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Modelling of Pollutant Removal in Subsurface-Flow Constructed Wetlands

Thesis Proposal Document

Jane Stokeld 12472414
Supervisor: Guangzhi Sun
JAMES COOK UNIVERSITY

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1 INTRODUCTION

Being the world's driest inhabited continent [1], Australia has had strict water restrictions throughout its history. Whether it be for drinking, recreation, or agriculture, Australians consume over 2250 cubic meters of water per year per capita [2].This make the country one of the highest water consumers in the world. So the quantity and quality of water recovered from industry must obtain high standards to be sustainable.

There are several waste water quality indicators. These include biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrogen, total suspended solids (TSS) and others. Water quality requirements and thus indicator standards vary from region to region as do water treatment methods. Common treatment options include activated sludge systems, trickling filters and rotation biological contactors. These options can be difficult to operate and are therefore unsuitable for small communities in particular [3]. They also incur considerable capital and energy costs, whilst occupying land that'd otherwise act as a habitat. An alternative treatment option is required, preferably an option with minimal environmental impacts.

The most commonly implemented ecological water treatment system utilized is the constructed wetland. Constructed wetlands are artificial wetlands that act as bio filters that remove heavy metals, sediments and other pollutants. Pollutants are separated and subsequently bound to the wetland via filtration, sedimentation, absorption, adsorption and ion exchange [3]. Some remain bound to the wetland whilst others are transformed by chemical and biological processes into more inert compounds. Constructed wetlands exist in two categories, subsurface and surface flow.

Surface flow (see figure 1) involves water passing across the roots horizontally. This design is outdated as it requires a large land area and is sensitive to colder climates [4].

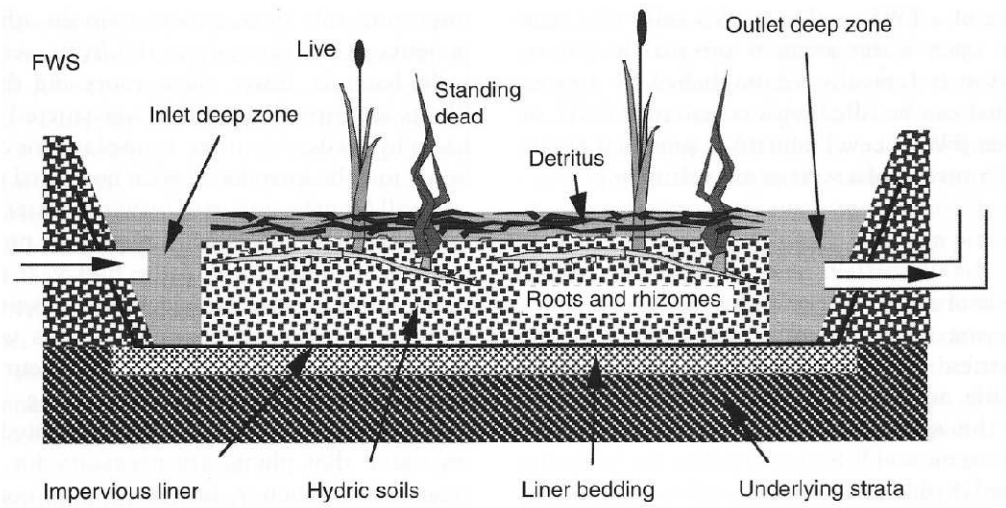

Figure 1 - Surface flow aka free water surface flow (FWS) [5]

Sub surface flow (see figure 2) is characterized by flow within substrates where water runs both horizontally and vertically. The system is prone to clogging however it requires less land area and is less odiferous. This option also minimizes mosquito breeding in the wetlands. The exposure of humans and wildlife to contaminated water is limited by the system as well.

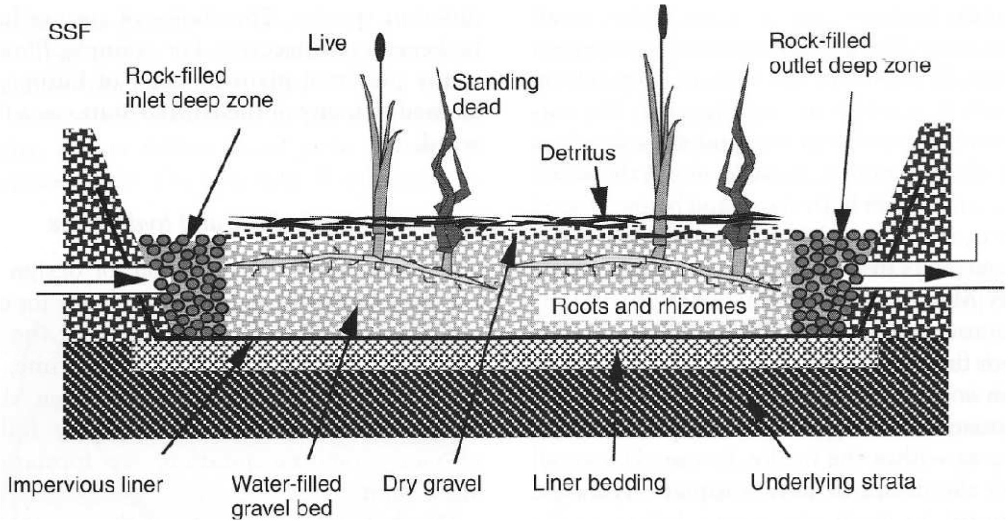

Figure 2– Sub surface flow (SSF) [5]

Wetlands have been used for wastewater treatment as far back as 1912 and research into the design and performance of these systems has been underway since the 1950s [5]. However in design, subsurface flow (SSF) wetlands have always been treated as “black boxes”, only their in and outputs have been considered. Some current design methods have utilized the first order Kickuth or KC* models, however these models have proved inadequate [5], [6]. Progress has been made into the modelling of pollutant removal in wetlands, particularly organics. However models are not yet reliable, especially with regards to metals and suspended solids.

So, significant progress needs to be made in the modelling of SSF wetlands in terms of both horizontal and vertical flow. Wetlands offer a viable alternative to more industrial type water treatments. However before they can be relied upon on a large scale, design equations need to be developed. Modelling SSF wetlands will contribute to the generation of these design equations.

2 PROJECT INTENT

2.1 AIMS AND OBJECTIVES

The aim of this project is to develop a model of sub-surface flow constructed wetlands for the removal of a variety of pollutants. These pollutants include manganese, iron, zinc, copper and suspended solids BOD, COD and NH4-H. The project will seek to establish a relationship between pollutant concentrations before and after treatment. Specific objectives include:

- A comparative review of models utilized for both vertical and horizontal flow
- The preparation of models to be applied to pollutant removal in the wetlands
- A comparison of model and collected data to establish model validity

2.2 SCOPE

This project seeks to model the removal of pollutants from wetlands, organic pollutant removal has been well described in literature. So the project will seek to focus on metal and suspended solid removal. Design equations are needed for wetland design, and the development of these equations should originate from research like this project. However other design factors need to be considered in equation development. So the development of these equations is beyond the scope of this project. Surface flow and tidal wetland modelling is considered beyond the scope of the project as well.

3 LITERATURE REVIEW

Rules of thumb have been widely used in the construction of wetlands. Whilst they are fast, they are also the roughest of design methods [7]. The rules are based on observations from a wide range of systems with differing climate conditions and waste waters. Rules of thumb have large levels of variation and uncertainty, more extensive calculations need to be utilized in the design of treatment wetlands. These calculations should be based on models. Models are determined by three major factors; flow direction (horizontal or vertical), reaction kinetics hydraulic behavior.

3.1 HYDRAULIC BEHAVIOR

The hydraulic behavior of wetlands is often assumed to be similar to that of tanks or tubes. The system can be approximated by a constantly stirred tank reactor (CSTR- see figure 3) or a plug flow reactor (PFR- see figure 4). They act as a single unit or as several units in series (or parallel). Multiple reactors will approximate changing conditions over the wetland. Also a mix of both CSTR and PFR can be implemented to approximate hydraulic conditions

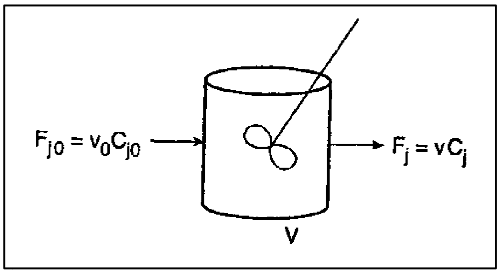

Figure 3 – Constantly stirred reactor [8]

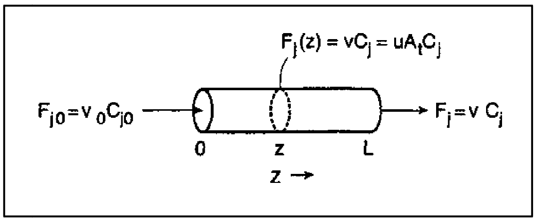

Figure 4 – Plug flow reactor [8]

3.1.1 CSTR

The CSTR flow pattern has been well utilized in wetland modelling. It describes the system as a constantly stirred reactor which is perfectly mixed throughout instantaneously. Composition throughout the reactor is consistent and the outlet stream has the same composition as the reactor itself. To assume a wetland is equivalent to a constantly stirred reactor is optimistic. Substrate media, site topography, plants and changing environmental conditions all impinge on the consistency of reactions in wetlands. A mass balance over the system will give reactant accumulation in the CSTR (see Equation 1). Reactant flow into the system is F_{j0} , flow out is F_j, V gives volume and v_j& r are the volumetric flow rate and reaction rate.

Equation 1 – CSTR Mass balance [8]

$$\frac{dN_j}{dt} = F_{j0} - F_j + Vv_jr$$

Where:

N_j= number of moles of reactant in reactor, mol/s

t= time, s

F_{j0}= inlet flow rate of reactant, mol/s

F_j=outlet flow rate of reactant, mol/s

V= volume of reactor,

v_j= volumetric flow rate, m^3/s

r= reaction rate, mols/ m^3 s

3.1.2 PFR

PFRs have also been utilized for modeling; their accuracy has been shown on horizontal flow in particular [7]. A basic mass balance for a PFR is listed in equation 2, where u is velocity, C_j is concentration and z is distance [8]. PFRs assume all water is treated to some degree so the system ignores short circuiting and extended retention. The system also assumes that the sole composition modifier is travel time. Realistically this cannot be the case in wetlands, environmental factors and kinetics will change along the path. Plug flow assumes no material will diffuse back throughout the process (including the inlets and outlets). Eddies will be abundant in the wetlands so to assume no back flow occurs is unrealistic [9]. Constant tube diameter, steady state and constant velocity profile are all assumed with this model, not one can be considered a reasonable assumption in wetlands.

Equation 2 – PFR mass balance

$$u\frac{dC_j}{dz} = v_jr$$

Where:

u= average velocity, m/s

C_j= concentration of jth component, mol/m^3

A model combining plug flow with dispersion (PFD) has been developed for free water surface flow wetlands (cite me). The system does not consider retention and bypassing, which gives rise to problems where precipitation or un-vegetated "dead" zones occur. The PFD assumes reaction occurs instantaneously at the inlet, ignoring any diffusion back into the inlet. Whilst it does consider some interaction with the surrounding environment, it only considers eddy transport. Flow is often laminar (in FWS in particular) and thus the model is unrealistic.

Multiple CSTRs and PFRs can be used in series or parallel to model a constructed wetland. Multiple CSTRs can reflect the lack of homogeneity in wetlands whilst multiple PFRs can describe path length variation. Urban [10] developed three models; three CSTRs in series, eight PFRs in series and three PFRs in parallel. All three fitted data reasonably well. A combination of the two hydraulic behaviors will characterize a wetland even more completely.

3.1.3 Multiple reactors and CSTR & PFR Hybrids

Zones of diminishing mixing

The zones of diminishing mixing (ZDM) model [11] utilizes a large number of side CSTRS connected to main PFR channels. The simple algorithm allowed for contaminant routing that models both advection and dispersion. The result effectively described tracer effluent concentrations and was thus extended in [12] to model nitrate reduction. The simulation utilized first order kinetics but was none the less effective in providing performance distributions. The effectiveness of this model on other pollutants has not been investigated.

Tanks in Series

The tanks in series (TIS) model characterize wetland flow as flow through a series of N CSTRs. This model has been used to compare FWS and SSF [13] but is not widely used in literature. This may be because the model assumes the reaction rate constant does not vary with time. There are a few variations of TIS, one of which considers two flow paths [14]. The variations have accurately described hydraulic performance

3.1.4 Flow direction

Pollutant removal mechanisms change in different directions of flow. Mechanisms will change in the vertical plane due to varying substrate media, decreasing root density, decreasing oxygenation levels, changes in the microbial population and other factors. It is known that vertical flow provides good nitrification conditions while the horizontal plane contains limited oxygen and thus provides de-nitrification conditions [15]. So a combination of horizontal (HF) and vertical flow (VF) will provide ideal conditions for nitrogen removal. This result may be extended to other pollutants that degrade via more than one pathway. So combined HF and VF constructed wetlands are called “hybrid constructed wetlands” [16].

3.2 KINETICS

Flow direction, reactor model variations and the number of reactors may describe the flow pattern of reactants, but they do not describe the reactions occurring. The reaction rate (or rate of removal r) is described by Equation 3a combination of rate constants and reaction order (m).

Equation 3 – Removal rate

$$r = kC^m$$

3.2.1 Zero Order

Zero order ($m = 0$) kinetics assume the removal rate remains constant regardless of contaminant concentration. Constant rates are only postulated occasionally for constructed wetlands [9]. It is used most for high pollutant concentrations or for characterizing return flux.

3.2.2 First Order

Many pollutant removal mechanisms are first order. Volatilization, sedimentation, sorption and mass transport are all first order processes. So it is reasonable to assume that for the combination of these processes, the removal rate is first order. This rate is highly prevalent in literature (e.g. [7]). However first order kinetics cannot account for sequencing (i.e. vegetated and open water zones in sequence). Kadlec, one of the creators of the model, noted the inadequacy of first order kinetics [6]. It has been shown that rate constants depend on hydraulic loading rates and inlet concentrations and are not universally applicable. Even with the addition of a third parameter (dispersion) models have no met design performance standards. A new model is needed that incorporates short circuiting and vegetation distribution.

3.2.3 Monod

Microbially mediated processes and other biological reactions are only first order where concentration is below saturation. So Monod kinetics (see Equation 4) were developed to interpolate between zero and first order kinetics. For low concentrations it is a first order model and for high it is zero order. The model was reported appropriate for phosphorus, BOD [9] and nitrogen removal [17]. However kinetic coefficients were strongly correlated with higher pollutant loading and influent concentrations as was the case for first order kinetics. Neither the zero nor the first order approximations were considered appropriate models. So this first/zero order combination suffers from the same drawbacks noted for each model respectively.

Equation 4 – Monod kinetics

$$r = k\left(\frac{C}{K + C}\right)$$

(Note: K= half saturation constant g/m^3)

3.2.4 Other factors to consider in kinetics

Limiting reactants

Occasionally more than one substrate limits the rate of pollutant degradation. This is the case with nitrogen removal, which requires oxygen and carbon for nitrification and denitrification respectively. In combination with Monod kinetics, the effect of limiting reagents (out 1 and out 2) can be expressed like so:

Equation 5 – Multiple Monod kinetics

$$r = k_{max}\left(\frac{C_{out_1}}{K_{half_1} + C_{out_1}}\right)\left(\frac{C_{out_2}}{K_{half_2} + C_{out_2}}\right)$$

Kadlec and Wallace [9] suggested limitations are implicit in overall rate constants unless supply is very low. However it has been shown that multiple Monod kinetics correlate more closely than Monod kinetics to collected data [17].

Return fluxes

There will be significant pollutant uptake in constructed wetlands, however the return rate of pollutants from the wetland is not negligible. No scientific study has been conducted into return rates and their dependencies. So a lumped rate equation has been postulated by Kadlec and Wallace:

Equation 6 –Zero order return flux

$$r = kC - r^* = k(C - C^*)$$

Where:

C^*= background concentration

r^*= return rate of chemical

Zero order return flux is assumed as it is the simplest option. C^*, the background concentration, is achieved when no uptake occurs (i.e. when $C = 0$). Non zero background concentrations can be attributed to 5 factors:

1) Portions of chemicals resistant to storage
2) Particulate matter transport
3) Hydraulic bypass of reactive wetland
4) Pollutants from ground or rain water
5) Seasonality (mineralization due to the wetting of previously bound substances

Seasonality has been extensively considered in literature, wetting is a major factor contributing to kinetic variations. However seasonality has a wide impact beyond this, temperature and atmospheric conditions display seasonal patterns as well.

Temperature and season

Pollutant removal mechanisms are changed to varying degrees by seasonality. It has been shown that the removal of nutrients is strongly effected by temperature. This is a result of the solubility of oxygen in water being temperature dependent. So temperature has a strong influence on biogeochemical processes, this is particularly evident below 15°C [18]. Sedimentation is weakly temperature dependent, with enhanced rates at higher temperatures. The effects of temperature dependence on rate constant has been summarized by the modified Arrhenius equation [9]:

Equation 7 – Modified Arrhenius Equation

$$k_t = k_{20}\theta^{T-20}$$

Where:

k_{20}= reaction rate constant at 20°C, units will vary depending on kinetics

k_t= rate constant at temperature T, units will vary depending on kinetics

θ= temperature correction factor, unitless

The temperature correction factor depends on the wetland's unique microbial population, biofilms and plant uptake characteristics. So no one pollutant specific temperature coefficient can be applied to all wetlands, they must be formulated for each individual system. Temperature changes are strongly influenced by seasonality but they should not solely represent seasonal effects on wetlands. Rain, evapotranspiration and reaeration also follow seasonal patterns. Kadlec [19] proposed an equation (Equation 8) to represent the cyclic, sinusoidal nature of the outlet concentration over a year related to the mean outlet concentration, C_{avg} .

Equation 8 – Kadlec random variability equation

$$C = C_{avg}[1 + A\ \cdot \cos(\omega(t - I_{max})] + E$$

Where:

A= fractional amplitude of seasonal cycle (dimensionless)

E= random portion of the outlet concentration, mg/L (this represent random variability or error)

t= time of year, Julian day

t_{max}= time of year for the maximum outlet concentration, Julian day

Seasonal patterns change over time, a prime cause of this is climate change. A weakness of this equation is that it does not consider these changing seasonal patterns.

Water losses and gains

The models above do not specifically consider water gain and loss from wetland. Atmospheric interactions and plant harvesting will remove moisture from the system. Rainfall will increase the hydraulic loading across the system, not just at the input. So a mass balance can be conducted over the system to account for this non uniform flow

Equation 9 – Concentration after water loss

$$C_1 = \frac{Q_i C_i + (k \cdot A_1 \cdot C^*)}{Q_i + A_1 \cdot (P - ET) + (k \cdot A_1)}$$

Where

Q_i= inlet flow rate m^3/d

A_1= area of the mass balance segment, m^2

ET= evapotranspiration, m/d

P= precipitation m/d

Note that here it is assumed that the rainfall and atmosphere do not contain any pollutants. Also moisture lost to plant harvesting has not been considered. This mass balance can be conducted over the whole wetland, however it is most effective when applied to wetland segments. So it is very effective in ZDM and TIS.

Weathering

Many contaminants are mixtures lumped together (e.g. BOD, COD and TSS). The composition of these mixtures will change over time as each individual component has its own reaction rate. So as a mixtures composition changes, it becomes weathered. If it is assumed that all components have the same kinetic order, there will be a distribution of k values in the mixture. So the k value at any given time during a process is given by Equation 10 :

Equation 10 – k value distribution

$$k = \frac{k}{(1 + \beta t)^n}$$

Where

k_i=inlet rate constant, units depend on the order of reaction

n= mixture k-value distribution breadth parameter, dimensionless

β= mixture k-value distribution weathering parameter, d^{-1}

3.3 MODELING LIMITATIONS

There are many and varied models applied wetlands, both for kinetics and hydraulic conditions. Each has its own limitations so no single equation can be used universally on all wetland. Some large limitation exist for all models.

3.3.1 Universal Model Limitations

The extrapolation of wetland performance models and data for the design of new wetlands comes with many inherent dangers. Some models are only valid for site specific conditions, others will not be correct above saturation limits. Detention times in wetlands will vary greatly, due to plant layout, plant density, rainfall, substrate density, microbial activity and more. The detention time of a single wetland will change due to plant growth over time. Neither of these factors have been considered in models above. Topography will also have an effect on pollutant detention time, where ZDM is used this can be considered. However there are so many topography changes in all wetlands that no model has yet shown the relationship between a wetlands topography and its pollutant removal effectiveness.

Compositions of pollutants will change over time, this has been factored into weathering for COD, BOD and TSS (see Equation 10 – k value distribution). But for metals, which may exist in wetlands as different ions with their own reactions, no such weathering data exists. The effectiveness of different plants has not been considered either. Some plants have an affinity for certain compounds (e.g. rice has an affinity for arsenic [20]). The magnitude of different plant species effects on pollutant removal has not been considered. Also the ecology of wetlands will change over time. Metals in particular will build up in sediment or plant life and decrease the effectiveness of wetlands over time. Some wetlands will grow too rapidly (particularly in the presence on nitrogen and phosphorus pollutants) and their death will build a layer of organic matter on the surface of the wetland decreasing wetland effectiveness. So dead or overgrown plant life is sometimes harvested to reduce metal and biological buildup. Harvestings effect on wetland effectiveness has not been investigated.

3.3.2 Longitudinal transect limitations

To avoid the "black box" approach it has been suggested to use longitudinal transect data for wetland analysis. Whilst transect data will describe concentrations within the system and thus describe the wetland more completely, transect data has its own limitations. It is notoriously difficult to find as it is so difficult to collect. It is hard to take spatially uniform data due to plant life, bogs and water, depth also becomes an issue as varying mechanisms act at different wetland depths. Even when spatially uniform data is collected it does not always represent flow paths in the system correctly. Flow will go backwards and may change at different depths. Where spatially uniform data is not collected, samples are usually taken from the easy access, open water areas. Open water will not accurately reflect pollutant removal in wetlands as they represent the shortest paths in the systems.

3.3.3 Pollutant specific limitations

Most of the above models have only been used on organic pollutants, but research into metal removal has been limited. Allende et al. [21] have researched arsenic removal, but the removal of other metals like copper, manganese, zinc and iron has not been extensively characterized. The buildup of suspended solids in wetlands has been discussed, but the net removal of suspended solids has not been discussed (if it exists at all – many pollutant removal mechanisms will actually produce suspended solids).

3.4 CONCLUSIONS

So there are significant knowledge gaps with regards to metal and suspended solid removal mechanisms in wetland matrices. The effects of environmental factors on these mechanisms is also unknown. Models proposed each have their own limitations as do kinetics. ZDM appear to have the least limitations, however its use of first order kinetics is questionable. Whilst 1^{st} order and zero order kinetics are not recommended the Monod option appears the most viable of all kinetic options. This is because it accounts for variability in reaction rate order. So a combination of ZDM and Monod kinetics will be used to model constructed wetland pollutant removal.

4 METHODOLOGY

The modelling of constructed treatment wetland systems will be undertaken in 3 stages:

4.1 MODEL DEVELOPMENT

Work will be done in this stage to develop new constitutional equations to predict the removal of target pollutants in constructed wetlands. These equations will be based on literature. Choices of hydraulic and kinetic models should be made.

4.2 DATA ANALYSIS

Field performance data is to be obtained from the data base of the Constructed Wetland Association (CWA). Longitudinal transect data will be used where possible to avoid the "black box" approach prevalent in literature. The use of transect data will allow for analysis of reaction progression within the wetland. Not all data collected will consider pollutants to be analyzed, and such irrelevant data will be excluded. Comparisons will be made to current literature to ensure data is within the operational bounds of equations to be used.

4.3 MODEL IMPLEMENTATION

The developed model will be applied based on wetland conditions from CWA. These conditions will include inlet flows, wetland size, plant distribution, average rainfall and others. From these parameters the outlet pollutant concentration will be modelled. If the model is to reflect transect data or use multiple reactors (i.e. ZDM or TIS modelling), pollutant concentrations across the wetland system will be modelled.

4.4 MODEL VERIFICATION

In this stage the model will be compared with CWA data. Where the model does not predict concentrations within reasonable limits it will be reviewed. Literature has shown a strong correlation between hydraulic loading and input concentrations with reaction rates (see section 3.2.2 First Order page 9 for more detail). The aim of this report is to provide model/s that are as close to universally applicable as possible, so they can be applied in design equations. So this strong correlation is to be avoided and will be considered grounds for model revision.

5 PROJECT MANAGEMENT PLAN

5.1 TIMELINE

The stages of the proposed project are set out in the project management plan. The stages correlate with methodology, wherever methodology proves inadequate the plan should be reviewed. The plan should be continually updated to account for project changes. Refer to Appendix A: Thesis Project Gantt Chart for further details. Note that significant risk is involved with regards to model verification, if a model cannot be verified and a new model needs to be developed there will be significant time consequences. All tasks should be completed as soon as possible, even before the deadlines described below.

Note that resources required for this project are minimal. Matlab will be used as the primary modelling software. The university owns licenses for this software, as does the modeler. The constructed wetland database will provide data for model comparison and calibration. This data is to be obtained by thesis supervisor, Guangzhi Sun.

Project Management Plan:
Semester 1:

Stage 1: 4th March – 11th March, 2013

- Topic Selection
- Preliminary research for understanding of topic

Stage 2: 11th March – 6th May, 2013

- Literature review with regards to:
    - Wetland kinetic models
    - Hydraulic models

Stage 3: 15th April – 10th May, 2013

- Modelling Methodology
- Risk Assessment

Stage 4: 11th March – 10th May, 2013

- Completion and submission of final thesis proposal document

Mid-Year University Break & Semester 2:

Stage 5: 3rd June – 29th July, 2013

- Model design and application
- Thesis report drafting

Stage 6: 29th July – 19th August, 2013

- Comparison of Constructed Wetland Database data with prepared model
- Thesis report drafting

Stage 7: 19th August – 30th October

- Completion and submission of final thesis proposal document
- Seminar preparation, submission and preparation

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Appendices

Appendix A: Thesis Project Gantt Chart

ACTIVITY	PLAN START	PLAN DURATION	ACTUAL START	ACTUAL DURATION	PERCENT COMPLETE
Topic Selection	2	1	2	1	100%
Literature Review	3	9	3	8	100%
Modelling Methodology	8	4	8	4	100%
Risk Assessment	4	8	10	1	100%
Proposal submission	4	8	4	8	100%
Model Design	15	8			0%
Model Verification	23	3			0%
Thesis Report Drafting	15	11			0%
Final Thesis Report	26	3			0%
Seminar drafting and submission	29	4			0%
Seminar presentation	32	2			0%