Table C 4). The 5 VSS components include, i.e. (i) OHO biomass (X_{BH}), (ii) OHO endogenous residue (X_{EH}) and (iii) unbiodegradable particulate organics (X_I), (iv) PAO biomass (X_{BG}) and (iv) PAO endogenous residue (X_{EG}). Whereby (i) to (iii) are associated with the MLE system and (i) to (v) associated with the NDEBPR AS system. With these VSS components determined, the unbiodegradable fraction of the WAS can be determined by adding up the calculated UPO and ER component masses (i.e. X_I, X_{EH} and X_{EG}) and dividing them against the total reactor VSS. Further, accepting that organically bound biomass P/VSS ratio is 0.025 mg P/mgVSS (Wentzel et al., 1990), the PP content of PAOs could be calculated from the PP/PAO ratio that allowed for the best match between model predicted and experimentally measured P removal.

Table C 4. Waste Activated Sludge Composition (Aerobic)

	Active OHO	Endogenous OHO	Active PAO	Endogenous PAO	PP	USO	FSA	OP	Total
OHO"s	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)	mg/l (conc.)
COD	372.0	163.3	3043.9	278.5	0.0	70.1	0.0	0.0	3927.8
Nitrogen (N)	41.1	9.0	335.9	15.4	0.0	3.5	1.2	0.0	406.0
Phosphorous (P)	7.4	2.9	60.7	4.9	694.7	0.1	0.0	38.8	809.4
VSS	284.9	110.8	2331.5	188.8	0.0				2916.0
COD/VSS	1.3	1.5	1.3	1.5	0.0				
TKN/VSS	0.1	0.1	0.1	0.1	0.0				
TP/MM	0.0	0.0	0.0	0.0	0.3				
Fraction in VSS	0.1	0.0	0.8	0.1	0.0	0.0	0.0	0.0	1.0

For the NDEBPR AS system, the contribution of accumulated influent UPO to the WAS is deemed to be significantly small (< 50 mg/l) as most of the influent COD (818mgCOD/l) was acetate (~75%) and the sewage added (25% of COD) was from settled wastewater (which was mostly soluble, with about 10% already contributing to soluble USO). Also, because it contains an enhanced culture the X_{BH} and X_{EH} contribution to WAS is significantly low. Hence the main contributor to the biodegradable mass of WAS was X_{BG} (80% of WAS, when calculated using the mass balanced steady state equations of Henze et al. (2008)) and the unbiodegradable mass of WAS was mostly X_{EG}, with a small contribution from X_{EH}. This was required for the experimental plan towards estimating the endogenous fraction of the PAOs, using the AD batch tests later.

STEADY STATE ANAEROBIC DIGESTION (AD) SYSTEM RESULTS

Description of AD system operation

The WAS collected from the full scale WWTP was used to feed a completely mixed 16-litre laboratory scale anaerobic digestion (AD) system. This AD system was fed batchwise, once a day and operated at mesophilic temperatures of 34˚C. The pH was kept in the range of 6.8-7.4 to accommodate growth of methanogenic bacteria and a consistent COD (of 10gCOD/l) of the WAS was fed daily.

The AD system used in this experiment was made of a 20-litre Perspex cylinder (with a working volume of 16 litres and 4 litres headspace) with two Perspex lids, one at the top and one at the bottom of the cylinder. The top lid was fit with a motor connected to a paddle which was placed in the reactor and used to stir its contents and keep the contents fully mixed at all times. For this experiment the motor was set to stir at 20 rpm.

The top lid was fit with a 90 mm opening to allow a temperature probe into the reactor. This measured the temperature of the contents of the reactor and showed this on an LED (light-emitting diode) display. A fish tank heater, set at 34˚C, was suspended in the reactor and kept the mixed liquor at this constant temperature for mesophilic activity. Methanogenic bacteria are temperature sensitive and so had to be kept at this temperature to ensure optimum performance. The digester was also placed in a 32˚C air-conditioned room as an extra precaution.

A second opening was made at the top of the digester to allow for daily feeding and was only opened once a day; for this purpose. Special precaution was taken to make sure that the system was gas tight (it was kept fully anaerobic) and that the only gas escaping the system, did so through an outlet at the top of the digester which was fitted to allow for the measurement of any gas produced. This was done by making sure that all openings, cracks or crevices were thoroughly sealed with silicon and cable ties used to tighten any opening where a tube was attached. A silicon tube was attached to the gas opening and then connected to a wet-tipping gas meter. This meter uses a metal ball to tip a scale placed under water and a counter tallied the number of times the scale was tipped. Once the volume of gas needed to tip the scale once was known, then the total amount of gas produced by the digester was easily calculated. Further, gas samples were collected in 5-litre impermeable Tedlar gasbags connected to the AD gas outlet pipes. The gas was analysed to determine the CO_2 and CH_4 content as a requirement to establish a COD and carbon balance over the digesters.

The AD system effluent/waste sludge was removed from the system through an outlet at the base of the reactor. This outlet was fitted with a ball valve and a silicon tube and used to open and close the outlet (once daily for wasting). In order to maintain a 20 days sludge age, the same volume of feed (800 ml) was added as volume of waste that was removed. The steady state for this AD system was achieved after it had been operated consistently for a period equivalent to three times the set SRT (i.e. >60days) had elapsed.

Various steps were taken to prepare the 800 ml influent feed to the AD system: Once a day, WAS from the stored collection in the cold room was thoroughly mixed and fed to the system. The required volume was measured out in a beaker (to allow for a COD of 10g/l) and tap water used to top up the beaker to the required volume. The beaker was then put into a bucket of hot water and left to heat up before feeding into the AD. This was done so as not to cause a temperature shock to the temperature sensitive methanogens. The WAS fed to the system was adjusted accordingly after each new batch of WAS collected or after the running of a COD test of the WAS currently stored in the cold room. This was done to make sure that a constant COD of 10gCOD/l was fed to the system. Although the volume of WAS would alter according to the COD of each new batch collected, the total volume of feed that was fed to the system remained constant at 800 ml. The AD was fed by opening the feed valve and placing a funnel into the opening and thereafter pouring the feed from the beaker into the opening.

In order to check the stability of the ADs on a routine basis, a five-point titration was conducted on a filtered effluent sample at least every second day. The in-situ pH and five-point titration method (Moosbrugger R.E., Wentzel M.C., 1992) gives the H_2CO_3 alkalinity and VFA concentration. For optimal operation, the in-situ pH should be above 6.5 but preferably within the range of 7 and 8 (McCarty, 1974) and the H_2CO_3 alkalinity to VFA ratio should be maintained at more than 3:1 (Ripley et al., 1986). Once the AD reached steady state, the influent and effluent unfiltered and membrane filtered VFA, COD, TKN and FSA, TP, OP and metallic ions (i.e. magnesium (Mg), potassium (K) and calcium (Ca)) tests were performed to determine the extent of digestion and the material mass balances over these digesters. Figure C 2 is a depiction of the AD system that was operated and tested on in this study.

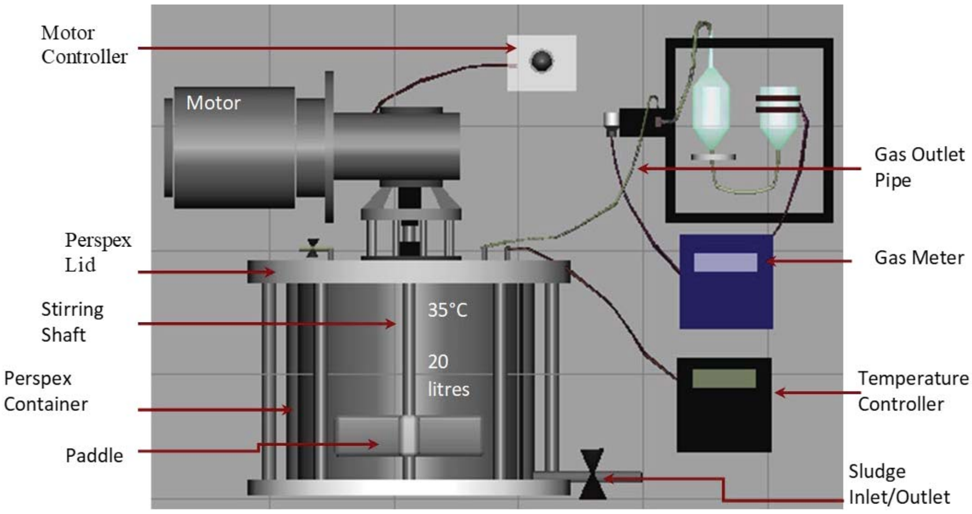


Figure C 2. Experimental set up for Anaerobic digester used in research project

The AD System Results

Anaerobic digestion (AD) systems were operated and tested with the objective of generating inoculum seed for the ABMP tests, which were in turn useful for determination of the WAS comprehensive characteristics and to reveal required information required for modelling the PAO metabolism (i.e. using parameter estimation to determine the stochiometric pathway of PAOs in AD; Ikumi and Ekama, 2019). To ensure steady state the AD systems were operated for a period equivalent to at least three time the given system sludge age. The following Table C 5 provides a summary of the results obtained from the testing of the AD system.

Table C 5. Steady state results for AD fed was from Zandvliet WWTW full scale system

Steady State	15-day ADr		32-day ADr	
Sample Point	Influent	Effluent	Influent	Effluent
COD Total (mg/l)	9956.3	7223.8	9946.2	5838.2
COD Soluble (mg/l)	81.3	177.6	92.7	188.9
TKN (mg/l)	698.8	675.5	677.2	672
FSA (mg/l)	6.2	257.5	5	287.4
TP (mg/l)	201.4	214	207.2	180.2
OP (mg/l)	3.2	108.9	2.1	114.7
TSS (mg/l)	8761.2	6157.8	8388.7	4912.8
VSS (mg/l)	6820.5	46754.1	6836.7	3767.8
ISS (mg/l)	1940.6	1403.7	1552	1145
H_2CO_3* Alk (mg as CaCO3/l)	101.5	1059.8	98.2	1137.5
pH	7	6.7	7	6.7
Mg Total (mg/l)	27.6	25.3	19.6	22.2
Mg Soluble (mg/l)	5.1	21	4.2	19.5

Ca Total (mg/l)	126.9	125	119.6	101.1
Ca Soluble (mg/l)	43.7	45.4	38.8	45.2
K Total (mg/l)	790.9	809.2	785.7	887.8
Steady State	15-day ADr	32-day ADr	Steady State	15-day ADr
Sample Point	Influent	Effluent	Influent	Effluent
K Soluble (mg/l)	14.2	401.6	10.9	419
Gas Production (litres)	-	1.41	-	1.47
CH_4 (%)	-	43	-	34
COD of CH_4 (mgCOD/l)	-	1152.6	-	2035.47

In AD systems, the AD biomass have a very low yield. This means that the only a very small portion of the COD feed is converted to new organism mass, while most of the biodegradable organics are converted to methane (CH4), which is insoluble and escapes the system as a gas. This means that most of the biodegradable COD escapes the system as methane gas. In order thus to achieve a COD mass balance over a methanogenic AD system, the difference between the COD influent and COD effluent should equal the COD that escaped as methane gas.

In order to obtain a 100% mass balance for N, P, Mg, K and Ca, the total unfiltered TKN, TP, Mg, K and Ca in the influent should equal the total unfiltered TKN, TP, Mg, K and Ca in the effluent. The AD mass balance results are given in Table C 6.

Table C 6. Mass Balances over the ADs

Components	Unit	15-day ADr	32-day ADr
COD	%	84.7	81.6
N	%	96.7	93.5
P	%	106.3	86.9
Mg	%	91.9	113.4
K	%	102.3	113.0
Ca	%	98.5	84.5

As can be noted from Table C 6, the COD balance is not > 90%, this can be explained by how the gas was either sampled from the ADs or prepared for testing. However, achieving a COD balance of > 80% over the lab scale ADs are deemed sufficiently accurate to meet the required objectives of this research. The N, P and counter-ion metals achieved average balance of > 85% which are very accurate mass balances in favour of this research. The results obtained, together with the steady state NDEBPR WAS AD model equations for Ikumi et al. (2015) were used to estimate the concentration of biomass in the control seed sludge fed to the ABMP tests (see Table C 9).

AUGMENTED ANAEROBIC DIGESTION (AD) BATCH TESTS

Augmented AD Batch Test Description

A bio-methane potential (BMP) test measures the biodegradability (biodegradable fraction of organics) of a substrate by comparing the methane production (along with other gases and compounds) of a control sample that contains anaerobic digestion seed inoculum, to that of a test sample that contains the anaerobic digestion seed inoculum as well as an organic substrate (Botha, 2015). The AD batch test performed in this study tests were augmented as shown by Gaszynski et al. (2019) to include the measurement of additional variables (H_2CO_3 alkalinity, pH, Free and saline ammonia (FSA) and ortho-phosphates) and the procedure is described below. Hence such batch tests are referred to as augmented biomethane potential (ABMP) tests.

Each test was conducted in a 2.5 litre glass aspirator bottle (hereinafter referred to as the reactor) with a rubber plug used to seal the top opening. Three (5 mm diameter) openings were made through the rubber plug to allow for the insertion of: (1) a fish tank heater which was completely submerged in the contents of the bottle and used to keep it at a constant temperature of 34˚C; the optimum temperature for an anaerobic digester, (2) a silicon tube which connected to a glass measuring column filled with water, which was used to measure the volume of gas produced per day by the system and, (3) a gas bag which was filled with nitrogen gas (N_2) and opened when samples were taken from the bottles. This was done in order to prevent the suction of air or water into the bottle caused by a negative pressure created when sampling. This bag was only opened and N_2 gas allowed to enter the system when samples were taken, it was otherwise kept sealed. The ABMP reactor generated biogas escapes through tubing connected at the top of each bottle and is bubbled through a barrier solution into a water-containing measuring column, where it displaces the water volume. Measuring the change in water level of the column continuously, by using fitted ultrasound and pressure sensors, allows for the volume of gas produced by the sample over time to be determined. An anaerobic environment was maintained in the reactors by flushing the bottles with nitrogen gas before tests began and by completely sealing them so that no gas was able to enter the system. The bottles were kept under anaerobic conditions at all times.

The bottom of each reactor was equipped with a small 20 mm diameter circular access hole with a tap attached to it, to allow for daily sampling. It was also stirred manually by shaking the bottles once a day in order to increase contact between the micro-organisms and the substrate.

Anaerobic digestion biomass is added to the ABMP reactor by a process known as seeding, in which a measured sample was drawn from the steady-state methanogenic AD system and placed into the ABMP reactor vessel at the start of the experiment. The control (containing AD biomass seed supplied from the steady state AD effluent) and test (containing both the biomass seed and substrate) ABMP reactors were subjected to a long sludge age (> 40 d) in the ABMP reactors. The initial starting concentrations of the ABMP reactor contents (inoculum and substrate) are sampled and then tested and characterised as thoroughly as possible. In particular, the COD was determined in order to ensure a substrate, inoculum (SI) COD ratio within an acceptable range. An SI ratio of 1:1 was used. Also, sample is drawn from each reactor every 24 h for the first 12 d, after which a sample is taken every second day. This is done to ensure that enough mass remained inside the reactor until the end of the test. Reaction endpoint (no further biodegradation to occur) will be observed the moment gas production stops. The Figure C 3 depicts the ABMP test set up that used in the performed experimental campaign.

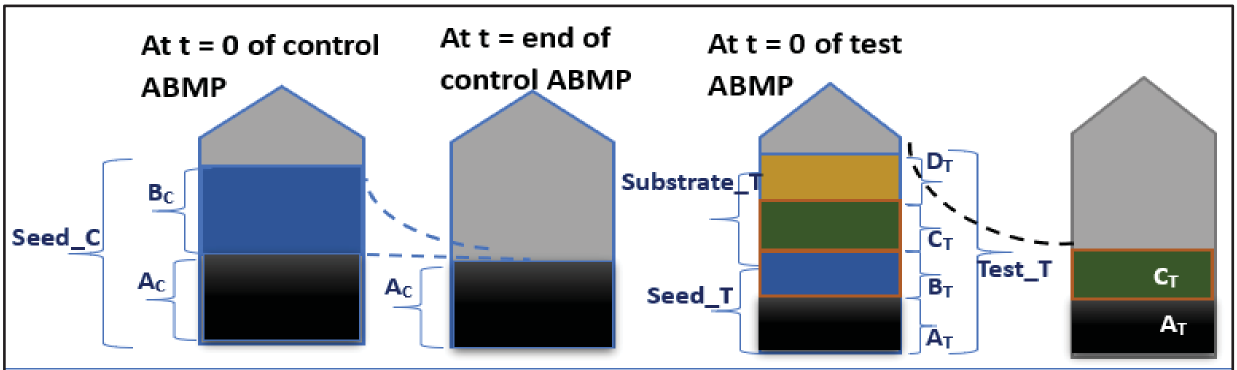
Figure C 3. ABMP Test Setup in WQL at UCT

The composition of the biomass can be identified by using the bioprocess stoichiometry for methanogenic AD. The control test contains only the sludge seed, therefore, the carbon (C), nitrogen (N) and phosphorus (P) in the biomass endogenously respired becomes part of both the gaseous and aqueous products. Therefore, by measuring the difference in the various concentrations before the start of the test and at the end of the test, the COD, VSS, C, N and P of the biomass endogenously respired can be calculated. Therefore, the biomass composition can be calculated provided accurate measurements are taken for the above-mentioned mass ratio parameters. The same procedure is then repeated for the batch test which contains biomass and a known concentration of organics. The results obtained indicate the concentrations of the various elements transferred to the gas and aqueous phases for both the biomass and the biodegradable organics (see Chapter 3 below).

Augmented AD Batch Test Results

The Augmented AD batch tests were operated and tested for solids retention time of about 40 days. The inoculum seed sludge source for these AD batch tests was the steady state AD system. The control AD batch reactors were fed diluted effluent from the steady state AD systems and the test AD batch reactors were fed half the mass of this diluted steady state AD system effluent (to provide inoculum seed) and the mass of substrate being tested. The substrates tested included (i) The WAS from the full scale ZWWTW, fed to the steady state AD system, (ii) the WAS from the laboratory scale UCT MBR AS system, containing enhanced cultures of PAOs and (iii) WAS from an MLE AS system. The AD batch control and tests reactors were tested daily for the first week and then less often as the solid’s retention time increased. The results from the tests performed on the control and test AD batch reactors are shown in Table C 7.

The first stage of the data analysis involved estimating the various ABMP reactor component masses (i.e. the WAS BPO (biomass), WAS UPO (mainly endogenous residue), inoculum seed BPO (AD biomass) and inoculum seed UPO). To estimate these values, it is assumed that all biodegradable organics in the ABMP reactors have been utilised by the end of the ABMP test (give that they are operated for a very long sludge age until there is no further biogas production observed). Hence the remaining organics at the end of the ABMP reactor operation is deemed unbiodegradable. With the biodegradable and unbiodegradable masses known for the control reactor (seed sludge) and test reactor (substrate), the intuitive knowledge of how the substrate is transformed during the ABMP test is used towards the analytical procedures employed (i.e. nonlinear regression for determination of kinetic constants and parameter estimation to determine the elemental composition of the WAS organics): essentially it is important to note that the organics (measured as chemical oxygen demand, COD and volatile suspended solids, VSS) shall be utilised (i.e. decreased through AD biodegradation) and converted to methane while the ammonia (FSA), orthophosphate (OP) and alkalinity is expected to increase via release of nitrogen (N) and Phosphorus (P) bound in the biodegradable particulate organic (BPO) material as the BPO gets degraded. Figure C 4 shows how the component masses for the ABMP reactors are determined.



A_C: Baseline values containing unbiodegradable material obtained at end of control ABMP test.
B_C: Mass of biodegradable organic material (BPO) in control ABMP reactor added (includes biomass fractions added as parameters) = VSS at t_0 – VSS at t_{end}
A_T – Equivalent mass of unbiodegradable material (UPO) from seed added that remains till end of exp.
B_T - Equivalent mass of seed biodegradable material (BPO) with characteristics determined using data from the control ABMP reactor.
C_T - Mass of UPO in substrate added = VSS at end of test – A_T.
D_T - Mass of BPO in substrate added = VSS at beginning of test – A_T – B_T.
Seed C: Has a mass (Xg) of sludge from continuous AD system containing AD biomass that at t=0 has a concentration of xmg/l (i.e., X/V in the volume V) in the control ABMP reactor.
Seed_T: Has a mass of Yg (which is Xg/2; i.e., half the mass of Seed_C) and added to half the Test ABMP reactor volume (V/2) to make up a concentration of Yg/0.5V (i.e., Xg/2/0.5V = Xg/V = x mg/l; same concentration as in Seed_C is added to the Test ABMP). However, the concentration of Seed_T in the entire reactor once mixed (at t=0) is equal to Xg/2/V = x/2 mg/l.
The Substrate_T is added at a mass of Zg (which is Xg/2; i.e., also half the mass of Seed_C and same mass as Seed_T and also = Test_T mass – Seed_T mass). Substrate_T is added at equal volume to Seed_T, hence the concentration of Substrate_T during its addition (zmg/l) is equal to that of Seed T (z=y). If Test _T mass is given as W (which equals X; i.e., Z+Y = X/2+X/2 = X) and its concentration is w(mg/l), then the concentration of Substrate T during addition is (W-X/2) /(V/2) = (X-X/2)/ (V/2) = (2X-X)/V = x(mg/l). Then at t=0, the concentration of Substrate_T in the test ABMP reactor is equal to (W-X/2)/V = (w * V – (x*V)/2)/V = w-(x/2). Hence because the equivalent concentration of the seed in the ABMP test reactor (seed T) is half that in the control ABMP the concentration of the substrate in the test is monitored by using this w-(x/2) formula.

Figure C 4. Determination of Biodegradable and Unbiodegradable Massed using AD Batch Tests

In order to determine these masses, the stated procedures in Figure C 4 were carefully followed using the ABMP data on COD. Table C 7 below shows the calculated control and test masses prior to the parameter estimation process.

Table C 7. Calculation of Control and Test Masses

Sludge Type	Samples	Unbiodegradable Particulates		Biodegradable Particulates		Total Organics	
		Concentration (mgCOD/l)	Mass (mgCOD)	Concentration (mgCOD/l)	Mass (mgCOD)	Concentration (mgCOD/l)	Mass (mgCOD)
UCT MBR WAS	Seed_C	2.1	10.5	2.7	13.5	4.8	24.0
	Test_T	2.0	9.8	3.7	18.3	5.6	28.0
	Seed_T	1.1	5.3	1.4	6.8	2.4	12.0
	Substrate_T	0.9	4.5	2.3	11.5	3.2	16.0
Full Scale ZWWTW WAS	Seed_C	3.7	18.5	1.8	9.2	5.5	27.7
	Test_T	5.6	27.8	4.5	22.3	10.0	50.0
	Seed_T	1.9	9.3	0.9	4.6	2.8	13.8
	Substrate_T	3.7	18.5	3.5	17.7	7.2	36.2
MLE WAS	Seed_C	2.1	10.5	2.7	13.5	4.8	24.0
	Test_T	2.8	13.8	4.1	20.3	6.8	34.0
	Seed_T	1.1	5.3	1.4	6.8	2.4	12.0
	Substrate_T	1.7	8.5	2.7	13.5	4.4	22.0
For the given AD batch tests, the 5-litre control reactor comprised 2 litres of seed sludge, sourced from the steady state AD system (which was at about 10gCOD/l), and 3 litres of water; The 5-litre test reactor fed UCT MBR WAS comprised 2.5 litres WAS (at about 4gCOD/l), 1 litre seed sludge and 1.5 litre of water; The 5 litre test reactor fed MLE WAS comprised 1.7 litres WAS (at about 6gCOD/l), 1 litre seed sludge and 2.3 litres of water.							

The ABMP test that virtually replicates the ones run experimentally (i.e. including both the control (run with inoculum only) and the test (with both inoculum and organics) are simulated separately. The test ABMP simulation is subsequent to the control ABMP simulation, to allow for the 'initial parameters' (i.e. the elemental composition of the seed sludge, whereby the x, y, z, a and b values of $C_xH_yO_zN_aP_b$ are determined via the parameter estimation (PE) process described below) to be determined first. Once the composition of the inoculum organics is known, the performance of PE using the test ABMP (with known inoculum and organics) output data, hence allows for determination of the composition of the WAS organics.

In order to use the WAS ABMP data towards determining the comprehensive characteristics of the WAS (i.e. including its biodegradability and the constants defining its hydrolysis kinetics), the characteristics of the inoculum seed sludge (i.e. the steady state AD system effluent that was added to the control ABMP reactor) are required. These required seed sludge characteristics include, amongst other variables, the estimate of the acidogenic biomass (Z_{AD}) and the biodegradable particulate organics COD (S_{bp}) concentration. Gaszynski et al. (2019) indicate that the characteristics of the inoculum seed can be determined with the measured steady state AD influent and effluent concentrations by calibrating the data against the UCT steady state AD model. In the UCT AD models (UCTADM (Sötemann et al.,2005); UCTSDM3P (Ikumi et al., 2015)) the hydrolysis of the three different organic materials (proteins, carbohydrates and lipids) of the International Water Association (IWA) ADM1 model (Batstone et al., 2002) is modified to a single hydrolysis process acting on a generic particulate biodegradable organic material representing sewage sludge, i.e. $C_XH_YO_ZN_A$. With complex organics, like in WWTP sludge, the hydrolysis process is usually the rate-limiting step so that the AD processes that follow it, being much faster, are dealt with stoichiometrically to yield the digester end products, i.e. biomass, CH_4, CO_2 (dissolved HCO_3^- and gaseous CO_2) and water (Ikumi et al., 2015).

For completely mixed flow through anaerobic digester conditions, the total COD concentrations (S_{ti}) is fractionated into (i) S_{bp}, (ii) unbiodegradable soluble and particulate COD (S_{us} and S_{up} respectively), (iii) fermentable readily biodegradable organics (FBSO, S_{bsf}) and (iv) volatile fatty acids (VFA, S_{bsa}; all assumed to be acetate).

Hence in the influent ($_i$) and effluent ($_e$) of the AD:

$$S_{ti} = S_{bpi} + S_{bsfi} + S_{bsai} + S_{usi} + S_{upi} \qquad [C1]$$

and

$$S_{te} = S_{bp} + S_{bsf} + S_{bsa} + S_{us} + S_{up} + Z_{AD} \qquad [C2]$$

Using this steady state modelling approach, it is possible to couple the FBSO (S_{bsfi}) with the BPO (S_{bp}) COD because it is a complex organic that also requires hydrolysis resulting in the generation of Z_{AD} (i.e. $S_{bp} = S_{bp} + S_{bsf}$). The acidogenic biomass (Z_{AD}) concentration, which has the largest yield value (0.089mgCOD organism/mgCOD substrate) represents the biomass formation of all the AD microorganism groups, i.e. not only the acidogens, (which are known to have much lower, yield values). However, to account for the growth of acetoclastic methanogen (Z_{AM}) and hydrogenotrophic methanogen (Z_{HM}) biomass, hence improve predictions on methane generation and sludge production, Sötemann et al. (2005) increased the yield coefficient (Y_{AD}) from 0.089 to 0.113 (mgCOD organism/mgCOD substrate). Although the Z_{AM} and Z_{HM} have very low yield coefficients ($Y_{AM} = 0.04$, $Y_{HM} = 0.01$), they still contribute to the overall biomass production. Since acidogenesis produces 67% acetic acid for Z_{AM} growth (and 33% hydrogen), 67% of the Y_{AM} value was added to Y_{AD}. The hydrogenotrophic methanogens (Z_{HM}), being a very small part of AD biomass were neglected in the adjustment of the Y_{AD}. In the ore complex dynamic simulation AD models, all AD biomass growth kinetics are modelled individually. With this steady state model set up, the Z_{AD} concentration was determined using the following equations established by Sötemann et al. (2005):

a. Based on a reactor at steady state and a mass balance on the acidogenic biomass, the hydrolysis rate of the organics is determined by:

$$r_h = \frac{Z_{AD}}{Y_{AD}}\left(\frac{1}{Rs} + b_{AD}\right) \qquad [C3]$$

Where: Y_{AD} = Biomass yield (*gCOD* biomass/ *gCOD organics)*

Rs = Sludge age (*d*)

: b_{AD} = Biomass death rate (*1/d*)

b. Similarly, the hydrolysis rate can also be determined based on a reactor at steady state and a mass balance of the biodegradable organics flowing through the reactor:

$$r_h = \frac{S_{bpi} - S_{bp}}{Rs} + b_{AD}Z_{AD} \qquad [C4]$$

c. The concentration of biomass present in the reactor can then be determined by:

$$Z_{AD} = \frac{Y_{AD}(S_{bpi} - S_{bp})}{[1 + b_{AD}Rs(1 - Y_{AD})]} \qquad [C5]$$

The calculated Z_{AD} is shown in Table C 8 below

Table C 8. Determination of AD Biomass Concentration

COD (unfiltered) – influent average	gCOD/l	11.22
COD (unfiltered) – effluent average	gCOD/l	8.79
AD sludge age	d	20
AD biomass yield coefficient (Y_{AD})	gZAD/gCOD	0.113
AD biomass death rate (b_{AD})	per d	0.04
Biomass, Z_{AD}	gCOD/l	0.17
Z_{AD} in control batch AD	gCOD/l	0.11

Using ABMP Dataset to Determine Hydrolysis Rate Constants

Saturation kinetics formulation is often used in models to represent the utilization of slowly biodegradable particulate organics (BPO) in activated sludge models (Henze et al., 1995) and hydrolysis of sewage sludge (McCarty, 1974; Ikumi et al., 2014). It includes acidogenic biomass growth (ZAD) and incorporates a maximum rate of hydrolysis under conditions of high substrate/biomass concentration ratio (Sbp/ZAD). Saturation kinetics is based on the quantity of BPO (substrate broken down by ZAD) attached to the organic ZAD active sites, whereby the rate of hydrolysis reaches a maximum at saturation of the active sites of the acidogens. This way saturation kinetics the hydrolysis rate is independent of the bulk liquid residual biodegradable COD concentration (Sbp), but rather dependent on its concentration with respect to the acidogenic biomass concentration (ZAD). Thus, the saturation kinetic equation used to predict the rate of hydrolysis is:

$$r_{HYD} = \left(\frac{k_M \cdot \left(\frac{S_{bp}}{Z_{AD}} \right)}{K_S + \left(\frac{S_{bp}}{Z_{AD}} \right)} \right) \cdot Z_{AD} \qquad \text{[gCOD/ (}l\text{.d)]} \qquad \text{[C6]}$$

Where K_S is the substrate and acidogenic biomass concentration ratio, at which the specific hydrolysis rate is half its upper limit (k_M) at saturation.

The mass balance-based principles (similar to those used by Sötemann et al. (2005) and Ikumi et al. (2015)) are adopted here to determine the kinetic constants (k_M and K_S) in the hydrolysis rate equations.

The S_{bpi} is connected to the residual one (S_{bp}; i.e. in the effluent) via the volumetric hydrolysis rate (r_{HYD}) derived below.

The derivation of volumetric hydrolyses kinetic rate constants was accomplished using the principle of mass balance over the AD system. For hydrolysis kinetics the components of interest include the BPO and Z_{AD}. Hence using the mass balance principles, the system's change in BPO can be equated to the BPO entering the AD, subtracting the amount exiting the AD and the quantity utilized via hydrolysis, and that generated through death of AD biomass (i.e. Z_{AD}) the so a mass balance on BPO yields:

$$V \cdot \partial S_{bp} = Q_i \cdot \partial t \cdot S_{bpi} - Q_e \cdot \partial t \cdot S_{bpe} - r_{HYD} \cdot V \cdot \partial t + \left(b_{AD} \cdot Z_{AD} \right) \cdot V \cdot \partial t \qquad \text{[C7]}$$

Where b_{AD} (/d) is the acidogen endogenous respiration rate constant.

In the above Equation C7, it is accepted that, negligible endogenous residue (Z_{EAD}) accumulates in the AD. For AD batch tests, without influent or effluent flow rates (i.e. $Q_i = Q_e = 0$), whereby the change in BPO is a decrease (hence negative) the formulation can be accepted as:

$$-V \cdot \partial S_{bp} = -r_{HYD} \cdot V \cdot \partial t + b_{AD} \cdot Z_{AD_i} \cdot V \cdot \partial t$$

Hence, $V \cdot r_{HYD} \cdot \partial t = V \cdot \partial S_{bp} + V \cdot b_{AD} \cdot Z_{AD_i} \cdot \partial t$ [C8]

Where δS_{bp} equals the S_{bp} at current time (S_{bp_t}) subtracted from the S_{bp} at initial time (S_{bp_ti}), i.e. $S_{bp\_ti} - S_{bp\_t}$, dividing the above Equation C8 by V.δt, gives:

$$r_{HYD} = b_{AD} \cdot Z_{AD_i} + \frac{\left(S_{bp_{ti}} - S_{bp_t} \right)}{\partial t} \qquad \text{[gCOD/ (}l\text{.d)]} \qquad \text{[C9]}$$

Applying the mass balance to the acidogenic biomass (Z_{AD}) concentration in a flow through AD yields:

$$V \cdot \partial Z_{AD} = Q_i \cdot Z_{AD} \cdot \partial t - Q_e \cdot Z_{AD} \cdot \partial t + Y_{AD} \cdot r_{HYD} \cdot V \cdot \partial t - b_{AD} \cdot Z_{AD_i} \cdot V \cdot \partial t \qquad \text{C10]}$$

Noting that $Q_i = Q_e = 0$, for AD batch tests, and dividing the above Equation C10 by V, gives0
:

$$\partial Z_{AD} = Y_{AD} \cdot r_{HYD} \cdot \partial t - b_{AD} \cdot Z_{AD_i} \cdot \partial t \qquad [C11]$$

Hence the Z_{AD} at current time (Z_{AD_t}) should equal the Z_{AD} at initial time (Z_{AD_ti}) added to the change in ZAD over the time (δZ_{AD}), i.e.:

$$Z_{AD} = Z_{AD_i} + \partial Z_{AD} = Z_{AD_i} + \left(Y_{AD} \cdot r_{HYD} - b_{AD} \cdot Z_{AD_i}\right) \cdot \partial t \qquad [C12]$$

Equations C1 to C12 establish the link between the initial and current COD concentration (S_{ti} and S_t) in the batch test and is computed as follows in the simplified model, for the determination of kinetic constants:

1. Coupling S_{bsf}) with S_{bp} as shown above and assuming that the S_{bsa} is used up very rapidly (hence dealt with separately). This allows for the residual biodegradable COD to be simplified to a single component.
2. Using the increased the yield coefficient (Y_{AD}) from 0.089 to 0.113 (mgCOD organism/mgCOD substrate) as explained in the above section.
3. Setting S_{up_ti} (influent UPO COD) = $f_{SL'up}$ S_{ti}, where $f_{SL'up}$ is the unbiodegradable COD fraction of the sludge and $S_{up\_te} = S_{up\_ti}$. Where S_{up_te} is determined as the particulate COD that remains after batch AD has continued for a long solids' retention time (i.e. > 40d R_s).
4. Hence, $S_t = S_{bp} + f_{SL'up} \cdot S_{ti} + Z_{AD} + S_{us}$ and therefore,

   $$S_{bp} = S_t - f_{SL'up} \cdot S_{ti} - Z_{AD} - S_{us} \qquad [C13]$$

   Hence, the best $f_{SL'up}$ estimate is selected that ensures the S_{bp} value of zero (for the long solids retention time) when calibrating the hydrolysis kinetics. The Sus can be assumed to be negligible as it is a significantly small contribution to the total COD.
5. Substituting Equation C12 for Z_{AD} in Equation C13 yields:

   $$S_{bp} = S_t - f_{SL'up} \cdot S_{ti} - Z_{AD_i} - \left(Y_{AD} \cdot r_{HYD} - b_{AD} \cdot Z_{AD_i}\right) \cdot \partial t \qquad [C14]$$

6. Further, substituting Equation C5 for r_{HYD} in Equation C4 yields:

   $$S_{bp_e} = S_t - f_{SL'up} \cdot S_{ti} - Z_{AD_i} - \left(Y_{AD} \cdot \left(b_{AD} \cdot Z_{AD_i} + \frac{\left(S_{bp_i} - S_{bpe}\right)}{\partial t}\right) - b_{AD} \cdot Z_{AD_i}\right) \cdot \partial t, \text{ hence}$$

   $$S_{bp_e} = \frac{S_t - f_{SL'up} \cdot S_{ti} - Z_{AD_i} - Y_{AD} \cdot b_{AD} \cdot Z_{AD_i} \cdot \partial t - Y_{AD} \cdot S_{bp_i} + b_{AD} \cdot Z_{AD_i} \cdot \partial t}{(1 - Y_{AD})} \qquad [C15]$$

Therefore, with an estimate of $f_{SL'up}$, the COD characteristics (S_{bp_ti} and Z_{AD_ti}) calculated from the parent steady state AD system. This estimate $f_{SL'up}$ is the selected value that, at the longest solids retention time (SRT > 40d) AD batch reactor, yields a calculated S_{bp} of zero. With S_{bp_t} known (calculated using Equation C15), r_{HYD} and Z_{AD_t} can be calculated from Equations C9 and C12 respectively. With S_{bpe}, Z_{AD} and r_{HYD} calculated for each time interval (where there is a corresponding measurement of S_t), the hydrolysis rate kinetic constants (k_M and K_S for saturation hydrolysis kinetics, see Equation C6) can be obtained through non-linear regression methods (such as sum of least squares; Fox, 2002; Uncini, 2015) via the utilization of curve fitting software (e.g. the R Studio software; an open source statistical package based on the S language). The model to be fitted (i.e. in this case the saturation hydrolysis kinetic formulation) and the model parameters to be estimated (i.e. the k_M and K_S values) are first specified. Thereafter, the R software determines the best parameter values by calculating fitted values for all the data points of the fitting regression model together with the residuals (differences between the fitted and observed values) such the minimum residual sum-of-squares (i.e. calculated from the totaling of residual squares) is obtained. From this process, the kinetic rate constants (k_M and K_S for saturation hydrolysis kinetics) that would provide the closest predictions are selected for application to the AD reactor. Once the kinetic constants have been determined, the calibrated hydrolysis rate equation can be applied to predict the residual biodegradable organics at a given time (S_{bp_t}).

To find the S_{bp} in terms of the saturation kinetics with k_M and K_S known, Equation C9 for r_{HYD} and Equation C12 that defined Z_{AD} are applied to the saturation kinetic Equation C6 in the following way:

1. Using the initial concentration at time t = 0 and the determined k_M and K_S values, the transient terms in the biological kinetic equations with finite difference terms are determined, e.g.

   $\delta S_{bp}/\delta t = (S_{bp\ time\ 1} - S_{bp\ time\ 2})/\Delta t$
   hence $S_{bp\ time\ 2} = S_{bp\ time\ 1} - \Delta t\ (\delta S_{bp}/\delta t)$ [C16]

   where Δt is the time interval between time 2 and time 1.

2. Where $r_{HYD\ time1}$ is from Equation C6 can be given as:

   $$r_{HYD_{time1}} = \frac{k_M \cdot \left(\frac{S_{bp_{time1}}}{Z_{AD_{time1}}}\right)}{K_S + \left(\frac{S_{bp_{time1}}}{Z_{AD_{time1}}}\right)} Z_{AD_{time1}} \qquad [C17]$$

   and δS_{bp} from Equation C8 can be given as:

   $$\partial S_{bp} = \left(r_{HYD} - b_{AD} \cdot Z_{AD_i}\right) \cdot \partial t \qquad [C18]$$

   The transients in the finite difference equations (e.g. $\delta S_{bp}/\delta t$) are then substituted by the respective biological kinetic equations, i.e.:

   $$Z_{AD_{time2}} = Z_{AD_{time1}} + \partial Z_{AD} = Z_{AD_{time1}} + \left(Y_{AD} \cdot r_{HYD} - b_{AD} \cdot Z_{AD_{time1}}\right) \cdot \Delta t \qquad [C19]$$

   $$S_{bp_{time2}} = S_{bp_{time1}} - \partial S_{bp} = S_{bp_{time1}} - \left(r_{HYD} - b_{AD} \cdot Z_{AD_{time1}}\right) \cdot \Delta t \qquad [C20]$$

3. A computer programme or spreadsheet can then be written to repeat the calculation from the initial conditions by stepping forward in time. This is done by setting the previous step end value equal to the beginning value of the next step. It is best to do this with selected low step length (Δt = 10 min, i.e. 5760 steps to make 40 days of integration) to ensure a stable integration.

With the Z_{AD} and S_{bp} values calculated using Equations C12 and C15 respectfully, the S_{bp} / Z_{AD} values for the different time points of the AD batch tests are determined. Following this, the r_{HYD} for each time point is calculated; (i) from data using Equation C9 and (ii) predicted using the saturation kinetic formulation (Equation C1), where the kinetic constants have been determined via non linear regression, using the R software as shown in the above section.

The above procedure, outlined by Equations C6 to C20, allows determination of the unbiodegradable particulate COD fraction ($f_{SL'up}$) and saturation kinetic rate constants for hydrolysis from experimentally measured batch AD results. This procedure is applied below to determine the hydrolysis kinetic rate constants in ADs fed waste activated sludge (WAS) from (1) a full scale nitrification-denitrification (ND) Excess biological removal (EBPR) activated sludge (AS) systems fed municipal wastewater and operated at a long sludge age (>30d), (ii) a laboratory scale UCT process configured NDEBPR AS system operated at a short sludge age (10d) and (iii) a laboratory scale MLE process configured ND AS system operated at a short sludge age (10d). The detailed description of the systems used in the experimental campaign are given in Chapter 2. The raw data collected from the ABMP reactors fed the various WAS are given in Table C 7 above. Figures C 5 (a and b) below show, for the different solids retention times, plots for specific hydrolysis rates (r_{HYD}/Z_{AD}) versus residual BPO (S_{bpe}) per acidogenic biomass (S_{bp} / Z_{AD}) values, when directly calculated from experimental data and compared to those predicted using the using the determined saturation kinetic constants from the curve fitting function of R program. The calculated data used in developing the plots is given in Table C 9. When preparing these plots, the measured ABMP data that did not conform to the form of the saturation equations was ommited to ensure reasonable correlation coefficient (R^2) values. The main focus of this hydrolysis kinetics evaluation is determining the unbiodegradable fraction $f_{SL'up}$ of the sludge and the hydrolysis kinetic rate to be able to calculate as accurately as possible the biodegradable COD utilized, for input to the stoichiometric model (Ikumi et al., 2015). Therefore, finding a precise $f_{SL'up}$ is deemed more important than accurate kinetic constants determination because even inaccurate kinetic constants do not change S_{bpe} much (< 0.1gCOD/*l*) particularly at long sludge age. However, an inaccurate value of $f_{SL'up}$ has a much bigger effect on ΔS_{bp}.

Table C 9. Determination of saturation hydrolysis kinetic constants for AD of WAS from the full scale ZWWTW and lab scale NDEBPR systems

ABMP Test Feed	Time	Test ABMP COD	Control ABMP COD	Residual BPO COD (S_{bp})	AD biomass (Z_{AD}^{*})	Volumetric hydrolysis rate (r_{HYD})	S_{bp}/Z_{AD}	Specific r_{HYD} (Mead.)	Specific r_{HYD} (Pred.)
	(days)	(gCOD)	(gCOD)	(gCOD)	(gCOD)	(gCOD/l/d)	(gCOD/ gCOD)	gCOD/ (gCOD.l.d)	gCOD/ (gCOD.l.d)
ZWWTW full Scale NDEBPR AS system (Rs>30d) WAS (k_M = 2.51; K_S = 4.04; $f_{SL'up}$ = 0.51)	1	7.78	5.53	0.94	0.37				
	2	8.78	4.25	2.8	0.15	0.33	18.31	2.16	2.06
	5	7.9	4.41	1.73	0.27	0.35	6.51	1.32	1.55
	6	7.45	4.97	0.92	0.35	0.43	2.59	1.21	0.98
	9	7.09	4.52	0.76	0.36	0.3	2.11	0.84	0.86
	10	7	4.48	0.7	0.37	0.28	1.91	0.76	0.81
	11	6.8	3.99	0.75	0.36	0.25	2.1	0.7	0.86
	14	6.64	4.89	0.07	0.42	0.25	0.16	0.58	0.1
	16	6.43	4.03	0.33	0.39	0.2	0.85	0.51	0.44
	24	6.07	3.91	0.01	0.4	0.15	0.03	0.37	0.02
	40	5.58	4.28	0	0.37	0.09	0	0.24	0
UCT MBR NDEBPR Lab Scale AS system (Rs = 10d) WAS (k_M = 2.64; K_S = 9.11; $f_{SL'up}$ =0.28)	0	5.6	4.8	2.26	0.04				
	2	4.44	2.92	2.02	0.06	0.12	33.46	2.05	2.07
	5	3.68	2.76	1.26	0.14	0.2	8.81	1.42	1.3
	9	3.6	3.48	0.77	0.19	0.17	3.98	0.87	0.8
	12	3.24	2.68	0.82	0.18	0.12	4.45	0.67	0.87
	25	2.76	2.68	0.29	0.23	0.08	1.3	0.36	0.33
	27	2.52	2.6	0.07	0.25	0.08	0.29	0.33	0.08
	29	3.16	3.36	0.37	0.21	0.07	1.73	0.31	0.42
	40	2.36	2.28	0.09	0.23	0.06	0.39	0.24	0.11

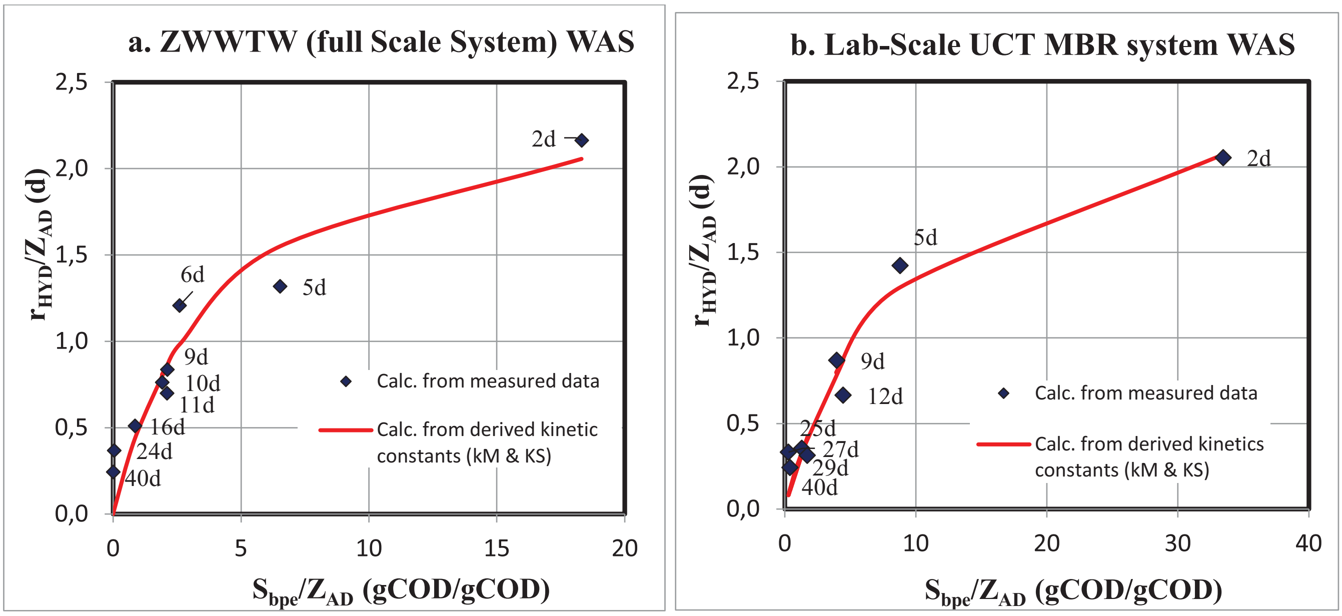


Figure C 5 (a and b). Hydrolysis saturation kinetics formulation curves plotted using experimental data and calculated from kinetic constants acquired using the R programme non-liner regression function for the (a) ZWWTW WAS and (b) UCT MBR WAS.

It can be noted that a reasonably good match is obtained between the experimental and model predicted residual S_{bp} concentrations. Hence, we can adopt these kinetic constants in the AD model used to simulate the AD system fed this same WAS.

Table C 9 shows the saturation kinetic constants for the saturation kinetics hydrolysis constants together with the unbiodegradable COD fraction of the WAS fed to the AD batch tests, for ZWWTW WAS (i.e. k_M = 2.51; K_S = 4.04; $f_{SL'up}$ = 0.51) and the UCT MBR WAS (i.e. k_M = 2.64; K_S = 9.11; $f_{SL'up}$ = 0.28). Mass components of the UCT MBR WAS, fed to the AD batch tests were calculated in Table C 10 below and the theoretical the UPO fraction of WAS ($f_{SL'up}$) from determined to be 0.34gCOD/gCOD, using the activated sludge model endogenous fraction values of OHO and PAO (f_{E_OHO} = 0.20; f_{E_PAO} = 0.25 respectively), which is marginally higher than the given 0.28 value. However, according to Table C 11, the $f_{SL'up}$ of 0.28 would require for the f_{EG} value to be decreased to 0.17gCOD/gCOD.

Table C 10. Estimating the PAO unbiodegradable fraction in AD systems

	Active OHO	Endogenous OHO	Active PAO	Endogenous PAO	USO	Total
COD concentrations of WAS components (see Table C 3)	372	163.3	3043.9	278.5	70.1	3927.8
Mass in 2.5 litre WAS fed to AD batch reactor.	930.0	408.3	7609.8	696.3	175.3	9819.5
I UPO mass expected in Effluent at end of AD batch test (Theoretical)	186.0[a]	408.3	1902.4[b]	696.3	175.3	3192.9
I. Where UPO at end of batch test for Active OHO and PAO are (a) f_{EH} * Active OHO & (b) f_{EG} * Active PAO respectfully. The f_{EH} of 0.2 and f_{EG} of 0.25 from Henze et al. (2008) were applied to get the values of 186gCOD and 1902gCOD respectfully. The endogenous OHO and PAO values were deemed to stay the same without any change due to AD bioprocesses. This results in the UPO mass of 3192.9mgCOD that results in the $f_{SL'up}$ of 0.34gCOD/gCOD.						
II. For a given (measured from the AD batch test) $f_{SL'up}$ value of 0.28 (see Table C 9) the same procedure as indicated in (I) above (i.e. no change in endogenous mass for OHO and PAO, and maintaining f_{EH} of 0.2) requires for an f_{EH} value of 0.17gCOD/gCOD.						

Table C 11 (a, for ZWWTW WAS and b, for UCT MBR WAS) below show a comparison of the experimentally determined and model predicted (using Equation C20) biodegradable COD concentrations (plots shown in Figures C 6 a and b) for the AD batch reactor at the different time points. The correlation between measured and predicted COD removal would serve as step towards verification of the kinetic constants obtained using the non-linear regression technique, as discussed earlier.

Table C 11. Measured and Model Predicted Residual Biodegradable Particulate COD concentration (S_{bp}) and associated COD Removal (%)

a. Full Scale ZWWTW WAS ABMP					b. Lab Scale UCT MBR WAS ABMP				
Time (days)	Residual Total BPO COD (S_{bp})		COD Removal (%)		Time (days)	Residual Total BPO COD (S_{bp})		COD Removal (%)	
	From Measd. Data	From Model Predictions	From Measd. Data	From Model Predictions		From Measd. Data	From Model Predictions	From Measd. Data	From Model Predictions
0	3.54	3.54	0.00	0.00	0	2.30	2.30	0.00	0.00
1	1.31	3.35	30.80	2.62	2	2.08	2.13	6.87	5.40
2	2.95	3.12	8.11	5.74	3	2.04	2.02	8.12	8.82
3	1.73	2.86	24.99	9.39	5	1.40	1.76	28.13	16.98
5	1.99	2.23	21.39	18.12	6	2.90	1.61	0.00	21.59
6	1.27	1.88	31.36	22.91	7	1.70	1.46	18.75	26.40
7	2.11	1.54	19.73	27.65	8	0.88	1.30	44.38	31.25
8	2.27	1.22	17.52	31.99	9	0.96	1.15	41.87	35.98
9	1.13	0.96	33.35	35.65	11	1.60	0.87	21.88	44.56
10	1.06	0.75	34.20	38.48	12	1.00	0.76	40.63	48.22
11	1.10	0.61	33.63	40.49	23	1.24	0.22	33.12	64.86
14	0.49	0.51	42.07	41.84	25	0.52	0.20	55.63	65.66
16	0.72	0.26	38.98	45.24	27	0.32	0.18	61.88	66.26
20	1.65	0.25	26.04	45.50	29	0.58	0.16	53.75	66.75
24	0.41	0.23	43.20	45.73	40	0.32	0.11	61.88	68.52
29	0.98	0.21	35.32	45.95					
40	0.03	0.14	48.50	46.92					

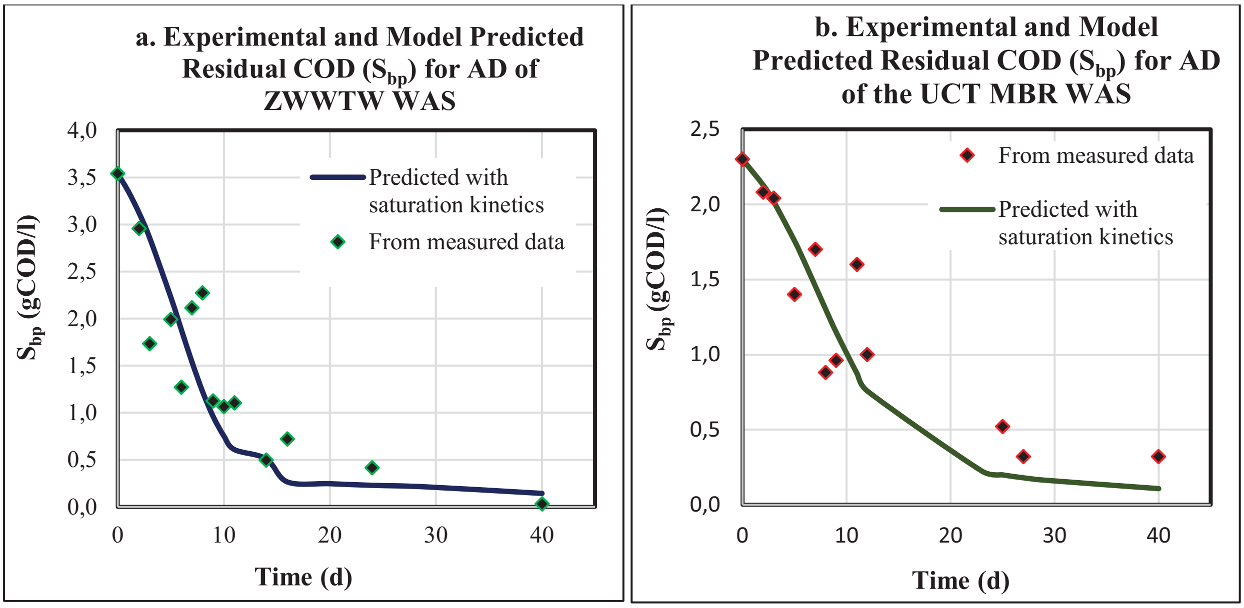


Figure C 6. Comparison of experimentally determined reactor biodegradable COD concentration (S_{bp}, gCOD/l) with those predicted using the derived saturation kinetic constants (see Table C 9) for (a) the ZWWTW WAS and (b) the UCT MBR WAS at different solid retention times of the batch AD period.

PHOSPHATE RELEASE DURING BATCH- AD OF NDBEPR WAS

Apart from COD removal, the AD batch tests were also useful to observe the rate of AD phosphorus release. For the AD batch tests that was fed the UCT MBR WAS, Ikumi and Ekama (2019) report that there is potential for polyphosphate (PP) breakdown via (i) a similar manner as would have occurred in the anaerobic environment of the parent AS system or (ii) with the ultimate death and breakdown of PAO mass. This PP ($Mg_cK_dCa_ePO_3$) breakdown would result in OP and metals release (Mg^{2+}, K^+ and Ca^{2+}) into the aqueous phase. Consequently, there would be mineral precipitation potential due to the high concentrations of these ions. Mainly, Mg^{2+} and OP would react with NH_4^+ (available from the release of N organically bound in disintegrating WAS biomass) to form struvite ($MgNH_4PO_4.6H_2O$). According to Musvoto et al. (2000), other precipitates that could form include newberyite ($MgHPO_4$), amorphous calcium phosphate ($Ca_3(PO_4)_2$), calcite ($CaCO_3$) and magnesite ($MgCO_3$). The potassium struvite ($MgKPO_4.6H_2O$) is not expected to precipitate (Harding et al., 2010; Ikumi et al., 2015), hence the concentration of K^+ in the aqueous phase shall be a good gauge on the PP release rate (this shall be confirmed by comparing the measured total K against the filtered K in the aqueous phase at the end of the batch AD experiment).

To quantify the polyphosphate available in the UCT MBR WAS required reconciliation of P removal and metal (Mg^{2+}, K^+ and Ca^{2+}) removal, together with reactor ISS generation using the method shown by Ikumi (2011). The P removed as part of the solid phase in the WAS could exit as the organically bound P in biomass (for both OHOs and PAOs) and endogenous residue (this was taken as 0.025 mg P/mgVSS as recommended by Wentzel et al. (1990)) or the P used to form PP ($Mg_cK_dCa_ePO_3$), that is stored in the PAOs. In the AS system (i.e. calculation of the total P that for the NDEBPR AS system. This PP contributes to the higher ISS values observed in EBPR systems, containing PAOs – according to Ekama and Wentzel (2004), OHOs have an ISS content of 0.15 mgISS/mgOHOVSS while the ISS content of PAOs increases significantly due to PP that has 3.826 mgISS/mg PP-P. The maximum PP/VSS ratio for PAOs is accepted at 0.35 mg P/mg VSS, hence the PAOs a maximum P/VSS of 0.38 mg P/mg PAOVSS (i.e. 0.025 + 0.35) (Wentzel et al., 1990). To allow for the P and metals removals shown and to ensure good mass and charge balance, the elemental composition of PP was determined as $Mg_{0.23}K_{0.34}Ca_{0.1}PO_3$, using the methods shown by Ikumi (2011). Hence the PP molar mass is calculated to be 101.89 g and the K contribution is 13.29 g (i.e. from 0.34 mols in PP × 39.098 gK/mol) and the mass/K ratio of PP is 7.66 g PP/gK. For the PP concentration in WAS (694.7 mg P/l) that allows for the measured P removal in the AS system, the inorganic particulate K (as component to PP) is 297.1 mgK/l. The soluble K in the WAS is given as 186 mgK/l (Table C 2), hence the total K concentration is calculated to be 483.1 mgK/l (i.e. the 297.1 + 186). Hence at the beginning (t=0) of the AD batch test for UCT MBR WAS, the contribution of total and soluble K from WAS is 0.24 gK/l and 0.09 gK/l respectfully (i.e. calculated from 0.483 g/2 and 0.186 g/2, since half the WAS substrate occupies half the volume (2.5 litres) of the AD batch reactor volume (5 l), the other half is fed control inoculum). To determine the K released from the UCT MBR WAS as AD batch test substrate ($K_{substrate}$) during the AD batch tests, a similar approach as that for COD removal was adopted, whereby the mass measured in the control ($K_{Control}$, which is halved because the inoculum seed sludge in the AD batch test reactor was equivalent to half of the control AD batch reactor mass) is subtracted from the mass measured in the test reactor (K_{Test}); $K_{Substrate} = K_{Test} - K_{control}/2$. With this approach, the K released from the WAS appears to be consistent from the period of around 6 days, with all the PP released within the 10-day period, as was also observed by Harding et al. (2010). The quantity of total K at this period (after 10 days) is about 0.29 g/l. This includes the original 0.24 g/l of total K from the MBR WAS (now all available in soluble form due to PP release), and the added quantity of K in the inoculum seed (which is about 0.05 g/l). With this maximum $K_{substrate}$ that could be released from the PP (K_{sub_max} = 0.29 g/l) determined the particulate K, which was component to in the substrate PP (K_{subPP}), could be calculated as by subtracting the total the $K_{substrate}$ release values from K_{sub_max}. At the point where all the K is released from PP, the K_{subPP} is equal to zero (i.e. within around 10 days of the AD batch test). The PP mass concentration (i.e. in mg PP/l) for each time period (X_{PP_t}) could then be calculated by multiplying the K_{subPP} value by the PP mass/K ratio (i.e. the 7.66 g PP/gK is assumed to remain constant), i.e.:

$$X_{PPt} = K_{subPP\_t} * (\text{g per mol PP})/\text{gK per mol PP}) = K_{subPP\_t} * 7.66 \qquad [C21]$$

The initial PAO biomass concentration (X_{BG} at t = 0; X_{BG_t0}) was estimated by converting the PAO mass estimate of 7.6 g from Table C 10 into its concentration in the AD batch reactor; hence dividing by the AD batch volume of 5 litres to give 1.52gPAO/l. The PAO concentration at each time period of the AD batch test (X_{BG_t}) was then calculated by multiplying this initial PAO concentration (X_{BG_t0}) by the fraction of residual S_{bp} (i.e. $f_{Sbp\_t} = S_{bp}$ at time (t) ÷ initial S_{bp} at time zero) due to sludge hydrolysis during the AD process (i.e. $X_{BG\_t} = f_{Sbp\_t} \times X_{BG\_t0}$). With the PAO and PP concentrations estimated at the various time period of the AD batch test, the corresponding X_{PP_t}/X_{BG_t} values could also be determined. Moreover, the rate of PP release ($r_{PP} = \delta X_{PP}/\delta t$) could be calculated for each time point as $\Delta X_{PP}/\Delta t = (X_{PPt} - X_{PP\ time\ 0})/\Delta t$ and the specific r_{PP} at that given time $(r_{PP}/X_{BG})_t$ is then given by:

$$(r_{PP}/X_{BG})_t = \{(X_{PPt} - X_{PP\ time\ 0})/\Delta t\}/ X_{BG\_t} \qquad [C22]$$

The PP release saturation kinetic formulation adopted in Activated sludge model no 2. (Henze et al., 1995) and PWMSA (Ikumi et al., 2015), for anaerobic PP is release with PHB uptake, is:

$$r_{PP} = \frac{q_{PHA} \cdot \left(\frac{X_{PP}}{X_{BG}}\right)}{K_{PP} \cdot \left(\frac{X_{PP}}{X_{BG}}\right)} \cdot X_{BG} \qquad [C23]$$

Where r_{PP} is the volumetric rate of PP release, q_{PHA} is the rate constant for PP release with PHB storage, K_{PP} is the saturation coefficient for PP, X_{PP} is the PP concentration (in PWMSA, the units are given as mg PP/l) and X_{BG} (mgVSS/l) is the concentration of PAO biomass.

With $(r_{PP}/X_{BG})_t$, X_{BG_t} and X_{PP_t}/X_{BG_t} calculated for each time interval, the hydrolysis rate kinetic constants (q_{PHA} and K_{PP} for the PP release saturation kinetics formulation; see Equation C23) can be obtained through non-linear regression methods (with the R software used, as was done for the previously described determination of the hydrolysis kinetic constants). Using the initial X_{PP} concentration at time t = 0 and the determined kinetic constants (q_{PHA} and K_{PP}), the transient terms in the biological kinetic equations with finite difference terms can be determined, i.e. where Δt is the time interval between time 2 and time 1:

$$\delta X_{PP}/\delta t = (X_{PP\ time\ 1} - X_{PP\ time\ 2})/\Delta t;\ \text{hence}\ X_{PP\ time\ 2} = X_{PP\ time\ 1} - \Delta t\ (\delta X_{PP}/\delta t) \qquad [C24]$$

where Δt is the time interval between time 2 and time 1, selected to have a low step length (Δt = 10 min; i.e. 5760 steps to make 40 days of integration) to ensure a stable integration. The $\delta X_{PP}/\delta t$ is calculated using Equation C25 for each time step, i.e.:

$$r_{PP_{time1}} = \frac{q_{PHA} \cdot \left(\frac{X_{PP_{time1}}}{X_{BG_{time1}}}\right)}{K_{PP} \cdot \left(\frac{X_{PP_{time1}}}{X_{BG_{time1}}}\right)} \cdot X_{BG_{time1}} \qquad [C25]$$

The PP release % is then calculated as $100 * (X_{PP\ time\ 0} - X_{PP\_t}) / X_{PP\ time\ 0}$, for the PP determined via Equation C21 and predicted using Equation C25. Table C 12 below shows the calculated values used in the above-described procedure, towards using the AD batch results to calibrate the PP release kinetics.

Table C 12. Determination of PP release (%) from AD batch test data and derived PP release kinetic constants

Time	$K_{substrate}$ (K^+)	K_{subPP} (PP-K)	X_{PP} (PP)	X_{BG} (PAOs)	X_{PP}/X_{BG} (PP/PAO)	r_{PP} ($\delta X_{PP}/\delta t$)	r_{PP}/X_{BG}		PP Released	
							From data	predicted	From data	Model predicted
(days)	(gK/l)	(gK/l)	(gPP/l)	(gVSS)	gPP/ gPAOVSS	gPP/l/d	gPP/ gPAOVSS	gPP/ gPAOVSS	%	%
0	0.10	0.19	1.59	1.52	1.04				0	0
1	0.19	0.09	0.76	1.46	0.52	0.83	0.57	0.49	52.20	48.72
2	0.23	0.06	0.49	1.39	0.35	0.55	0.39	0.48	69.16	90.77
3	0.27	0.02	0.14	1.31	0.11	0.48	0.37	0.39	90.89	100.00
5	0.27	0.02	0.15	1.12				0.40	90.36	100.00
6	0.28	0.01	0.06	1.01	0.06	0.25	0.25	0.29	96.18	100.00
7	0.28	0.01	0.05	0.90	0.06	0.22	0.24	0.27	96.71	100.00
8	0.28	0.00	0.01	0.78	0.01	0.20	0.25	0.09	99.36	100.00
9	0.29	0.00	0.00	0.67	0.00	0.18	0.26	0.00	100.00	100.00
UCT2-C1 (Q_{pha} = 0 52; KS_{PP}=0.05)										

DETERMINATION OF WAS ELEMENTAL FORMULATION

Parameter estimation (PE) is a process that adjusts the input parameters of a model, by using collected experimental data as an objective for the simulated data. This occurs via the calculation of minimum error towards the identification of the closest match between the simulated model variable components and experimentally measured variables. Therefore, in order to find a substrate (in this case WAS) composition that better fits the observed AD batch experimental data, parameter estimation (PE) was conducted on a virtual AD batch experimental reactor that was simulated using the UCTSDM3P model (Ikumi et al., 2015; Ghoor, 2020). In this case, the parameters that were used as the unknowns were the hydrogen (H), oxygen (O), nitrogen (N) and phosphorus (P) molar fractions of the WAS biodegradable particulate organics (i.e. x, y, z, a and b values of $C_xH_yO_zN_aP_b$; the parameters used to define the elemental composition of the PAO biomass) in the WAS. Five observed or known variables were set as the simulation objectives: total COD, FSA, OP, VSS concentrations and the system pH. A PE tool found in WEST ® software (where the virtual AD batch reactor is simulated using the UCTSDM3P model) was then used to perform hundreds of iterative simulations, while adjusting the parameterized molar fractions of the substrate (PAO biomass), until the input substrate elemental composition achieved the lowest error, in the comparison of the AD batch test model predictions to the AD batch test experimental data (i.e. those set as simulation objectives) (Botha & Ekama, 2015; Gaszynski et al., 2019).

The following PE procedure, similar to that as used by Botha and Ekama (2015) was applied towards simulation of the experimental data within the AD batch experimental environment:

i. Setting the initial values in the 5-litre batch AD virtual systems to zero, apart from 5000 *ml* of water comprising some as the initial reactor contents in order to prevent model errors that would occur due to initialisation equations that require division by mass of water in the system (i.e. the mass of H_2O has to then be > 0). Table C 13 shows the start and end values of the batch AD reactors that were used to form the initial reactor mass (t=0) components, prior to simulation, and the target values (i.e. the simulation objectives) for the PE procedure, when simulating the virtual batch AD reactor in WEST®.

Table C 13. AD batch reactor initial and end point concentrations for selected variables

ABMP Reactor set up		period	Variables								
			COD	FSA	OP	VSS	ISS	Ca	Mg	K	pH
Control ABMP values	Control 1	t = 0	2560.00	3.05	44.51	1687.84	493.00	14.20	10.95	99.00	7.01
		t = end	1140.00	11.52	52.95	728.38	249.00	14.27	5.77	139.00	6.89
	Control 2	t = 0	2400.00	2.97	42.24	1579.73	299.00	13.84	10.13	101.50	6.90
		t = end	1140.00	11.86	50.40	728.38	230.00	16.67	7.70	130.00	6.84
	Control Average	t = 0	2480.00	3.01	43.38	1633.78	396.00	14.02	10.54	100.25	6.96
		t = end	1140.00	11.69	51.67	728.38	239.50	15.47	6.74	134.50	6.87
Measured Test ABMP Values	MLE Test	t = 0	4800.00	2.96	45.19	3201.35	914.00	21.30	12.56	108.00	6.98
		t = end	2000.00	18.97	68.49	1309.46	445.00	29.82	16.80	151.00	6.72
	UCT Test	t = 0	5600.00	2.76	187.08	3741.89	1180.00	42.96	48.50	247.00	7.08
		t = end	2360.00	22.39	326.53	1552.70	1225.00	26.93	86.99	499.00	6.69
Equivalent Control concentrations relative to Test ABMPs	Control 1 (C1)	t = 0	1280.00	1.53	22.26	843.92	246.50	7.10	5.47	49.50	
		t = end	570.00	5.76	26.48	364.19	124.50	7.13	2.89	69.50	
	Control 2 (C2)	t = 0	1200.00	1.48	21.12	789.86	149.50	6.92	5.07	50.75	
		t = end	570.00	5.93	25.20	364.19	115.00	8.33	3.85	65.00	
	Control Avg. (CA)	t = 0	1240.00	1.50	21.69	816.89	198.00	7.01	5.27	50.13	
		t = end	570.00	5.84	25.84	364.19	119.75	7.73	3.37	67.25	
Calculated Substrate	MLE – C1	t = 0	3520.00	1.44	22.94	2357.43	667.50	14.20	7.09	58.50	
		t = end	1430.00	13.21	42.02	945.27	320.50	22.69	13.92	81.50	
	MLE – C2	t = 0	3600.00	1.48	24.07	2411.49	764.50	14.38	7.50	57.25	

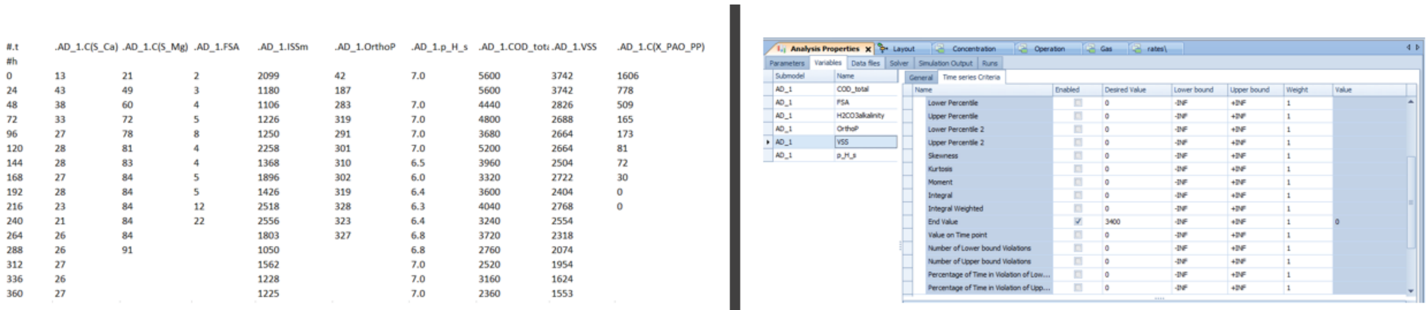
			Variables								
ABMP Reactor set up		period	COD	FSA	OP	VSS	ISS	Ca	Mg	K	pH
concentrations in ABMP Tests		t = end	1430.00	13.04	43.30	945.27	330.00	21.49	12.95	86.00	
	MLE – CA	t = 0	3560.00	1.46	23.51	2384.46	716.00	14.29	7.29	57.88	
		t = end	1430.00	13.13	42.66	945.27	325.25	22.09	13.43	83.75	
	UCT – C1	t = 0	4320.00	1.24	164.82	2897.97	933.50	35.86	43.03	197.50	
		t = end	1790.00	16.63	300.06	1188.51	1100.50	19.80	84.11	429.50	
	UCT – C2	t = 0	4400.00	1.28	165.96	2952.03	1030.50	36.04	43.44	196.25	
		t = end	1790.00	16.46	301.34	1188.51	1110.00	18.60	83.14	434.00	
	UCT – CA	t = 0	4360.00	1.26	165.39	2925.00	982.00	35.95	43.23	196.88	
		t = end	1790.00	16.55	300.70	1188.51	1105.25	19.20	83.62	431.75	

The control AD batch reactor is simulated first in order for the information generated during this PE (i.e. the characteristics of the inoculum seed, is added prior to simulation of the test AD batch reactor, which is simulated afterwards. Hence, in the simulated control AD batch reactor, the PE and measured output variables are used to determine the elemental composition of biomass in the inoculum seed. This process involves

a. Estimating the biomass concentration at the beginning (t = 0) of the batch AD control reactor. Because the inoculum seed sludge is sourced from the steady state AD system, the steady state AD equations of Sötemann et al. (2005) were used, with a combined AD organism yield (Y_{AD}) value of 0.113, to estimate the biomass concentration. This biomass concentration is keyed into WEST® as the initial total AD biomass concentration for the AD batch reactor to be simulated.
b. The AD biomass components, defined in the UCTSDM3P model (i.e. acidogens, acetogens, acetoclastic methanogens and hydrogenotrophic methanogens) are then fractionated from the total AD biomass concentration (determined in (a) above) using fractionating parameters (whereby each AD biomass component is given a contributing value as a fraction of the total biomass such that all the AD biomass component fractions add up to a value of 1). The fractionating parameters and the total AD biomass concentration are then used in calculation of the component AD biomass concentrations, during the batch AD simulation.
c. The experimentally measured data for the batch AD control reactor is entered into WEST® in a text file that contains the measured batch AD output values of variables such as COD, VSS, ammonia (FSA), orthophosphates (OP), pH and alkalinity (see Figure C 7 below).
d. The required parameters (those that would define the elemental composition of the sludge being digested, i.e.: the y, z, a and b values of $C_1H_yO_zN_aP_b$) are inputted as the WEST® PE target (adjustable) parameters for the PE iterative simulations and given realistic constraints (upper and lower bound values) to adhere to.
e. The WEST PE tool is switched on to carry out multiple iterations, whereby (via parameter variations within the given constraints) the theoretically predicted variables are adjusted towards meeting the experimentally measured data. The multiple iterations progress until the combination of parameter values allowing for the best match between model predicted and experimentally observed variables is achieved.

ii. A batch AD test reactor that replicates virtually replicates the one run experimentally (i.e. with both inoculum and organics added) is simulated. This batch AD test reactor simulation is subsequent to the batch AD control reactor simulation, with the ‘initial parameters’ that are associated with the inoculum seed and the AD biomass present, having already been determined from the batch AD control reactor simulation. From the batch AD test reactor simulation, the elemental composition of the substrate (in this case WAS biomass) can now be calculated, using the same PE exercise described above (i.e. steps c to e of (ii)).

Figure C 7 shows an example of the WEST® simulation platform set up, including the batch AD configuration for parameter estimation, the parameters defined in WEST® for proposed simulation, the variables added as simulation objectives and the iterative simulation process.



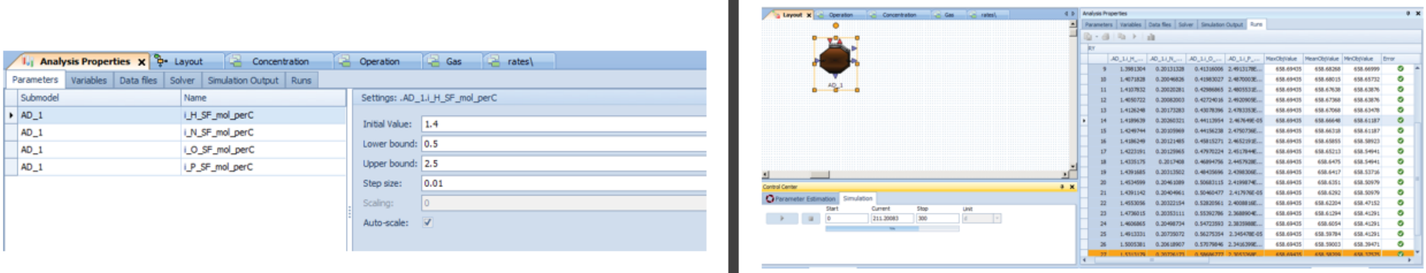
#.t #h	.AD_1.C(S_Ca)	.AD_1.C(S_Mg)	.AD_1.FSA	.AD_1.ISSm	.AD_1.OrthoP	.AD_1.p_H_s	.AD_1.COD_tot	.AD_1.VSS	.AD_1.C(X_PAO_PP)
0	13	21	2	2099	42	7.0	5600	3742	1606
24	43	49	3	1180	187		5600	3742	778
48	38	60	4	1106	283	7.0	4440	2826	509
72	33	72	5	1226	319	7.0	4800	2688	165
96	27	78	8	1250	291	7.0	3680	2664	173
120	28	81	4	2258	301	7.0	5200	2664	81
144	28	83	4	1368	310	6.5	3960	2504	72
168	27	84	5	1896	302	6.0	3320	2722	30
192	28	84	5	1426	319	6.4	3600	2404	0
216	23	84	12	2518	328	6.3	4040	2768	0
240	21	84	22	2556	323	6.4	3240	2554	
264	26	84		1803	327	6.8	3720	2318	
288	26	91		1050		6.8	2760	2074	
312	27			1562		7.0	2520	1954	
336	26			1228		7.0	3160	1624	
360	27			1225		7.0	2360	1553	

Submodel	Name
AD_1	COD_total
AD_1	FSA
AD_1	H2CO3alkalinity
AD_1	OrthoP
AD_1	VSS
AD_1	p_H_s

Name	Enabled	Desired Value	Lower bound	Upper bound	Weight	Value
Lower Percentile	☐	0	-INF	+INF	1	
Upper Percentile	☐	0	-INF	+INF	1	
Lower Percentile 2	☐	0	-INF	+INF	1	
Upper Percentile 2	☐	0	-INF	+INF	1	
Skewness	☐	0	-INF	+INF	1	
Kurtosis	☐	0	-INF	+INF	1	
Moment	☐	0	-INF	+INF	1	
Integral	☐	0	-INF	+INF	1	
Integral Weighted	☐	0	-INF	+INF	1	
End Value	☑	3400	-INF	+INF	1	0
Value on Time point	☐	0	-INF	+INF	1	
Number of Lower bound Violations	☐	0	-INF	+INF	1	
Number of Upper bound Violations	☐	0	-INF	+INF	1	
Percentage of Time in Violation of Low...	☐	0	-INF	+INF	1	
Percentage of Time in Violation of Upp...	☐	0	-INF	+INF	1	

a. Text file that contains the measured batch AD output values of variables

b. The selection of variables to be added as simulation objectives



Submodel	Name
AD_1	i_H_SF_mol_perC
AD_1	i_N_SF_mol_perC
AD_1	i_O_SF_mol_perC
AD_1	i_P_SF_mol_perC

Settings: .AD_1.i_H_SF_mol_perC
Initial Value: 1.4
Lower bound: 0.5
Upper bound: 2.5
Step size: 0.01
Scaling: 0
Auto-scale: ☑

c. Addition of WEST® PE target (adjustable) parameters

d. The iterative simulation process during WEST® parameter estimation

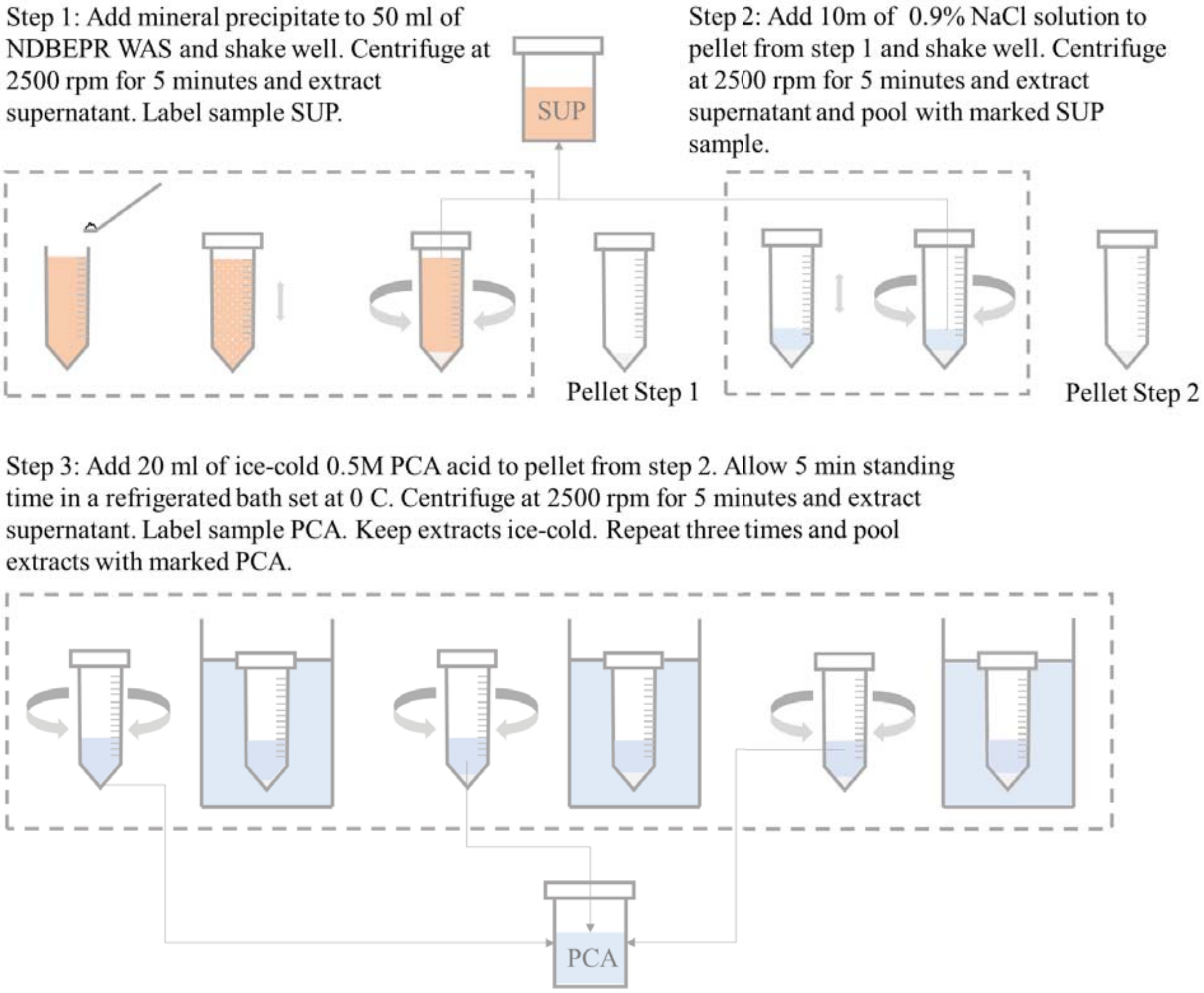
Figure C 7. An example of the WEST® parameter estimation (PE) set up and process

ISS Characterization Test

In this study the ISS characterisation test was an ancillary yet necessary aspect. Towards the development this procedure, a modified cold PCA fractionation procedure (MCPFP) of De Haas et al. (2000) is augmented to broadly fractionate EBPR sludge-P content into mineral precipitate-P and polyphosphate-P. The MCPFP augmentation involves including other analytical measurements to fully characterize inorganic solids into their component concentrations (see Table C 14 and Figure C 8).

Table C 14. Analytical measurements on ISS characterization test samples

Test Case	SUP	PCA	RES
A	Mg^{2+} FSA OP	Mg_T Mg^{2+} TKN FSA TP OP	Mg_T Mg^{2+} TKN FSA TP OP
B	Ca^{2+} OP	Ca^{2+} Ca_T TP OP	Ca^{2+} Ca_T TP OP
C	Mg^{2+} Ca^{2+} FSA OP	Mg^{2+} Mg_T Ca^{2+} Ca_T FSA TKN TP OP	Mg^{2+} Mg_T Ca^{2+} Ca_T FSA TKN TP OP
D-G	Mg^{2+} Ca^{2+} FSA OP K^+	Mg2+ MgT Ca2+ CaT FSA TKN TP OP K_T K^+	Mg2+ MgT Ca2+ CaT FSA TKN TP OP K_T K^+
Where SUP denotes supernatant after centrifuging the sample, prior to PCA addition, the PCA denotes the extracted solution sampled after centrifuging post PCA addition and the RES denotes the remnant residue extracted after centrifuging the sample. The procedure towards obtaining these samples is detailed below.			



Step 1: Add mineral precipitate to 50 ml of NDBEPR WAS and shake well. Centrifuge at 2500 rpm for 5 minutes and extract supernatant. Label sample SUP.

Step 2: Add 10m of 0.9% NaCl solution to pellet from step 1 and shake well. Centrifuge at 2500 rpm for 5 minutes and extract supernatant and pool with marked SUP sample.

Step 3: Add 20 ml of ice-cold 0.5M PCA acid to pellet from step 2. Allow 5 min standing time in a refrigerated bath set at 0 C. Centrifuge at 2500 rpm for 5 minutes and extract supernatant. Label sample PCA. Keep extracts ice-cold. Repeat three times and pool extracts with marked PCA.

Figure C 8. Schematic diagram of the ISS characterization test

Figure C 8 shows a schematic of the ISS characterization test. The experimental procedure adopted in this study is similar to De Haas et al. (2000), although additional analytical measurements were taken on the extractants. First, a 50 ml sample was centrifuged in a centrifuge tube at 3000 rpm for five minutes. The supernatant was extracted and transferred to a sampling flask labelled SUP. To the pellet from this first step, 10 ml of 0.9% NaCl solution was added. The supernatant was then extracted after further centrifugation. The extract was pooled together in sampling flask SUP. For each test case the SUP content was tested for soluble ion concentrations as outlined in figure C 9. This step aimed at determining the concentrations of soluble or loosely bound ions inherently present in the sample.

Using the pellet from step 2, an ice-cold acid extraction was then carried out. A solution of 0.5M perchloric acid was made up using a standard concentrated solution of perchloric acid (>98%). The acid solution was allowed to reach 0°C in a freezer set to -18°C. The centrifuge tube, containing the pellet from step 2, was placed in a jacketed reactor at 0^oC. To it, 20 ml of the ice-cold 0.5M perchloric acid was added. The centrifuge tube was allowed to stand in the jacketed reactor for five minutes. Thereafter, it was centrifuged at 6000 rpm for five minutes in a refrigerated centrifuge and the acidic solution was then extracted and transferred to a sampling flask (labelled PCA). The acid extraction step was repeated three times and the acidic solutions pooled in sampling flask PCA. Immediately, analytical measurements were then taken on the PCA samples. De Haas et al. (2000) showed that cold PCA acid can effectively solubilize mineral precipitate with negligible hydrolysis of PP. In these circumstances, the ISS components are in forms that are distinguishable in analytical measurements. This is illustrated in Figure C 9.

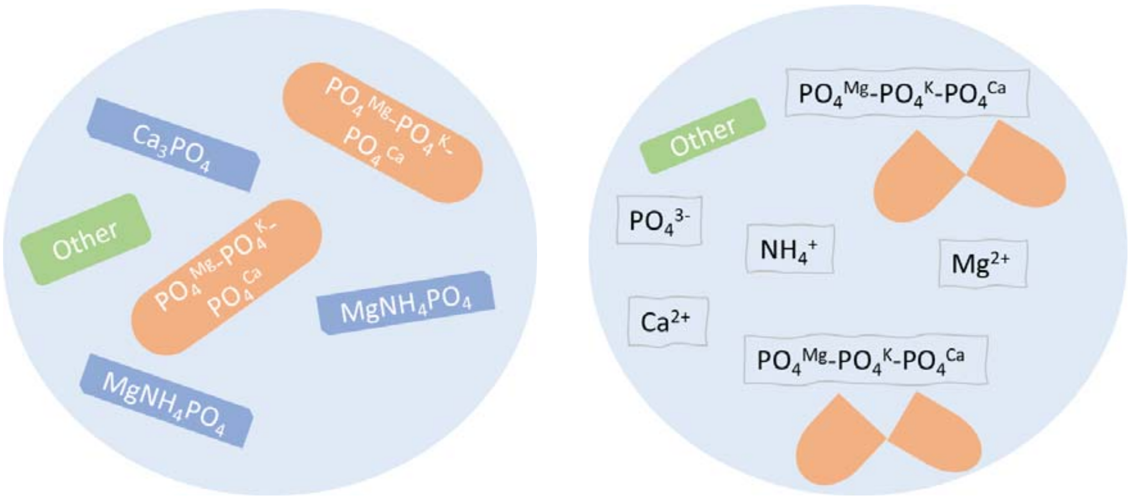


Figure C 9. Effect of cold PCA extraction of NDEBPR WAS. Left: Original NDBER WAS. Right: PCA extract

In addition to dissolving mineral precipitates, the cold PCA also lyses the bacteria cell wall and therefore all cell contents, including PP, are released into the bulk solution. However, as the extraction is carried out at a low temperature, the hydrolysis of PP is negligible in a short timespan (<5 minutes). Hence, the dissolved ion concentrations in the PCA extract corresponds to the mineral precipitates. The difference between the total soluble and ion concentration therefore corresponds to the PP ions concentrations (considering ions from the hydrolysis of biomass). In this study, the NDEBPR AS system was used to provide the sample of WAS containing PP. It was noted that the influent feed to this NDEBPR AS system was largely synthetic and soluble with a small (<30%) of filtered raw wastewater – it is therefore assumed very low concentrations of unbiodegradable particulate organic and inorganic solids were present in the influent feed. This was useful towards validation of the approach because result would not be impacted by the UPO and ISS that may have accumulated in the AS reactors when raw sewage is used. However, with this initially validated approach, the next phase would require testing the procedure against systems fed raw sewage.

Application of a Data-Modelling Procedure

A data-modelling procedure (Table C 15) was developed to allow for a rigorous and robust analysis of the data generated by the ISS characterization test. At certain points in the model, stoichiometric relations could be verified, such as the PP counter-ion molar ratios, or the Ca:P in ACP. This verification provided confidence in the data-driven model. The development of the data-modelling procedure is explained below.

Table C 15. Data-Modelling Procedure

	N	Mg	P	Ca	K	ISS
Soluble ($X_{soluble}$)	FSA_{SUP}	$Mg^{2+}{}_{SUP}$	TP_{SUP}	$Ca^{2+}{}_{SUP}$	$K^{+}{}_{SUP}$	
Struvite (X_{struv})	$a = FSA_{PCA}$	$b = a \times (24.3/14)$	$c = a \times (31/14)$	$d = 0$	$e = 0$	$\alpha = c/31 \times 245$
ACP (X_{ACP})	$f = 0$	$g = 0$	$h = PO_4^{3-}{}_{PCA} - c - 0.15w$	$i = h/31 \times (3/2) \times 40$	$j = 0$	$\Theta = h/31 \times 310$
Complex (X_{cpx})	$k = TKN_{PR} - a$	$l = Mg_{T,PR} - Mg^{2+}{}_{PCA}$	$m = r + w$	$n = Ca_{T,PR} - i$	$o = K_{T,PR} - K^{+}$	ND
Biomass (X_{bio})	$p = 0.100 \times X_V$	$q = 0$	$r = 0.010 \times X_V$	$s = 0$	$t = 0$	$\mu = 0.015 \times (X_{BH} + X_{BG})$
PP (X_{PP})	$u = 0$	$v = l$	$w = v/(24 \times 0.35) \times 31$	$x = n$	$y = o$	$\Omega = 3.19 \times w$
MLSS(X_{MLSS})	TKN_{MLSS}	$Mg_{T,MLSS}$	TP_{MLSS}	$Ca_{T,MLSS}$	$K_{T,MLSS}$	ISS

The following points gives the rationale behind the data-driven modelling procedure.

- The soluble content ($Mg^{2+}{}_{SUP}$) is obtained by measuring the total magnesium in the supernatant. The magnesium ($Mg^{2+}{}_{struv}$) in struvite is equal to the measured concentration of soluble magnesium in PCA ($Mg^{2+}{}_{PCA}$). This implies that there is negligible interference of Mg from polyP hydrolysis and complete solubilisation of struvite in PCA.
- Due to the release of PP counter-ions in the PCA extract, the measurement of soluble magnesium in the PCA extract does not correspond only to the magnesium from struvite. The analysis in test case D and E, F and G showed that FSA in the PCA extract was solely from struvite, and no contribution to FSA from biomass was observed. This has two positive implications for the data-driven model. The concentration of struvite can be obtained from the N measurements directly. Secondly, using the stoichiometric ratio of Mg:N in struvite (1:1), the soluble concentration of Mg (also P) corresponding to struvite (Mg_{st}) can be obtained.
- The magnesium content of PP phosphate (or complex magnesium, Mg_{cpx}) is given the difference between the total magnesium in the PCA and residue extract ($Mg_{T,PR}$; Which is equivalent to the total Mg in the solid phase (i.e. unfiltered – filtered Mg of sample) and the struvite magnesium concentration (Mg_{st}; calculated as shown in the above point).
- Using the molar ratio of Mg:P in the approximate formula of PP, the P content of PP was determined.
- The potassium content of each ISS component is determined as explained in data-driven model I. The K measured in the PCA extract is generated by the hydrolysis of PP, since it is deemed that there are negligible K precipitates found in the sludge samples. This way the K released could be used to calibrate the % of PP that is hydrolysed to OP in the PCA This value was parameterised as a measurable unknown α. In this study it was observed that the α value was 15% (i.e. 15% of PP is released with cold PCA extraction). The quantity of K that was originally in the PP and released to the extract was determined as the difference between the total K in the PCA and residue extract ($K_{T,PR}$; which is equivalent to the total K in the solid phase).
- The contribution of P from ACP in the PCA extract was determined by subtracting the P contribution from struvite and PP. It was previously concluded that approximately 15% of PP is hydrolysed to orthophosphates in the PCA extract, and hence this proportion was included in the formula.
- The calcium concentration in the PCA extract corresponding to ACP was determined by using the molar ratio of Ca:P in ACP ($Ca_3(PO_4)_2$) is (3:2).
- The calcium content of PP phosphate (or complex calcium, Ca_{cpx}) is given the difference between the total calcium in the PCA and residue extract ($Ca_{T,PR}$) and the ACP calcium concentration (Ca_{ACP}).
- The validity of the output from the data-driven model can be checked by comparing the measured ISS with the sum of ISS from each component.

APPENDIX D: EVALUATIVE FRAMEWORK FOR WRRFs BASED ON PERFORMANCE INDICES

The evaluation of the performance of WWTPs under different design and operational options is traditionally performed using the performance indices adopted by the IWA BSM task group (Jeppsson et al., 2007). More recently, works by De Ketele et al. (2018) provided improvements on the original formulation of the EQI and OCI equations. In spite of the improvements, the performance indices are still lacking from a point of view of resource recovery and holistic environmental impact. This Appendix provides detail on the modified EQI and OCI formulations according to Coothen (2022).

EFFLUENT QUALITY INDEX

The EQI is a useful tool to quantitatively describe effluent quality at WWTPs. It allows for the total pollutant load to a receiving water body to be quantified into a single term by applying weighting factors to each pollutant.

With the aim of becoming more environmentally conscious, it was deemed necessary to take into consideration the impact of wastewater treatment processes on the atmosphere and on land, instead of solely focusing on the impact on water. In light of the latter, three separate EQI equations were developed as described below.

EQI water

The discharge of wastewater effluent to water bodies or its reuse by irrigation in South Africa is regulated by the National Water Act, No. 36 of 1998 (1998: s39). The revision of General Authorisation under Section 39 of the Act (National Water Act, No. 36 of 1998. Regulation, 2004) specifies the volumes of wastewater effluent that can be discharged to water bodies or used for irrigation within the stipulated limitations of their respective effluent quality requirements (Nozaic & Freese, 2009).

The limiting concentrations of pollutants in wastewater effluent that may discharged into water resources at a rate not exceeding 2 ML/d (i.e. for small WWTPs) are shown in Table D 1 below. The special limit applies to all the listed water resources under the revision of General Authorisation under Section 39 of the Act (National Water Act, No. 36 of 1998. Regulation, 2004).

Table D 1. Pollutant limit values for wastewater discharges not exceeding 2 ML/d (National Water Act, No. 36 of 1998. Regulation, 2004)

Pollutant/Parameter	General limit	Special limit
Faecal Coliforms (per 100 ml)	1 000	0
Chemical Oxygen Demand (mg/l)	75	30
pH	5.5-9.5	5.5-7.5
Ammonia (ionised and un-ionised) as Nitrogen (mg/l)	36	2
Nitrate/Nitrite as Nitrogen (mg/l)	15	1.5
Chlorine as Free Chlorine (mg/l)	0.25	0
Suspended Solids (mg/l)	25	10
Electrical Conductivity (mS/m)	70 mS/m above intake to a maximum of 150 mS/m	50 mS/m above background receiving water, to a maximum of 100 mS/m
Ortho-Phosphate as phosphorus (mg/l)	10	2.5
Fluoride (mg/l)	1	1
Soap, oil or grease (mg/l)	2.5	0
Dissolved Arsenic (mg/l)	0.02	0.01

Pollutant/Parameter	General limit	Special limit
Dissolved Cadmium (mg/l)	0.005	0.001
Dissolved Chromium (VI) (mg/l)	0.05	0.02
Dissolved Copper (mg/l)	0.01	0.002
Dissolved Cyanide (mg/l)	0.02	0.01
Dissolved Iron (mg/l)	0.3	0.3
Dissolved Lead (mg/l)	0.01	0.006
Dissolved Manganese (mg/l)	0.1	0.1
Mercury and its compounds (mg/l)	0.005	0.001
Dissolved Selenium (mg/l)	0.02	0.02
Dissolved Zinc (mg/l)	0.1	0.04
Boron (mg/l)	1	0.5

The EQI$_{water}$ is formulated as shown in Equation D1 below. The original EQI expression, developed by Jeppsson et al. (2007), calculates the impact of effluent discharge on water bodies as a sum over time of the amount of each pollutant discharged per day. The EQI$_{water}$ expression of the current EQI formulation is similar to the original EQI expression, with some added modifications, which include:

1. The addition of the term X(t). This term represents any other pollutant that may be taken into consideration in future evaluations where more advanced models can predict and track more pollutants than current models do; and
2. Allowing flexibility in the calculation of pollutant weighting factors. This acknowledges that different plants or regions within the same country (or different countries) may have different effluent goals, thus allowing the EQI to be a better representation of plant performance with respect to plant-specific or regional goals. The weighting factors are calculated based on the environmental impact of each pollutant with respect to COD. (e.g. $\beta_{TSS} = \frac{COD\ limit}{TSS\ limit}$)

$$EQI_{water} = \frac{1}{T \cdot 1000} \int_{t_0}^{t_{end}} \left(\beta_{TSS} \cdot TSS(t) + \beta_{COD} \cdot COD(t) + \beta_{FSA} \cdot FSA(t) + \beta_{NO} \cdot NO(t) + \beta_{OP} \cdot OP(t) + \beta_x \cdot X(t) \right) \cdot Q_e(t) \cdot dt \qquad [D1]$$

To illustrate the above, two types of WWTPs are considered – Plant A being a small WWTP with effluent limits stipulated in Table D 2, and a larger WWTP Plant B with stricter effluent quality standards based on the special standard of the Water Act No. 54 of 1956 Regulation No. 991 (1984). From Table D 2, it can be seen that the Beta weighting factors for each plant are different. This allows the evaluation of the effluent quality using Equation D1 to be tailored towards the effluent quality goals specific to each plant.

Table D 2. Comparison of Beta factors for different WWTPs

Parameter	Plant A		Plant B	
	C$_{limit}$ (mg/l)	Beta	C$_{limit}$ (mg/l)	Beta
COD	30	1	30	1
FSA	2	15	1	30
OP	2.5	12	1	30
NO	1.5	20	1.5	20
TSS	10	3	10	3

While in the example above, the weighting factors for the EQI calculation were determined on the premise that the effluent would be discharged in water bodies, it is acknowledged that different applications of water reclamation from WRRFs have different standards to be met. The flexibility in the weighting factors and the term X(t) (which is intended to be used as a generic term for any additional component/pollutant to be considered in the EQI calculation) allow for application specific EQI evaluations.

EQI gas

Greenhouse gases, gases that trap heat in the atmosphere, are regarded as a major driver of human-induced climate change. Greenhouse gases comprise carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases such as chlorofluorocarbons. The impact of each greenhouse gas on climate change is essentially dependent on three factors:

i) The concentration of greenhouse gases on the atmosphere

ii) The length of time the gases remain in the atmosphere

iii) The Global Warming Potential (GWP) of each gas (EPA, 2017).

The expression for EQI_{gas} specific to the impact of wastewater treatment processes on the atmosphere is formulated as shown in Equation D2 below. This expression includes greenhouse gases that evolve from WWTPs bioprocesses such as CO_2, CH_4 and N_2O that escape into the atmosphere. The weighting factors assigned to each gas are set equal to their respective average global warming potentials (Table D 3) – a measure of the amount of heat greenhouse gases trap relative to CO_2 (EPA, 2017).

$$EQI_{gas} = \frac{1}{T \cdot 1000} \int_{t_0}^{t_{end}} \left(\beta_{CO_2} \cdot FCO_2(t) + \beta_{CH_4} \cdot FCH_4(t) + \beta_{N_2O} \cdot FN_2O(t) \right) \cdot dt \qquad [D2]$$

Where:

T : Total length of evaluation period (days)

β : Pollutant weighting factor

F : Flux of gas evolved (kg/d)

Table D 3. Pollutant weighting factors (gas)

Gas	GWP range	Beta value
CO_2	1	1
CH_4	28-36	32
N_2O	265-298	281

EQI sludge

The handling of sludge generated at South African WWTPs is regulated by the Guidelines for the Utilisation and Disposal of Wastewater Sludge (Snyman & Herselman, 2006a). The guidelines offer various sustainable sewage sludge management options dependent on the quality of the sludge. The selection of appropriate sludge management options requires the classification of the sludge. More specifically, characteristics of sewage sludge pertaining to microbiological parameters, stability indicators and pollutant content need to be determined.

The microbiological classification is a function of the concentration of faecal coliforms and helminth ova in the sludge. It is divided into three classes A, B and C, where class A sludges have the least allowable concentrations and class C sludges have the highest allowable concentrations. (Snyman & Herselman, 2006a)

The stability classification is deemed to be of high importance when it comes to beneficial use of sewage sludge. This is because odour is recognised as the most important factor that has an impact on public perception. Since the amount of volatile solids in the sludge directly influences the odour, it is desirable to maximise reduction of volatile solids. The stability is divided into three classes (1, 2 and 3), where each class is determined by the level of compliance to a 38% minimum reduction of volatile solids. (Snyman & Herselman, 2006a)

The pollutant classification is related to the concentration of potentially toxic metals and elements in the sludge which limit the applications of sewage sludge. The pollutant characterisation is split into three classes a, b and c, with class a having the lowest concentration limits and class c having the highest concentration limit. (Snyman & Herselman, 2006a)

Table D 4 below gives a summary of every possible sludge classification and their suitability relative to each available management options. In this diagram, “i” indicates that for this specific sludge characteristic class (i.e. microbiological, stability or pollutant), usage of the sludge is permitted without any restriction; “ii” indicates that the sludge may be used with restrictions and good management practices; “iii” indicates that the sludge may only be used under strict restrictions involving costly and major management practices; “iv” indicates that the sludge may not be used unless unique conditions are met; and “v” indicates that usage of the sludge is not permitted. While each sludge management option has distinct sludge characteristic requirements, the preferred option as stipulated in the guidelines is agricultural use (Snyman & Herselman, 2006a). It can be seen that the poorest quality sludge that may be used in agriculture with restriction is B2b classification, which would be a suitable basis for the formulation of an EQI for sludge. However, since the goal is to transition towards resource recovery, it is important to consider options such as beneficial use of sludge to rehabilitate degraded soils (Herselman & Moodley, 2009), and the use of sludge to produce commercial products such as fertiliser or certain construction materials (Herselman et al., 2009). From Table D 4, it can be seen that sludge with classification A1a is the only one that may be used in agriculture, for beneficial use and to produce saleable products. Therefore, A1a classification is most suitable for use as a basis for the formulation of the EQI for sludge (i.e. to benchmark WRRFs that include sludge re-use).

Table D 4. Sludge classification (Adapted from Snyman & Herselman, 2006a: 31)

Sludge classification	Available management options for each sludge classification														
	Agricultural use at agronomic rates			On-site or off-site disposal			Beneficial use (other than agricultural use at agronomic rates)			Thermal treatment methods			Produce saleable products		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
A1a	i	i	i	iii	i	iv	i	ii	i	v	iii	i	i	i	i
A1b	i	i	ii	iii	i	iii	i	ii	iii	v	iii	ii	i	i	iii
A1c	i	i	v	iii	i	iii	i	ii	iv	v	iii	ii	i	i	iii
A2a	i	ii	i	iii	ii	iv	i	iii	i	v	ii	i	i	iv	i
A2b	i	ii	ii	iii	ii	iii	i	iii	iii	v	ii	ii	i	iv	iii
A2c	i	ii	v	iii	ii	iii	i	iii	iv	v	ii	ii	i	iv	iii
A3a	i	v	i	iii	iv	iv	i	iv	i	v	i	i	i	v	i
A3b	i	v	ii	iii	iv	iii	i	iv	iii	v	i	ii	i	v	iii
A3c	i	v	v	iii	iv	iii	i	iv	iv	v	i	ii	i	v	iii
B1a	ii	i	i	iii	i	iv	iii	ii	i	iv	iii	i	iv	i	i
B1b	ii	i	ii	iii	i	iii	iii	ii	iii	iv	iii	ii	iv	i	iii
B1c	ii	i	v	iii	i	iii	iii	ii	iv	iv	iii	ii	iv	i	iii
B2a	ii	ii	i	iii	ii	iv	iii	iii	i	iv	ii	i	iv	iv	i
B2b	ii	ii	ii	iii	ii	iii	iii	iii	iii	iv	ii	ii	iv	iv	iii
B2c	ii	ii	v	iii	ii	iii	iii	iii	iv	iv	ii	ii	iv	iv	iii
B3a	ii	v	i	iii	iv	iv	iii	iv	i	iv	i	i	iv	v	i

Sludge classification	**Available management options for each sludge classification**														
	Agricultural use at agronomic rates			**On-site or off-site disposal**			**Beneficial use (other than agricultural use at agronomic rates)**			**Thermal treatment methods**			**Produce saleable products**		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
B3b	ii	v	ii	iii	iv	iii	iii	iv	iii	iv	i	ii	iv	v	iii
B3c	ii	v	v	iii	iv	iii	iii	iv	iv	iv	i	ii	iv	v	iii
C1a	iv	i	i	i	i	iv	iv	ii	i	i	iii	i	v	i	i
C1b	iv	i	ii	i	i	iii	iv	ii	iii	i	iii	ii	v	i	iii
C1c	iv	i	v	i	i	iii	iv	ii	iv	i	iii	ii	v	i	iii
C2a	iv	ii	i	i	ii	iv	iv	iii	i	i	ii	i	v	iv	i
C2b	iv	ii	ii	i	ii	iii	iv	iii	iii	i	ii	ii	v	iv	iii
C2c	iv	ii	v	i	ii	iii	iv	iii	iv	i	ii	ii	v	iv	iii
C3a	iv	v	i	i	iv	iv	iv	iv	i	i	i	i	v	v	i
C3b	iv	v	ii	i	iv	iii	iv	iv	iii	i	i	ii	v	v	iii
C3c	iv	v	v	i	iv	iii	iv	iv	iv	i	i	ii	v	v	iii

1 = Microbiological class 2 = Stability class 3 = Pollution class

Tables D 5, D 6 and D 7 below show the characteristics of wastewater sludge with A1a classification.

Table D 5. Microbiological class 1 (Adapted from Herselman et al., 2009:45)

Microbiological class A	Target value	Maximum permissible value
Faecal coliform (CFU/g_{dry})	<1000	10 000
Helminth $_{ova}$ (Viable ova/g_{dry})	<0.25 (or 1 ova/4 g_{dry})	1
Compliance requirements	90% compliance	The 10% samples that exceed the Target value may not exceed this value

Table D 6. Stability class 1 (Adapted from Herselman et al., 2009:46)

Stability class 1	
Product must **always** comply with one of the options below.	
Applicable Vector attraction reduction options	
Option 1	Reduce the mass of volatile solids by a minimum of 38 percent
Option 2	Demonstrate vector attraction reduction with additional anaerobic digestion in a bench-scale unit
Option 3	Demonstrate vector attraction reduction with additional aerobic digestion in a bench-scale unit
Option 4	Meet a specific oxygen uptake rate for aerobically treated sludge
Option 5	Use aerobic processes at a temperature greater than 40°C (average temperatures 45°C) for 14 days or longer (e.g., during sludge composting)
Option 6	Add alkaline material to raise pH under specific conditions
Option 7	Reduce moisture content of sludge that do not contain unstabilised solids (from treatment processes other than primary treatment) to at least 75 percent solids

Table D 7. Pollutant class a (Adapted from Herselman et al., 2009:46)

Aqua regia extractable metals (mg/kg)	Pollutant class
	a
Arsenic (As)	<40
Cadmium (Cd)	<40
Chromium (Cr)	<1200
Copper (Cu)	<1500
Lead (Pb)	<300
Mercury (Hg)	<15
Nickel (Ni)	<420
Zinc (Zn)	<2800

The expression used for the evaluation of sludge quality (EQI_{sludge}) is formulated as shown in Equation D3 below. It is based on the consideration of the pollutant class, microbiological class and stability class. The weighting factors used in the expression (Table D 8) are based on the concentration limits of pollutants and microorganisms in wastewater sludge. Similar to EQI_{water}, the weighting factors in EQI_{sludge} reflect the regional sewage sludge standards and would therefore be different for another region/country.

On the basis of the stability classification described above, a minimum reduction of volatile solids mass of 38% was chosen as the sludge stability criterion for the formulation of the EQI_{sludge}. Thus, the term $\frac{38}{x(t)}$ was introduced in the expression such that any reduction in volatile solids x(t) less than 38% will result in an increase in the EQI_{sludge} by a factor greater than 1. Conversely, a desirable reduction in volatile solids greater than 38% translates into a decrease in the EQI_{sludge} by a factor less than 1.

$$EQI_{sludge} = \frac{1}{T\cdot 1000}\int_{t_0}^{t_{end}} \frac{38}{x(t)} \cdot \big(\beta_{As}\cdot As(t) + \beta_{Cd}\cdot Cd(t) + \beta_{Cr}\cdot Cr(t) + \beta_{Cu}\cdot Cu(t) + \beta_{Pb}\cdot Pb(t) + \beta_{Hg}\cdot Hg + \beta_{Ni}\cdot Ni + \beta_{Zn}\cdot Zn + \beta_{CFU}\cdot CFU + \beta_{ova}\cdot ova\big)\cdot F\ Sludge(t)\cdot dt \qquad [D3]$$

Where:

T : Total length of evaluation period (days)
β : Pollutant weighting factor
F : Flux of sludge produced (kg/d)

Table D 8. Pollutant weighting factors (sludge)

Weighting factor	Value
β_{As}	70
β_{Cd}	70
β_{Cr}	2.33
β_{Cu}	1.87
β_{Pb}	9.33
β_{Hg}	186.67
β_{Ni}	6.67
β_{Zn}	1
β_{CFU}	0.28
β_{ova}	2800

OPERATIONAL COST INDEX

The new OCI is formulated by modifying the existing one used by De Ketele et al. (2018) through considerations of post-treatment investments and benefits together with WRRF processes. The OCI includes the operating cost factors as well as any potential savings arising from the implementation of WWTP design or control operating strategies and non-compliance fines (Equation D4).

Recovery of resources, for instance struvite or calcium phosphate, is incorporated into the OCI as a benefit in terms of tangible costs. Additionally, any operational cost incurred related to side stream nutrient recovery are now included in the OCI. For instance, precipitation of struvite may require dosing lime to maintain pH and may also require dosing magnesium chloride.

Each of the costs in the OCI function vary regionally. For instance, the market price of additives and WRRF recovered products may not be the same in different regions/countries with different economies. Thus, similar to the EQI, the OCI allows operational cost evaluations tailored to specific regions. This was implemented in the model through parameterization of the market price values.

$$OCI = (AE + PE - MP + ME + HE)\cdot Energy\ cost + SP\cdot Sludge\ disposal\ cost + EC\cdot Carbon\ cost + Metals\ dosed\cdot Metal\ cost + Lime\ dosed\cdot Lime\ cost - NR\cdot Market\ price + Fines \qquad [D4]$$

Where:

AE : Aeration energy (kWh/d)
PE : Pumping energy (kWh/d)
SP : Sludge produced (kgTSS/d)
EC : External carbon addition (kgCOD/d)
ME : Mixing energy (kWh/d)
MP : Energy from methane produced (kWh/d)

HE : Total heat energy required by anaerobic digester for sludge treatment (kWh/d)
NR : Nutrient recovered, e.g. Struvite (kg/d)

Energy tariffs

In South Africa, the energy cost is determined by the tariffs set by Eskom. The latter makes use of "time of use" tariffs which vary during peak, standard and off-peak times during the day, and vary during high demand (June to August) and low demand (September to May) seasons. In addition to the aforementioned, Eskom tariffs also vary based on transmission zones. The average tariffs set by Eskom for 2019/2020 for the low demand season are shown in Table D 9 below.

The time-of-use tariff employed by Eskom is applied in the OCI formula through the addition of a time dependent price function P(t) as described by De Ketele et al. (2018). To illustrate the latter, the aeration energy cost is calculated with consideration of time-of-use tariffs as $AE\ cost = \int_{t_{begin}}^{t_{end}} AE \cdot \frac{P(t)}{100} dt$. Similarly, other energy costs relating to pumping, mixing and heating, as well as savings from methane production is calculated with the inclusion of the term "P(t)".

Table D 9. Eskom 2019/2020 tariffs (Eskom, 2019)

Hour of the day	Time of use	P(t), Price (incl. VAT) (c/kWh)
00:00-06:00	Off-peak	53.20
06:00-07:00	Standard	83.83
07:00-10:00	Peak	121.78
10:00-18:00	Standard	83.83
18:00-20:00	Peak	121.78
20:00-22:00	Standard	83.83
22:00-24:00	Off-peak	53.20

Non-compliance fines

To ensure that effluent quality is not compromised for lower operating costs while aiming to achieve optimal design and operation of WWTP, effluent violation charges are included in the OCI. Once a "unit fine" is decided, the total fines incurred is calculated as the product of the unit fine and the $EQI_{negative}$. The latter, as described by using the approach described by De Ketele et al. (2018), disregards all non-negative terms in Equation D6 below. As a result, the only terms left in the formula are pollutants that have exceeded the regulatory effluent limit. Therefore, as the pollutants are all standardised by application of weighting factors, the product of unit fine and EQI negative gives the total fine. This method of calculating fines is similar to the approach used in Flanders (Vanrolleghem et al., 1996). While currently in South Africa WWTPs do not get fined for non-compliance to effluent standards, this framework for calculating fines remains a potential solution to prevent compromise in effluent quality should lawmakers opt to implement fines in the future.

$$EQI_{water} = \frac{1}{T \cdot 1000} \int_{t_0}^{t_{end}} (\beta_{TSS} \cdot (TSS_{limit} - TSS(t)) + \beta_{COD} \cdot (COD_{limit} - COD(t)) + \beta_{FSA} \cdot (FSA_{limit} - FSA(t)) + \beta_{NO} \cdot (NO_{limit} - NO(t)) + \beta_{OP} \cdot (OP_{limit} - OP(t))) \cdot Q_e(t) \cdot dt \qquad [D5]$$

$$Fines = Unit\ fine \times EQI_{negative} \qquad [D6]$$