

# QUEENSLAND WATER MODELLING NETWORK



Water planning, integration and management

## MEDLI science review: Pond chemistry module Final report

Report prepared by  
Dr Mike Johns and Dr Bronwen  
Butler  
For the Queensland Water  
Modelling Network



The Queensland Water Modelling Network (QWMN) is an initiative of the Queensland Government that aims to improve the state's capacity to model its surface water and groundwater resources and their quality. The QWMN is led by the Department of Environment and Science with key links across industry, research and government.

Prepared by: Dr Mike Johns and Dr Bronwen Butler, Johns Environmental Group Pty Ltd.

© State of Queensland, 2021.

The Queensland Government supports and encourages the dissemination and exchange of its information. The copyright in this publication is licensed under a Creative Commons Attribution 4.0 Australia (CC BY) licence.

Under this licence you are free, without having to seek our permission, to use this publication in accordance with the licence terms. You must keep intact the copyright notice and attribute the State of Queensland as the source of the publication. For more information on this licence, visit <https://creativecommons.org/licenses/by/4.0/>.

#### Disclaimer

This document has been prepared with all due diligence and care, based on the best available information at the time of publication. The department holds no responsibility for any errors or omissions within this document. Any decisions made by other parties based on this document are solely the responsibility of those parties.

If you need to access this document in a language other than English, please call the Translating and Interpreting Service (TIS National) on 131 450 and ask them to telephone Library Services on +61 7 3170 5470.

This publication can be made available in an alternative format (e.g., large print or audiotape) on request for people with vision impairment; phone +61 7 3170 5470 or email [library@des.qld.gov.au](mailto:library@des.qld.gov.au).

#### Citation

Johns M and Butler B (2021). MEDLI science review: Pond chemistry module. Report to the Queensland Water Modelling Network, Department of Environment and Science by Johns Environmental Group Pty Ltd, Brisbane.

#### Acknowledgements

QWMN commissioned a review of MEDLI (Model for Effluent Disposal using Land Irrigation) to assess the science underpinning its Hydrology, Nutrient & Pond Chemistry modules, to identify gaps, and suggest possible improvements. This report is one of five reports written for the MEDLI Science Review by a team led by Prof Ted Gardner (Victoria University). Other reports from the MEDLI Science Review are "Hydrology – Model and process" by Dr Tony Ladson, "Methodologies used by biophysical models for simulating soil nutrient pools and processes in pasture systems - Carbon, nitrogen and phosphorus" by Dr Phil Moody, "MEDLI Science Review: Synthesis" by Prof Ted Gardner and "Modelling of Water and Solute Transport in MEDLI" by Prof Freeman Cook. The Executive Summary was taken from the MEDLI Science Review: Synthesis" by Prof Ted Gardner.

## Executive Summary

We argue that the current module used in MEDLI is really only fit for piggery effluent and even then, the partitioning factors for settling are too high, as is the N volatilization loss. The equation used to estimate volatilisation is extremely empirical – even by pond modelling standards – and appears to have little dependence on factors critical to volatilisation such as water temperature, pH, retention time and wind velocity.

The literature suggests that volatilization contributes < 5% NH<sub>3</sub>-N loss unless the effluent is very high strength (say 500mg/L) and the climate is tropical. Rather, the main N removal pathways are algal growth and its sedimentation, and associated nitrification/denitrification reactions.

Use of the Pano & Middlebrooks (1982) empirical equation is supported for use in MEDLI to calculate the removal of soluble N. Although it is based (incorrectly) on NH<sub>3</sub> loss via volatilization, its form captures N removal as a first order reaction. Moreover, use of NH<sub>3</sub>-N as the input variable is not a great drawback as it comprises the bulk of the **soluble N** in ponds.

If TN is the important variable to calculate, then the Reed et al. (1995) equation could be considered, but this needs an Arrhenius type temperature correction factor to be added.

Nitrogen loss by sedimentation of the influent particulate organic nitrogen and the N sequestered in the particulate biomass (algae and bacteria) remains an intractable issue. The net settling fraction (Fr-N) approach has merit, but the challenge is what this value should be. The value should be “reasonable and not overstated”.

The current MEDLI approach to estimate P removal in ponds is simple and brutal. All P loss is credited to the first (anaerobic) pond through use of the net settling fraction (Fr-P). The default value is 90%, which will substantially over-estimates P removal for sewage ponds and agri-industrial ponds.

However, the removal process of P in ponds is uncertain, with experts’ views split between biomass sequestration and settling, and natural precipitation reactions.

There are very few predictive equations for P removal from ponds, but we recommend that the Vijay and Yuan (2017) model should be considered. This is a three-term phenomenological equation where the first term accounts for P loss due to assimilation into biomass, and the other terms account for P precipitation reactions. Although developed in Canada on sewage effluent, we suggest it can be used in other climates provided a temperate correction is made (as described in this review) and it provides plausible P removal % even when the precipitation terms are ignored. However, predicted losses should be capped at 50%.

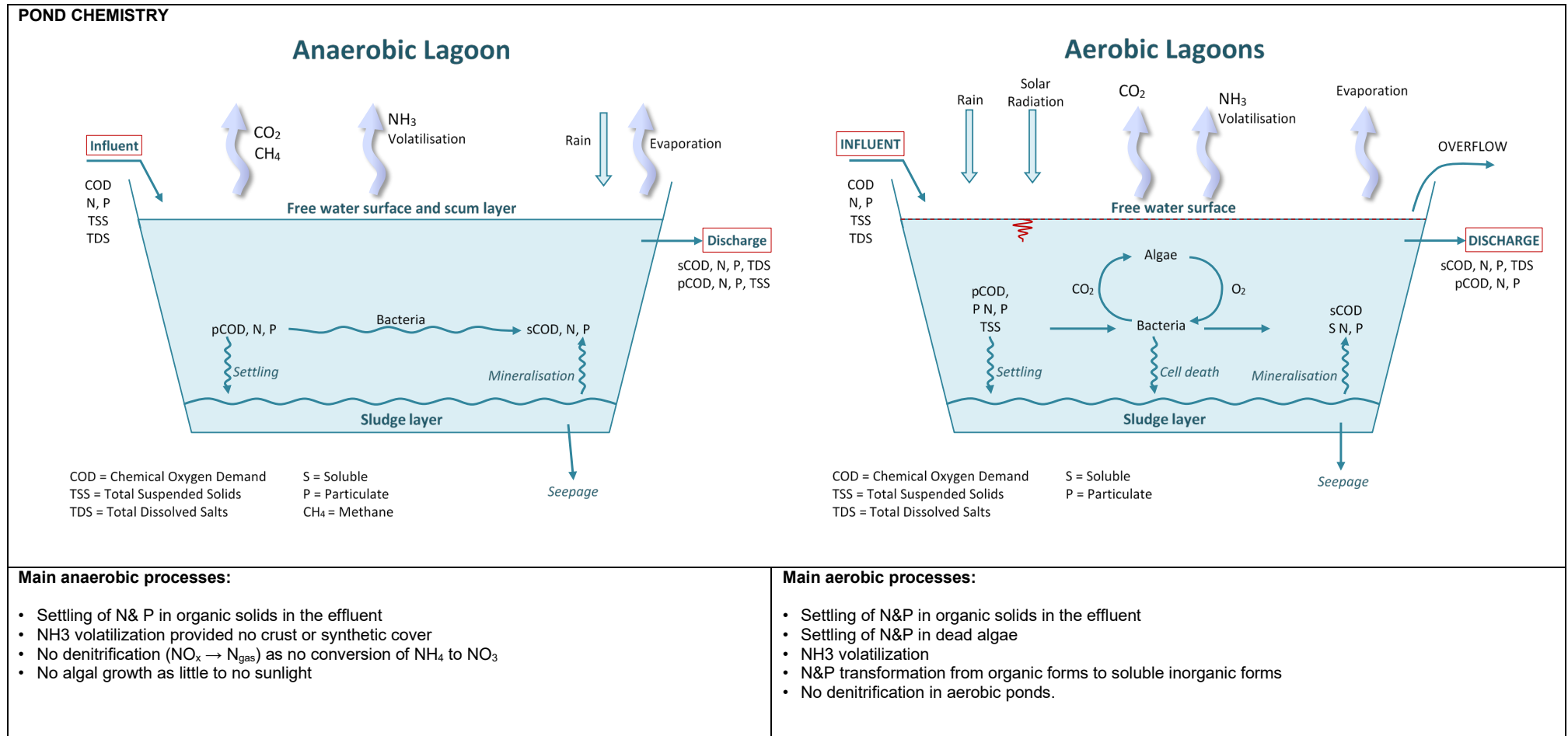
Overall, we believe that MEDLI should focus improvements on nitrogen and phosphorus removal for sewage waste stabilisation pond systems where traditional ponds remain in widespread use. Medium to large agri-industrial wastewater plants treating high nutrient loads (and concentrations) usually install intensive BNR and/or chemical precipitation systems to arrive at the required compliance P level. The output concentrations are relatively constant and can be inputted into MEDLI as the effluent composition of the final pond.

These issues are summarised below, along with their implications in Tables 4 (Pond hydrology) and 5 (Pond chemistry).

Table 4. Strategic overview of the issues and implications raised by this review – Pond Hydrology. (From p.29)

POND HYDROLOGY		Trapezoidal shaped pond used in MEDLI					
Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Pond geometry	Limited to trapezoidal-shaped ponds.	A “MEDLI-helper” spreadsheet is provided to allow users to enter in their own pond depth – water surface area – water volume data points and retrieve the trapezoidal inputs that best match their pond geometry.	Allow calculation of equivalent surface area and volume for irregular shaped ponds within MEDLI.	Addressing this issue to allow for user specification of pond geometry (e.g., for round, rectangular, trapezoidal or irregular ponds) will improve relevance to many users.	Low to moderate.	High. This has been raised by users frequently	Implement a module to generate the depth– water surface area – water volume relationship for each pond that can be directly used for all pond calculations. This relationship would be derived from user input for round, rectangular, trapezoidal or irregular ponds.
Pond evaporation	Check the assumed default Pan factors used for ponds. E.g., anaerobic, facultative/wet weather, and anaerobic ponds with a crust.	Evaporation takes place from all ponds if no crust or synthetic cover. A Pan evaporation factor is used to derive pond water evaporation from daily Class A Pan. The default Pan evaporation factor is 0.7 for anaerobic and facultative ponds.	Consider the WATHNET, IQQM or MIKE models that may have pan evaporation factors for ponds and eWater Source – Water Quality may have nutrient removal estimates.  Check for a more correct Pan factor or replace with Penman equation or similar.	Errors in evaporation prediction carry over into errors of pond overflow prediction.	low	high	Investigate alternatives as listed.

Table 5. Strategic overview of the issues and implications raised by this review – Pond Chemistry. (From p.30)



Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Pond treatment	MEDLI's pond treatment trains do not reflect the treatment trains now used by medium to large agro-industrial wastewater generators. Engineered pre-treatment systems have replaced the need for anaerobic ponds. More efficient to input the water <b>quality</b> characteristics of the irrigation pond.	The pond treatment trains currently offered are (1) "anaerobic pond first followed optionally by up to three "facultative/wet weather storage" ponds; (2) Up to four "facultative/wet weather storage" ponds. The last pond is always the irrigation pond.  Apart from calibrating MEDLI's predicted irrigation water quality by adjusting the wastestream inputs in MEDLI., there is no easy way of "turning off" pond treatment and inputting the irrigation water quality characteristics directly.	Add a new option to allow the direct input of water quality characteristics of the last pond used for irrigation. This will turn off pond treatment algorithms but allow pond hydrology modelling to continue.	This new feature will allow MEDLI's simple pond chemistry algorithms to be bypassed in favour of irrigation water quality. <b>This will have potentially large impacts on all post-irrigation processes including nutrient loading on the irrigation area and plant growth.</b>  <b>This option will need the MEDLI user to be provided with the irrigation water quality.</b>	Low	High	Add a new option to allow the direct input of water quality characteristics of the last pond used for irrigation.  Retain the option to use the MEDLI pond chemistry algorithms but investigate the recommendations N and P transformations as listed below in the future. E.g., the Pano and Middlebrooks model
Minimum pond treatment volume for odour control of anaerobic ponds	Minimum anaerobic treatment volume should be based on BOD.	Volatile Solids Loading Rate used to estimate malodour potential	Use mean BOD data for raw influent  Use a table of BOD loading vs Malodour generation to estimate minimum pond treatment volume.	An accurate estimate of minimum pond treatment volume will impact on rate of desludging and to a lesser extent, the pond hydrology.  Will need user to input BOD data.	Moderate	High for high strength waste streams (e.g., meat rendering plant, abattoir), low for low strength waste streams e.g., conventional STP.	Investigate adding the option for high strength wastestream.
Sludge generation and accumulation	MEDLI assumes only the anaerobic pond has settlement of solids. N&P are removed with the solids.  MEDLI ignores sludge accumulation from algae growth.	(1) Sludge accumulation is based on a simple user-specified sludge accumulation rate applied to total solids concentration of the influent. It only occurs in (the first) anaerobic pond.  (2) The sludge accumulation rate is based on experimental piggery and cattle data.	(1) Allow sludge accumulation to occur in all ponds, especially those with algal growth.  (2) Review literature to identify the likely sludge accumulation rates. Implement to all ponds considered in MEDLI.  (3) May be simpler to input final water quality leaving irrigation pond if available.	More user inputs needed to specify sludge accumulation rate across all ponds, and desludging protocols.  Modelling sludge will impact on pond water quality predictions and hence irrigation water quality (i.e., N and P).	Moderate coding task but need data and algorithms for sludge accumulation from algal growth / death.	Low to moderate particularly as alternatives exists to simply bypass the pond chemistry.	Input the final water quality as recommended in Pond Treatment row.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Nitrogen sedimentation in ponds	<p>(1) Recent work suggests uptake by algae and bacteria followed by biomass sedimentation is a major mechanism of N removal in <b>aerobic</b> ponds</p> <p>(2) The default value for TN settling in anaerobic ponds is based on piggery data.</p>	<p>Settling of organic N only occurs in anaerobic ponds.</p> <p>A two-compartment model is used – one for “soluble” TN; the second for the solid TN fraction. This accumulates as sludge in the anaerobic pond A settling fraction of about 25% is used based on piggery data.</p>	<p>(1) Predicting N uptake by algal growth remains an intractable issue. The existing sludge settling approach used in MEDLI seems warranted provided the value is not overstated (as occurs now).</p> <p>The settling fraction concept could be applied to all ponds, with its value decreasing down the pond series.</p> <p>(2) Review recent studies to evaluate sludge accumulation rates for different effluents.</p> <p>(3) May be simpler to input final water quality leaving irrigation pond if available.</p>	<p>Applying the settling fraction to all ponds causes sludge accumulation in all ponds. This would necessitate including sludge volume in the pond volume calculations as done currently for the anaerobic pond.</p> <p>N sedimentation impacts on the pond water TN concentration and hence irrigation water quality.</p>	Moderate	High if there were no alternative to bypass the pond chemistry.	Input the final water quality as recommended in Pond Treatment row.
Nitrogen transformation to ammonia in ponds	<p>Volatilisation of NH<sub>3</sub> is very limited in anaerobic ponds with a natural crust or a synthetic cover. However significant conversion of organic nitrogen to ammonia still occurs. MEDLI's volatilization approach is based on TN concentration.</p>	<p>Ammonia volatilisation occurs from all ponds according to a user-defined “N transfer” coefficient applied to pond TN concentration.</p> <p>The user can adjust the default value of 0.014 <b>m/day</b> towards zero if the pond has a crust or synthetic cover.</p>	<p>Biokinetic models for nitrogen transformations (e.g., Ho et al. 2019 and Senzia et al. 2002) allow discrimination between the various N removal mechanisms but are not recommended due to their complexity and lack of validation.</p> <p>The Pano and Middlebrooks model is recommended to replace the NH<sub>3</sub> volatilisation equations in MEDLI.</p>	<p>N transformation will impact on the TN concentration and hence irrigation water quality and TN for irrigation.</p>	Moderate	High if there were no alternative to bypass the pond chemistry.	Input the final water quality as recommended in Pond Treatment row.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Phosphorus sedimentation in ponds	MEDLI's default value of 90% removal is likely to over predict P removal in anaerobic ponds. Total phosphorus removal in aerobic ponds is driven by precipitation reactions and algal growth & settling. Phosphorus may also be re-released from sediments during warmer months. Contributions from the different removal mechanisms are hard to determine.	Settling of P in organic solids in the effluent only occurs in anaerobic ponds.  A two-compartment model is used – one for “soluble” TP fraction; the second for the solid TP fraction. A default value of 90% of solid TP is assumed to settle as pond sludge. This (number based on piggery data).	1) The phosphorus settling fraction could be replaced by the Vijay & Yuan model (2017) which appears suited for STP treatment ponds of any type. A temperature correction for some of the model coefficients is required as the model was developed in Canada.  2) Suggest implementing a maximum total P removal cap of 50%.	The Vijay & Yuan model lacks validation against real WSP data. A small local validation study may be warranted before use in MEDLI. The study would also provide an opportunity to quantify values for the temperature modifier.  P sedimentation impacts on the pond water P concentration and hence irrigation water quality.	1) Moderate  2) Low	1) Moderate if there were no alternative to bypass the pond chemistry.  2) High	1) Investigate the Vijay & Yuan model.  2) Set maximum total P removal cap of 50%.
Phosphorus transformation in ponds	Conversion of biologically available organic phosphorus to soluble phosphate is rapid and almost stoichiometrically complete in active anaerobic ponds.	Not considered in MEDLI	The Vijay & Yuan (2017) approach offers an encouraging but unproven approach for P transformation and losses in anaerobic systems.	P transformation will impact on the P concentration and hence irrigation water quality.	Moderate	Moderate if there were no alternative to bypass the pond chemistry.	Investigate the Vijay & Yuan model.
Pond pH	Pond pH is currently ignored in MEDLI. This is an issue if alternative models are considered such as Vijay & Yuan model.  This model was designed to operate between pH 8-10. Many ponds operate at lower pH. It can be expected this will impact P removal via precipitation reactions.	Pond pH is ignored	Implement a basic ionic model such as that used by Gehring et al. (2010) to estimate pH effects on precipitation (removing phosphorus) and dissolution (re-solubilisation) reactions.	Significant additional measurable data will be required to implement this model.  Pond pH will impact on the P concentration and hence irrigation water quality.	Moderate to high	High if the Vijay & Yuan model was implemented and simply inputting average pond pH is insufficient for this model.	Investigate the Vijay & Yuan model.



## Table of Contents

---

Executive Summary .....	3
Abbreviations .....	10
1. Introduction.....	12
1.1. Background.....	12
1.1.1. Treatment System Changes since 1996 .....	12
1.1.2. Scientific Advances in Pond Modelling: Scope for the Review .....	13
1.2. Methodology Statement.....	13
2. Current MEDLI Technical Document - Pond Chemistry Module.....	14
2.1. MEDLI Assessment .....	14
2.2. Vulnerable MEDLI Modules .....	16
3. Review of QWMN Models.....	17
4. Nitrogen Mass Balance.....	20
4.1. Current MEDLI equations and assumptions .....	20
4.2. Literature Review .....	20
4.3. Nitrogen Modelling.....	21
4.3.1. The Pano & Middlebrooks equation .....	21
4.3.2. Issues using Pano & Middlebrooks modelling.....	22
4.3.3. Dynamic Biokinetic Models.....	23
4.4. Recommendations for Nitrogen Modelling in MEDLI .....	25
5. Phosphorus Mass Balance .....	28
5.1. Current MEDLI Phosphorus Equations and Assumptions .....	28
5.2. Phosphorus Literature Review.....	28
5.3. Phosphorus Modelling .....	29
5.3.1. Gomez et al (2000).....	29
5.3.2. Vijay & Yuan (2017).....	29
5.4. Recommendations for Phosphorus Modelling in MEDLI.....	30
6. Anaerobic Pond Module .....	32
6.1. Current MEDLI Anaerobic Pond equations and assumptions.....	32
6.2. Anaerobic Pond and Sludge Deposition Literature Review .....	32
6.3. Anaerobic Nutrient Modelling Options .....	33
7. Implications of the issues raised .....	34
8. References .....	40

## Abbreviations

AOB	=	Ammonia Oxidising Bacteria
ASM3	=	Activated Sludge Model No. 3
BOD <sub>5</sub>	=	biochemical oxygen demand (measured in 5 days at 20°C) (mg/L).
BNR	=	biological nutrient removal
CAL	=	Covered Anaerobic Lagoon
CFD	=	Computational Fluid Dynamics
COD	=	chemical oxygen demand (mg/L)
CSTR	=	Completely (mixed) stirred tank reactor
DO	=	dissolved oxygen concentration (mg/L)
DS	=	dry solids (usually %)
EC	=	Electrical conductivity
EP	=	Equivalent Person
HRT	=	hydraulic retention time (days)
JEG	=	Johns Environmental Group Pty Ltd
LAR	=	Lagoon Activity Ratio
MBR	=	Membrane Bioreactor
MEDLI	=	Model for Effluent Disposal using Land Irrigation
MTC	=	Mass transfer coefficient (units dependent on type)
NH <sub>3</sub> -N	=	ammonia-nitrogen concentration (mg/L)
N	=	Nitrogen
NOB	=	Nitrite Oxidising Bacteria
NO <sub>2</sub> -N	=	nitrite-nitrogen concentration (mg/L)
NO <sub>3</sub> -N	=	nitrate-nitrogen concentration (mg/L)
P	=	Phosphorus
PP	=	Particulate phosphorus
QWMN	=	Queensland Water Modelling Network
STP	=	Sewage Treatment Plant
TDS	=	Total Dissolved Solids (mg/L)
TKN	=	Total Kjeldahl nitrogen (mg/L)
TN	=	Total Nitrogen concentration (mg/L)
TP	=	Total Phosphorus concentration (mg/L)
TS	=	Total solids (mg/L)

TSS	=	Total suspended solids (mg/L)
VSS	=	Volatile suspended solids (mg/L)
WSP	=	waste stabilisation ponds
WWS	=	wet weather storage
WWTP	=	wastewater treatment plant

## 1. Introduction

### 1.1. Background

The pond module in MEDLI receives inputs from waste generation and provide outputs calculated on a daily time-step basis as inputs to the irrigation modules. Key aspects of the pond module include:

- A focus on simple pond types.
- Hydraulic modelling to incorporate natural mechanisms affecting the daily volume of water in the ponds and discharged to irrigation including evaporation, overflows, seepage into soil, and rainfall.
- Pond chemistry modelling to close mass balances over ponds for nitrogen, phosphorus and salts. MEDLI captures the impact of volatilisation (nitrogen), sludge generation and accumulation, overflows and seepage on the partitioning and concentrations of these components between solid, atmospheric and liquid (irrigated effluent and overflow) phases in the pond system.
- This allows the module to output daily volumes requiring irrigation and/or storage with their corresponding nutrient and salt concentrations.

MEDLI originated in 1996 and has been used widely for the design of land application systems across Australia. Indeed, Johns Environmental (JEG) has used MEDLI extensively since 2000 to assess the sustainability of both existing and greenfield effluent irrigation systems in most States and Territories of Australia. Justin Galloway, a soil scientist with JEG and specialising in the impact of effluent on land, has applied MEDLI on an almost daily basis since 2002.

#### 1.1.1. Treatment System Changes since 1996

Achieving the stringent requirements for sustainable effluent irrigation systems in Australia has led to a reduction in the number of “traditional” pond systems featured in MEDLI. For many agri-industry sites relevant changes include:

- A transition to covered anaerobic lagoon (CAL) systems with biogas capture.
- Adoption of technologies including Biological Nutrient Removal (BNR) activated sludge systems, Membrane bioreactors (MBR), and aerated ponds to name a few.
- Chemical dosing for phosphorus reduction.
- A focus on minimising seepage through the use of low permeability liners including clay or synthetic geomembrane liners.
- Improved sludge management to control accumulation; and
- Improved sizing of wet weather storage (WWS) dams to permit more sustainable irrigation for example on the basis of soil moisture deficit control.

Clearly these changes in the MEDLI “marketplace” seriously impact the utility of the pond module especially for the larger treatment systems which are more likely to install the more complex treatment technologies. The changes significantly complicate nitrogen transformations occurring during treatment. For example, oxidised nitrogen species were rare in “traditional” pond systems but may predominate in the treated effluent of newer technologies. Also, ammonia volatilisation may be significantly reduced in CALs relative to open anaerobic ponds with long retention times.

Expanding the scope of the Pond Module to embrace all of these newer technologies would be an almost impossible task given the pace of change in treatment technologies. Instead, the value of the existing pond module structure in practice lies in:

- Its ability to allow MEDLI designers to explore the interaction between WWS dam sizing and irrigated land area. This is critical for all developments whether municipal, industrial or agricultural. WWS dams are expensive to construct to modern standard and can be challenging to manage to minimise nuisance issues such as wave control, algal blooms, vermin and odour. On the other hand, areas of land suitable for sustainable irrigation can be limited for existing facilities and/or expensive. So this aspect of MEDLI is particularly valuable

in practice. For this application of MEDLI, the user often already knows the typical composition of the treated effluent and it is the daily time-step variation in the component concentrations and water balance in the WWS dam that become important rather than trying to model sludge deposition and concentration changes in the treatment train.

- Evaluating sludge accumulation rates in anaerobic systems (including CALs) and the WWS dam and the effect on nitrogen and phosphorus concentrations in the effluent irrigated (or overflow). Active sludge management in CALs is becoming a significant issue for many of the industries who use MEDLI, and it would be very helpful to better model partitioning of nutrients into sludge and output the result.

An emphasis on these aspects of the Pond Module in the scientific review would be valuable.

#### 1.1.2. Scientific Advances in Pond Modelling: Scope for the Review

In terms of the Pond Module components, there is likely to be little gained from the review of hydraulic component which appears adequately modelled in the existing module. It is unlikely that the science has changed dramatically in this respect.

In terms of modelling of ponds themselves, there have been some significant developments particularly including the use of computational fluid dynamics (CFD) modelling to better understand pond hydraulic impacts on treatment performance (Ho, van Echelpoel, & Goethals, 2017). However, CFD modelling is likely to be too sophisticated to embody in MEDLI. Several pond specialists have nevertheless developed simplified models from the results of CFD studies that may be useful to review.

A major feature of the MEDLI pond module is its reliance on piggery models to estimate sludge accumulation rates, pond chemistry and nutrient partitioning. Using MEDLI for other industry sectors requires substantial adjustment of parameters to obtain a valid output. One example is the high partitioning of phosphorus to sludge in anaerobic ponds. This is not observed for meat processing systems. There is merit in reviewing recent studies to assess aspects such as sludge deposition and quality in a wider range of effluents treated through ponds, particularly anaerobic lagoons (including covered systems).

There is also value in reviewing scientific studies of sludge and nutrient transformations in WWS dams since in many cases, the impounded effluent may be held for long periods of time during which even slow acting mechanisms such as volatilisation and algal growth can profoundly influence nutrient levels.

## 1.2. Methodology Statement

The MEDLI pond chemistry review involved the following steps:

- A review of the current MEDLI Technical Reference Manual to:
  - Extract models and recommended default values in the pond chemistry module section.
  - Use experience to determine models and values that are either questionable, out of date, not applicable to non-piggery applications or based on assumptions.
  - Identify vulnerable aspects, especially when applied to STPs or food production facilities.
- Review QWMN Models to identify and assess models that may be valuable in updating the pond module in MEDLI.
- Review the recent pond-based publications relevant to the pond module. Two of importance are:
  - The excellent book by Shilton (2005) "Pond Treatment Technology" which encapsulates recent research on pond systems up to about 2006.
  - "Waste Stabilization Pond Design Manual" authored by Ashworth and Skinner (2011). This publication was specifically developed for tropical Australia and incorporates much of the work conducted by Duncan Mara over many decades for tropical and sub-tropical pond systems. There is strong Government interest in developing

agricultural and food production systems in Northern Australia (including North Queensland) and this publication is worth evaluation for its value to MEDLI upgrades.

- Review of scientific and technical publications published from 1995 to present focused on vulnerable aspects of the current MEDLI model.
- Collation of relevant information.
- It was then agreed that the subsequent work should particularly focus on nitrogen and phosphorus transformations and removals in ponds and how the modelling of removals of these nutrients in ponds could be improved.

## 2. Current MEDLI Technical Document - Pond Chemistry Module

This section describes the assessment of Chapter 3 “*Pond Chemistry and Water Balance*” in the MEDLI Technical Reference document.

### 2.1. MEDLI Assessment

The current models and default values in the pond chemistry section of the MEDLI Technical Reference were reviewed to determine aspects that are either questionable, out of date, generally not applicable to non-piggery applications or where recent research has provided an improved understanding of the field and/or generated superior approaches that can be realistically embedded in MEDLI.

Table 1 summarises our assessment of the equations and default values in the listed sections of the MEDLI Technical Reference, pond chemistry module section. The intent was to identify aspects:

- where the approach used in MEDLI was sound and there had been little or no change in the underlying science. These aspects are identified as “Strong” in Table 1.
- where the approach adopted in MEDLI was vulnerable to error, especially when applied to STPs or food production facilities. These “vulnerable” aspects were prioritised in the technical literature review.

Table 1: Review of MEDLI Technical Reference - Pond Chemistry Module Chapter

Model	Equation	Status	Comment
Pond Geometry	3.1 – Top dimensions	Strong	Minor improvement to allow calculation of equivalent surface area and volume for irregular shaped ponds recommended.
	3.2 & 3.3 – Bottom dimensions	Strong	
	3.4, 3.5, 3.6 & 3.7- Volume	Strong	Minor improvement to assume side slope of 30° not 45°
	3.8 - Depth	Strong	
Hydraulic Retention Time	HRT = Volume / Flow Assumes CSTR	Strong	Minor improvement to remove assumption that anaerobic ponds need 40d HRT recommended
Hydraulic Balance	3.9 – Water balance	Strong	Conservation of (water) mass equations and pathways for inputs/outputs remain valid

Model	Equation	Status	Comment
	3.10 & 3.11 – Rainfall	Strong	
	Runoff = 0	Strong	
	3.12 - Evaporation	Strong	Minor improvement to check the assumed default value of 0.7 anaerobic and 0.73 other ponds which do not appear to be based on research.  New addition. If covered pond then 0
	3.13 - Seepage	Strong	Includes advice that HDPE lined ponds would be zero
Nutrient Mass Balance	3.14 – TN mass balance	Vulnerable	Conservation of (nitrogen) mass equations and pathways for inputs/outputs remain valid but: <ol style="list-style-type: none"> <li>1. Modelled ammonia volatilization rate is high.</li> <li>2. Assumes 70-80% TN present as NH<sub>3</sub>. This is high for non-anaerobic ponds</li> <li>3. Does not account for pH, temp or mixing.</li> </ol>
	3.15 – TN mass in sludge	Strong	
	3.16 – TP mass in sludge	Vulnerable	Assumes that 90% of the P entering anaerobic pond settles in sludge. This is very high for non-piggery ponds.
	3.17 – TP mass balance	Strong	Conservation of (phosphorus) mass equations and pathways for inputs/outputs remain valid.
	3.18 – TDS mass balance	Strong	Conservation of (TDS) mass equations and pathways for inputs/outputs remain valid.
Anaerobic Pond	3.19- Sludge deposition	Vulnerable	Sludge deposition estimation is challenging for ponds. Among other aspects, MEDLI: <ol style="list-style-type: none"> <li>1. Only allows 1<sup>st</sup> pond to be anaerobic.</li> <li>2. Assumes only anaerobic ponds accumulate sludge</li> <li>3. Uses accumulation rate of 0.00303 and 0.004 m<sup>3</sup>/kg TS/d for pigs and cattle respectively.</li> </ol>

Model	Equation	Status	Comment
			Relevance for STPs & other pond effluents is questionable. 4. Ignores sludge from algae growth.
	3.20 – Fraction of nutrient settled	Vulnerable	1. Based on manure characteristics and estimated to be 0.0645 m <sup>3</sup> /kg TKN and 0.1894 m <sup>3</sup> /kg TP 2. Relevance for STPs & other pond effluents is questionable. 3. All settled fractions based on piggery solids.
	3.21 – Minimum anaerobic treatment volume	Vulnerable	1. Based on loading rate of 0.1 kg VS/m <sup>3</sup> /day and adjusted by temperature factor (LAR). 2. Relevance for STPs & other pond effluents is questionable.
	Minimum Volume for irrigation from anaerobic pond	Strong	
	Desludging protocol	Strong	

## 2.2. Vulnerable MEDLI Modules

The review of the MEDLI Technical Reference identified three major vulnerable aspects for particular focus:

- In the Nitrogen Mass Balance, the treatment of ammonia and its volatilisation from ponds.
- In the Phosphorus Mass Balance, the assumptions used in the partitioning of phosphorus between the solid and dissolved states.
- The estimation of sludge deposition and partitioning of nutrients in ponds.

In addition, the following aspects may benefit from small improvements:

- Pond Geometry
- Hydraulic retention time
- Evaporation
- Pond type allocation
- Anaerobic Pond minimum treatment volume
- Desludging protocol.



### 3. Review of QWMN Models

The Queensland Water Modelling Network (QWMN) Water Model Catalogue (Oct 2017) was reviewed to assess the possibility of suitable models for application to the MEDLI pond chemistry module.

Table 2 summarises the models, model use, description, and applicability to the MEDLI pond module.

It is possible that the WATHNET, IQQM or MIKE model may have pan evaporation factors for ponds and eWater Source – Water Quality may have nutrient removal estimates. The equations within each of these models would need to be examined to determine if this information is included and if it is relevant to the MEDLI pond chemistry module.

Table 2: Review of QWMN Models to MEDLI Pond Chemistry Module

Model Name	Model Use	Brief Description	Applicable to MEDLI Pond module
SoilWater App (SWApp)	Farmer decision support	Soil water balance simulation to explore irrigation approaches using historic rainfall data.	No
HOWLEAKY	Agricultural systems assessments	Estimates soil water balance, runoff, erosion, and constituent loads	No
APSIM	Agricultural systems assessments	Predictions of crop production in relation to climate, genotype, soil and management factors plus long-term soil management	No
GRASP & AussieGRASS	Agricultural systems assessments	Model of climate, soil, plant, animal management interactions in the perennial grasses of northern Australia	No
2CSALT	Planning Support	Predicts the quantity and timing of water and salt export from upland catchments	No
Sacramento	Catchment Policy	Simulated daily stream flows using moisture store capacities, lateral outflows, flow between stores and losses	No
SIMHYD	Catchment Policy	Simulates daily stream flow from daily rainfall and potential evaporation.	No
WATHNET	Catchment Policy	Uses network linear program to simulate a system of storages, transfer links and demand centres.	May contain evaporation factors
IQQM	Catchment Policy	Prime purpose is to simulate the impacts of water resource management strategies on flow to assess impact of water diversion scenarios	May contain evaporation factors

Model Name	Model Use	Brief Description	Applicable to MEDLI Pond module
eWater Source - Water Quantity	Catchment Policy	Runs a daily time step and is designed to assess the long-term impacts of water resources policy on system storages, flows and water shares.	No
eWater Source - Water Quality	Catchment Policy	Simulates catchment runoff generation and constituent generation from the addition of a number of functional units representing different land uses. Uses a number of filter and decay models within the stream network	No
MIKE	Catchment Policy	Model complex river channel networks, lakes and reservoirs	May contain evaporation factors
TUFLOW	Receiving water & coastal water quality reporting	Simulates free surface flows for urban waterways, rivers, floodplains, estuaries and coastlines	No
HEC-RAS	Catchment Policy	1D and 2D hydraulic calculations for a network of natural and constructed channels.	No
MODFLOW	Groundwater Policy	3D modular groundwater model.	No
BC2C	Groundwater Policy	annual time step model to estimate the impacts of changes in forest cover on stream volume and salt load to groundwater	No
Receiving Water & Coastland Models	Receiving water & coastal water quality reporting	links hydrodynamic model, sediment transport model and biogeochemical model in relation to the protection and preservation of the Great Barrier Reef	No

## 4. Nitrogen Mass Balance

### 4.1. Current MEDLI equations and assumptions

The nitrogen mass balance over a pond is calculated using MEDLI Technical Reference Equation 3.14 on a daily time step basis to estimate the total nitrogen concentration in the supernatant (effluent discharged from the pond). Essentially a two-compartment model is adopted – one is a “soluble” total nitrogen compartment comprising the non-settling nitrogen fraction; the second is the settled or solid total nitrogen fraction which accumulates in the base of the pond. The equations are solved on each pond but only the anaerobic pond has a settling fraction (e.g.,  $Fr\_N = 0$  for other ponds).

The phenomena modelled include entry & exit (to irrigation from the final pond) of nitrogen in the effluent streams, ammonia volatilisation, seepage, and overflow losses, recycle and solids settling. Mineralisation feedback of nitrogen from the sludge to the soluble form is discounted on the basis that its contribution is negligible.

MEDLI assumes that the only forms of nitrogen of consequence in the ponds are organic (TKN) and ammonia nitrogen. It predicts the concentration and mass of these forms in the pond effluent by applying a proportionality constant, rather than using a nitrogen species mass balance. Oxidised forms of nitrogen are ignored.

In our opinion, the primary weaknesses of the nitrogen mass balance approach in MEDLI are:

- Settling of nitrogen-containing solids is assumed in the anaerobic pond only.
- It assumes a single “proportionality constant” is sufficient to model ammonia concentrations and volatilization rate in the ponds. MEDLI assumes that the TN is comprised of 70 to 80% ammonia which whilst this is typically true after anaerobic treatment, it is not generally true to all wastewater ponds and effluent types. The MEDLI volatilization rate also ignores seasonal impacts, pH, temperature and mixing which can be profound especially in final storage lagoons with long retention times. For a daily time step model this simplification is prone to considerable error in the mass of nitrogen irrigated.
- The models assume no nitrogen loss due to biological uptake and subsequent sedimentation of the resulting biomass or from nitrification/denitrification reactions catalysed by bacteria in the pond.

### 4.2. Literature Review

Nitrogen removal in wastewater treatment ponds was until recently attributed to sedimentation of organic nitrogen and ammonia volatilisation (Shilton, 2005). This was probably due to the linkage of the widespread success of the Pano & Middlebrooks equations (Pano & Middlebrooks, 1982) in estimating nitrogen loss in real waste stabilization pond (WSP) systems with the fact that the equations were based on ammonia volatilisation as the primary N removal mechanism.

However, a number of more recent studies using  $^{15}\text{N}$ -labelled ammonia tracer (Camargo Valero & Mara, 2007; Camargo Valero, et al., 2009),  $^{15}\text{N}$ -labelled nitrite (Camargo Valero, et al., 2009), gas hoods and sediment collection (de-Assuncao & von-Sperling, 2012; Bastos, et al., 2018; Rodrigues, et al., 2017; Zimmo, et al., 2003) demonstrated that algal growth and subsequent sedimentation and simultaneous nitrification/ denitrification are the most significant total nitrogen removal pathways in ponds. Mayo & Abbas, (2014) through modelling and actual (small) pond measurements suggest that N removal occurs mainly:

- In primary facultative ponds mainly by uptake of ammonia to algal and microbial growth with subsequent sedimentation of the microbial-embodied organic nitrogen and secondarily through denitrification (a much lesser quantity of removal).
- In maturation ponds mainly through denitrification.

The major ammonium removal pathway in facultative ponds (also known as waste stabilization ponds) is now considered to be biomass (algal and bacterial) growth. The high pH conditions created by algal growth were assumed to be favouring volatilization for ammonia removal. But several studies have shown that volatilisation was measured to only account for 1.5 to 3.8% of total ammonia removal (de-Assuncao & von-Sperling, 2012; Zimmo, et al., 2003 and Camargo Valero & Mara, 2007) while algal growth accounted for ~70% (Camargo Valero & Mara, Nitrogen removal in maturation ponds: tracer experiments and <sup>15</sup>N-labelled ammonia, 2007). Algal growth rate is proportional to pond area and solar intensity (Ashworth & Skinner, 2011). These studies were conducted in sewage treatment ponds where ammonia levels are less than 50 mg/l.

Potentially for effluents where ammonia levels can be 200 – 300 mg/l, volatilisation may account for a higher proportion of the removal, since the process is concentration-dependent. In addition, algal growth inhibition occurs at high organic, ammonia and sulphate concentrations (Gehring, et al., 2010, Ashworth & Skinner, 2011) which explains the negligible algal growth in anaerobic ponds (in addition to poor light penetration) and to some extent perhaps in ponds treating meat processing wastewater.

The overall total nitrogen removal is typically less than the ammonia removal. Total nitrogen removal via the algal biological uptake route requires algae sedimentation as well. Algae discharged with the effluent stream is correctly included in effluent total nitrogen and has just simply transferred the nitrogen form from ammonia to organic nitrogen. The TN removed is typically around 55% of the ammonia removed from aerobic ponds (Bastos, et al., 2018; Silva, et al., 1995 and Camargo Valero & Mara, 2007).

The settled sludge in wastewater ponds will also re-release nitrogen into the water column as it digests and releases mineralised forms of nitrogen back to the soluble nitrogen compartment of the pond.

Nitrification and denitrification have been proven to be a significant pathway for nitrogen removal through <sup>15</sup>N-labelled ammonia and <sup>15</sup>N-labelled nitrite studies (Camargo Valero, et al., 2009). In the past this route was assumed to be insignificant due to very low nitrite and nitrate concentrations typically found in pond effluents and the generally low bacterial concentrations in ponds. However, this is found to be because the nitrification rate generally matches the denitrification rate (Ashworth & Skinner, 2011). Camargo Valero, et al. (2009) concluded that nitrification-denitrification is a major mechanism for nitrogen removal in all seasons whilst algal growth was seasonal. Rodrigues, et al. (2017) also found all bacterial groups (AOB, NOB, anammox and denitrifiers) present in the liquid and sludge of an established aerobic pond.

### 4.3. Nitrogen Modelling

This section focusses on the models describing nitrogen transformations and/or removal in WSP. Only models of significant relevance to MEDLI incorporation have been selected.

#### 4.3.1. The Pano & Middlebrooks equation

Camargo Valero & Mara (2010) provide an insightful, thorough and cogent review of the state of nitrogen modelling for WSPs treating sewage. They critically summarise the two main models most commonly applied to date in the light of the most recent scientific findings. This includes:

- Pano & Middlebrooks (1982) ammonia removal model.
- Stratton's contributions (Stratton, 1968 and Stratton, 1696) on volatilization widely used by subsequent authors.

They note that these models pre-suppose the dominance of ammonia volatilization for N removal in WSP. In the light of more recent science (mentioned above), this assumption now appears erroneous. In particular, Stratton's equations (used by many subsequent authors) seriously overestimate volatilisation contributions to N removal (Camargo Valero & Mara, 2010; de Assuncao & von Sperling, 2012) and use of this model cannot be supported.

The Pano & Middlebrooks model equations are as follows:

For temperatures up to 20°C:

$$\frac{C_e}{C_i} = 1 / [1 + \frac{A}{Q} (0.0038 + 0.000134T) * e^{\{(1.041+0.044T)(pH-6.6)\}}]$$

where:

- $C_{e,i}$  = ammonia-N concentration of effluent and influent, respectively  
 $Q$  = average flow rate into pond (m<sup>3</sup>/d)  
 $A$  = pond surface area (m<sup>2</sup>)  
 $T$  = pond water temperature (°C)

For temperatures of 21 - 25°C the following equation was recommended:

$$\frac{C_e}{C_i} = 1 / [1 + 5.035 * 10^{-3} * \frac{A}{Q} * e^{\{1.540(pH-6.6)\}}]$$

Ironically, the Pano & Middlebrooks equation along with its variants (Silva et al, 1995, Soares et al, 2001, Bastos et al 2007) continues to provide reasonably good average prediction of ammonia removal from ponds despite its development on the assumption of ammonia volatilization dominance. The reason for this according to Camargo Valero & Mara is that the model essentially describes N removal as a first order reaction in a completely mixed reactor (pond) system which reasonably describes (in a lumped fashion) most of the N removal or transformation mechanisms at work (e.g., incorporation into biomass, nitrification/denitrification) for similar pH and temperature ranges.

#### 4.3.2. Issues using Pano & Middlebrooks modelling

In the context of the MEDLI software, a reasonable prediction of ammonia levels in the effluent of the ponds is important. Ammonia levels are crucial for estimating volatilization losses during irrigation. In addition, ammonia N tends to represent the bulk of the soluble N present (except where ammonia effluent levels are very low) since concentrations of oxidized nitrogen in waste stabilisation pond effluents is typically negligible. The Pano & Middlebrooks model does this relatively well.

##### *Ammonia vs Total Nitrogen Removals*

An important issue is that the Pano & Middlebrooks model was developed around ammonia concentrations. It provides a less useful understanding of total nitrogen levels and removals in pond effluents (TN removal is generally less than for ammonia). Much of the non-ammonia TN in pond effluents is organic N incorporated into microbial or algal cells and is principally particulate nitrogen.

It could be argued that this is an acceptable trade-off. To some degree this particulate nitrogen form is less impacting on the irrigation environment since time is required to mineralize the nitrogen back to soluble (and potentially) mobile forms in the soil matrix. The soluble ammonia fraction is the more impacting nitrogen discharge to irrigation.

Nevertheless, from the viewpoint of using the Pano & Middlebrooks equation to estimate TN levels in the final effluent of the ponds for compliance concentrations, if TN is used rather than ammonia-N, then final predicted TN levels will tend to be lower than real levels.

Reed et al (1995) published a similar equation for TN removal in WSP using a rate constant with temperature dependence. Adoption of this equation may permit estimation of TN removal.

$$C_e = C_i e^{-K_T(t+60.6(pH-6.6))}$$

Where:

- $C_{e,i}$  = TN concentration of effluent and influent, respectively

$K_T$  = rate constant (1/d) at temperature  $T$  (°C) with relationship to temperature expressed as:

$$K_T = K_{20}\theta^{(T-20)}$$

$K_{20}$  = rate constant value at 20°C = 0.0064 /d

$\Theta$  = temperature constant, 1.039

$A$  = pond surface area (m<sup>2</sup>)

$T$  = pond water temperature (°C)

$t$  = hydraulic retention time (d)

The pond water temperature can be obtained from the widely used Mancini & Barnhart equation given in Shilton (2005).

#### *Effluents with Higher TN*

Almost all recent literature addresses STP WSPs characterised by low TN levels (50 mg/l or less). For industrial or intensive animal effluents where TN levels may be 200 - 400 mg/l (for meat processing plants) or even higher for intensive agriculture, some of the conclusions above may not be appropriate.

For example, where pH is high, temperatures warm (30°C or more), losses by volatilization may be proportionally higher than for STPs since the volatilisation rate is linearly proportional to liquid ammonia concentrations, whereas rates of other processes such as algal growth (and so growth assimilation of nitrogen) is described better as a Monod-style function where growth or activity rates flatten (become zero order) at higher concentrations.

Some evidence of this difference in behaviour is seen in the study of Gehring et al (2010) using a modified ASM3 model (see section below) for a pilot scale pond system in Brazil (similar latitude to Rockhampton) treating landfill leachate with high N concentrations (500 mg/l). These authors measured significant ammonia volatilisation rates of 18.2 and 4.5 gN/m<sup>2</sup>.d in the facultative and maturation pond, respectively. These are much higher than typical values of 0.01 – 0.02 gN/m<sup>2</sup>.d reported for sewage-based systems.

#### 4.3.3. Dynamic Biokinetic Models

More recent sophisticated dynamic biokinetic (using the nomenclature of Ho, et al., 2019) models have been published for nitrogen transformations in WSPs. The two prominent examples include:

1. The dynamic rational model of Senzia, et al., (2002) and Mayo & Abbas (2014). This model considers dynamic mass balances on ammonia, organic and nitrate nitrogen and captures six N loss/transformation pathways including mineralisation, nitrification, denitrification, microbial uptake (algae and bacteria), permanent sedimentation and ammonia volatilisation.
2. Dynamic modelling based on the ASM3 (Activated Sludge Model No. 3) modified to include processes specific to WSPs such as algal growth and ammonia volatilisation by Gehring et al (2010). This is a sophisticated model based on the Gujer matrix approach and using the current approach used to design intensive wastewater treatment systems.

In contrast to the empirical model of Pano & Middlebrooks, these models allow discrimination between the various N removal mechanisms based on equation sets for each mechanism. A quick description of each is provided below.

*Mayo & Abbas (2014) Biokinetic Rational model*

This model updates the earlier modelling work published by Senzia, et al., (2002) a decade earlier largely through updated model constant values rather than changes in model structure and is particularly focussed on nitrogen transformation and removal in WSPs. As noted above six main mechanisms are incorporated. Key elements of the model are:

- Nitrogen uptake into microbial (bacteria and algae) is modelled as the uptake of ammonia and nitrate using Monod kinetics. Unlike Gehring, et al., (2010), there appears to be no discrimination between algae and bacteria and no dependence on light conditions.
- Sedimentation of biomass nitrogen is incorporated as a linear function of the organic nitrogen concentration where the settling rate varies between 0.001 – 0.1/d. This is similar to the current MEDLI approach (net settling fraction) used for the first (anaerobic) pond.
- Nitrification and denitrification reactions are modelled using Monod kinetics with Arrhenius temperature adjustments and standard adjustment for inhibition (of nitrification) by pH and DO. It is not clear how pH changes are modelled.
- Ammonia volatilisation is estimated based on the Stratton equation. There is no clear dependence on wind velocity and in our opinion, this relationship is questionable and likely to underpredict volatilisation contributions to N removal.

The model gave reasonable prediction when compared to a WSP system based in Tanzania (Dar es Salaam). Sedimentation of biomass was the major contributor to N removal in the facultative pond and denitrification in the maturation pond, although overall reported removals in the pond system are quite small (< 15% per pond).

*Gehring et al (2010) Biokinetic modified ASM 3 model*

Gehring, et al., (2010) adopt the ASM3 dynamic model developed by Gujer, et al., (1999) for activated sludge systems and modify it to account for algal growth and ammonia volatilisation to attempt to describe pollutant removals (COD, TSS and nitrogen) in WSPs. It has therefore a broader focus than the model of Mayo & Abbas. Key features of the model include:

- Algal growth processes based on ammonia and nitrate and endogenous respiration are incorporated from the River Water Quality Model (RQWM) No. 1 by Reichert, et al., (2001). As per the ASM type models, the kinetics of biological reactions are modelled as Monod equations based on maximum growth rates and half saturation constants with allowances for inhibition by various factors. Light attenuation in the pond is included.
- Gas transfer processes are also modelled, especially ammonia volatilisation. Unlike most pond literature models which use “mass transfer coefficients (MTC)” based on static gas hood measurements and the largely discredited Stratton (1969) relationships, these authors use mass transfer relationships where the MTC incorporates the effect of wind velocity, which has a significant influence on mass transfer processes in ponds. This may help explain the higher volatilisation rates observed compared to earlier studies.
- Pond pH was calculated using solution of an ionic charge balance. This appeared to simulate dynamic pH change well. The pH is a critical factor affected by and affecting many processes including algal growth and ammonia volatilisation.
- Hydraulic behaviour was modelled as complete mix, which is the usual simplification for pond models.
- Other mechanisms in the pond were described per the usual ASM3 equations, although the high ammonia level (500 mg/l) in the leachate ponds had profound impacts (according to both the model and measured data) on bacterial and algal growth and activity and nitrification/denitrification.



- Strangely, sedimentation processes were ignored. This is potentially a significant weakness of the Gehring *et al* (2010) model given the importance of algal growth and sedimentation in nitrogen capture reported by many researchers (refer Section 4.2).

Gehring *et al* (2010) report reasonable prediction of nitrogen removal compared to the results from their pilot scale ponds (facultative and maturation) treating leachate wastewater. The mechanisms responsible for nitrogen loss, however, are significantly different to work by others with WSPs treating sewage with a tenth the TN concentration. The authors admit that validation of the model is difficult given the paucity of full-scale pond data of relevance and the uncertainty associated with many of the model constants.

#### 4.4. Recommendations for Nitrogen Modelling in MEDLI

In summary, there remains considerable dispute as to the predominant mechanisms for nitrogen removal in WSPs. While more recent literature suggests that the contribution of ammonia volatilisation has been overblown, the experimental techniques used to measure volatilisation have comprised stagnant chamber gas hoods and the models have incorporated relationships from Stratton's work which ignores the impact of wind velocity and fluid properties (density, viscosity) on ammonia mass transfer from large pond surfaces. Nevertheless, there is evidence that other mechanisms, especially incorporation of N into biomass and subsequent sedimentation and nitrification/denitrification play a significant role, the latter more likely in latter ponds in a series, the former important in primary facultative ponds.

In this respect, the current approach in MEDLI is not without merit:

- MEDLI incorporates a sedimentation loss of particulate nitrogen in the first pond but assumes none in subsequent ponds. Like the approach of Mayo & Abbas (2014) a simple linear function is assumed based on  $Fr_N$  – a net settling fraction. The challenge is what this value should be. Various estimates of sludge settling have been derived in literature and there is a very wide range. Gehring *et al* (2010) simply ignore it. The Pano & Middlebrooks approach works only with the soluble N fraction – an acknowledged weakness. There remains no clear simple solution.
- Ammonia volatilisation. The current MEDLI approach is based on the now disputed view that ammonia volatilisation is a predominant N removal mechanism. The equation used to estimate volatilisation is extremely empirical – even by pond modelling standards – and appears to have little dependence on factors critical to volatilisation such as water temperature, pH, retention time and wind velocity.

Other N removal mechanisms are neglected presumably on the basis that their contribution is minimal (as was accepted wisdom until recently).

Existing QWMN Models offer little benefit since nitrogen transformation and losses are either not included, or the models are not appropriate to WSPs.

In moving forward, it is useful to focus on the aims of this review which can be summarised as:

- The need to maintain a sensible balance between modelling complexity (user-friendliness) and output accuracy (per Saltelli, 2019); and
- To ensure that modelling is conservative. That is, the modelled N removals are not overestimated to the subsequent cost of environmental sustainability in the real system being modelled.

Our recommendations are:

1. Biokinetic models. It is our view that the biokinetic models are not suitable for incorporation into MEDLI for the following reasons:
  - Complexity. They add a fundamental complexity to the software due to the large equation set and the number of associated model parameters that need to be

quantified. This detracts from future user-friendliness without necessarily providing superior outcomes. With some effort it may be possible to provide a suitable set of parameter values, but little or any work has been published with values for Australian WSPs and conditions. Consequently, there would be a dependence on values derived and used for activated sludge BNR systems in Australia, which in some instances may not be appropriate for WSPs. It is important to use Australian derived values, as the nature of dissolved species from the unique Australian flora has been shown to impact rates of microbial processes compared to overseas.

- Validation Issues. As Ho et al (2019) indicate, biokinetic models have not been validated with full-scale WSP data. In contrast, the simpler Pano & Middlebrooks model outcomes has been widely supported by studies on full-scale systems across the world.

Consequently, it is perhaps too early to move to these kinds of models at this stage.

2. Any model based on the Stratton (1968, 1969) work in regard to ammonia volatilisation is likely to be compromised. More recent work has identified inconsistencies with this model, which has been widely incorporated into more recent WSP modelling work and is likely to under predict losses from ammonia volatilisation.
3. Soluble N removal. There is benefit in adopting the Pano & Middlebrooks (1982) model approach to replace the existing ammonia volatilisation equations in MEDLI. The model has been well validated with pond systems and provides a superior estimation of soluble nitrogen (ammonia) losses to the existing MEDLI equation. Although originally developed on the basis of ammonia volatilisation as the predominant mechanism of nitrogen loss in ponds, the model equations represent an aggregate biological/physicochemical removal process very satisfactorily, rather than a volatilisation-only process. In this sense, the Pano & Middlebrooks model is superior to the existing MEDLI equations.

It could be argued that the focus on ammonia ignores other soluble nitrogen species, but ammonia is the principal soluble form of nitrogen in most WSP and agro-industrial effluents with soluble biodegradable organic nitrogen species rapidly mineralised in ponds. The implementation of this model would strengthen estimation of soluble nitrogen removal in the model.

4. Pond pH. A challenge for adoption of the Pano & Middlebrooks model, however, is estimation of seasonal pond pH, which is especially impacted by algal growth. One option may be to include a simple ionic balance model such as that used by Gehring et al (2010). A weakness of this though is that it does not capture algal impacts. This suggests that the user would need to input a seasonal pH curve for the pond system based on historical behaviour for the most accurate results. Fortunately, the aggregated mechanism nature of the Pano & Middlebrooks model as used in practice (rather than as originally intended by the authors) reduces dependence on pH conditions.
5. Sedimentation. Nitrogen loss by sedimentation of (a) influent particulate organic nitrogen and (b) soluble forms transformed into particulate biomass (algae and bacteria) through uptake by growth remains a severely intractable issue. Whereas losses through settling of influent TSS can be readily determined through appropriate influent analysis (although more challenging for greenfield industrial sites), the estimation of net losses through biomass sedimentation is challenging. This is somewhat disturbing given the more recent pond work which suggests this is a major mechanism of N removal. Furthermore, estimates of sludge sedimentation rates in WSPs are hugely variable even for a single type of pond (e.g., primary facultative). The existing approach in MEDLI seems warranted (the use of a simple net settling fraction, Fr<sub>N</sub>) provided the value is reasonable and not overstated.
6. Net Settling Fraction (Fr<sub>N</sub>). Currently MEDLI allows settling fraction only for the first (anaerobic) pond in a series of four. While this is a not unreasonable simplification, an

alternate option would be to allow for this term to be available in all ponds if desired, but with the value decreasing down the pond series since settling fraction in the last 2 ponds is likely to be much lower due to the loss of settleable influent N in earlier ponds.

7. An alternative to estimating N loss through sedimentation is to use the Reed et al (1995) equation to estimate TN removal across the pond system. The challenge with this approach is that this modification of the Pano & Middlebrooks equation is fundamentally less appropriate for TN in the effluent (soluble & particulate).
8. Applicability. In our view, the model needs to focus improvements in nitrogen estimation for STP WSP systems where traditional ponds remain in widespread use and where the need for intensive or mechanically aerated pond systems is unnecessary for treatment. Consequently, the Pano & Middlebrooks model represents our preferred way forward. In contrast, current practice for medium to large agro-industrial wastewater plants (e.g., meat processing, dairy processing etc) treating high nitrogen load (and concentration) wastewaters is to adopt intensive BNR systems. The use of MEDLI for the latter typically focusses on irrigation of an effluent of known nitrogen concentration (usually a function of compliance limits and available irrigation area and wet weather storage volume) which can be input as the effluent composition from the final pond.

## 5. Phosphorus Mass Balance

### 5.1. Current MEDLI Phosphorus Equations and Assumptions

The total phosphorus (TP) mass balance over a pond is estimated using MEDLI Technical Reference, Equation 3.16 and 3.17. The same two-compartment model approach is used as for nitrogen with one compartment computing the soluble (non-settling) TP and the second compartment, the solid (settling) TP. The equations are solved on each pond but only the anaerobic pond has a settling fraction (e.g.,  $Fr_P = 0$  for other ponds).

The phenomena modelled include entry & exit (to irrigation from the final pond) of TP in the effluent streams, seepage and overflow losses, recycle and solids settling. Mineralisation feedback of phosphorus from the sludge to the soluble form is discounted on the basis that its contribution is negligible.

Speciation of phosphorus forms is neglected. This is entirely reasonable, since in most instances in pond systems biological activity rapidly and almost stoichiometrically converts organic and condensed forms of phosphorus into the inorganic phosphate form. Precipitation reactions involving precipitation of phosphorus by reactions with cations are omitted and perhaps encapsulated in the “settling fraction” constant.

In our view, the major weaknesses of the phosphorus mass balance approach are:

- Settling of solids is assumed in anaerobic ponds only.
- MEDLI’s default assumption that 90% of TP entering the pond settles into the sludge is not appropriate for STP and agro-industrial effluents and almost certainly underestimates TP loads to the irrigation area if this default is selected in these situations.

### 5.2. Phosphorus Literature Review

In most wastewater pond systems phosphorus is removed by biomass assimilation and subsequent settlement (Ashworth & Skinner, 2011) and phosphate precipitation reactions promoted by alkaline pH conditions in the ponds (Shilton, 2005). Total phosphorus removal is typically inconsistent (Powell, Shilton, Pratt, Christi, & Grigg, 2007) with widely varying observed values (20 - 51% removal) quoted for facultative ponds (Shilton, 2005; Ashworth & Skinner, 2011) and 2 to 43% in aeration ponds (Bastos, et al., 2007; Shilton, 2005) with the higher the pH the better the removal (Bastos, et al., 2007) which illustrates the importance of precipitation reactions. Phosphorus reduction is unlikely to exceed 50% without chemical addition (Ashworth & Skinner, 2011) and these reductions are typically much less in agro-industrial systems where initial TP levels are much higher than in sewage.

The predominance of the removal mechanisms remains unclear. Shilton (2005) reports that precipitation results in the largest fraction of phosphorus removed. This was supported independently by sediment sampling from three facultative ponds in France (Gomez, Paing, Casellas, & Picot, 2000), which found inorganic phosphates accounted for 92-94% of total sediment phosphorus (~66% iron hydroxides and ~ 33% bound to calcium) However, Vendramelli *et al.* (2016) reported that phosphorus removal by assimilation into biomass appeared to be the greatest contribution to removal in Manitoba facultative ponds with only a small portion precipitated. Powell et al (2007) conducted experiments showing luxury uptake of P by microalgae under summer conditions (temperature).

Phosphorus removal through algal growth is difficult to accurately calculate as the amount of phosphorus in algae differs between species (Shilton, 2005) and most biological microorganisms have low uptakes (~ 1-2% of dry cell weight). In addition, nitrogen supply can also limit phosphorus removal by biomass assimilation (Vendramelli, Vijay, & Yuan, 2016) with a typical N:P ratio in the dry weight of algae and bacteria of 15:1 (Shilton, 2005) - higher than the N:P ratio in domestic wastewater.

The calculation of phosphorus removal by precipitation requires measurement of cations such as iron, calcium and magnesium (in the water column and sludge) and pond pH and temperature which vary seasonally.

An additional challenge is that phosphorus may also re-release from sediments during warmer months (Vendramelli, Vijay, & Yuan, 2016) with sediment decay typically 25 to 50% faster in anaerobic and facultative ponds than maturation ponds (Shilton, 2005). This may also change pond pH and ORP, both of which potentially may lead to redissolution of chemical precipitated forms (Gomez et al, 2000).

### 5.3. Phosphorus Modelling

The modelling of phosphorus removal in WSP is almost non-existent. They can be summarised as:

1. A regression equation model by Gomez et al (2000) based on work on STP WSP in Meze, France in which the phosphate concentration out is related to influent P input and particulate P concentration (PP).
2. An empirical equation from work on STP WSP in Canada by Vijay & Yaun (2017). The equation relates phosphate concentration out to precipitation reactions (due to soluble iron and calcium) and assimilation into biomass in which P(out) has a linear relationship to VSS, biomass settling rate and pond HRT.

More sophisticated modelling published in recent years based on mechanistic biokinetic models have neglected phosphorus species. It would not be difficult to include phosphorus reactions into these types of models, but the work has not been done.

#### 5.3.1. Gomez et al (2000)

This work examined the removal of phosphorus from a large WSP 3 pond system at Meze, France and is a continuation of extensive WSP studies by Picot's research group. A conceptual model was used to discriminate between variables important to phosphorus (as phosphate-P) concentrations in the pond effluent. From this they generated simple regression equations of the form:

$$PO_4 = aIP - bPP$$

Where  $a$ ,  $b$  are model constants determined from pond data sets.  $PO_4$  is the effluent phosphate concentration,  $IP$  is input phosphorus and  $PP$  is particulate phosphorus (in the pond) comprising non-dissolved forms of any type. These equations described between 46 – 74% of variation in phosphate levels. Constant  $a$  varied between 0.37 – 0.49 (lower in winter) and  $b$  between 0.52 – 0.76 with little change seasonally. There was relatively small difference between the three ponds suggesting similar mechanisms of P removal were at work.

The challenge of this work is the degree to which it is applicable given there is no dependence on removal on factors such as temperature, hydraulic retention time, pH and so on.

#### 5.3.2. Vijay & Yuan (2017)

This research was somewhat unique in being almost entirely focussed on P removal in WSP. The ponds were a 4-set of facultative ponds in Manitoba, Canada which served a town of 5,000 persons. The model developed by Vijay & Yuan is shown below:

$$P_o = P_i \left( 1 - \frac{e^{(A*0.053)}}{4} \right) - \frac{K_{sp}(AlPO_4)}{Al_i} - \frac{K_{sp}(FePO_4)}{Fe_i}$$

The first term accounts for P loss due to assimilation into biomass (represented as VSS) and the second and third terms account for P precipitated through reactions with trivalent aluminium and iron, respectively assuming a pond pH in the range 8 – 10. Assimilation is estimated as a linear function of biomass VSS growth and the pond retention time. Values given in the definition of the variables is from their work and should be applied with caution elsewhere since there is no compensation for temperature differences which can be expected to be significant.

$$A = VSS * G * VPC * t$$

where:

- $P_{o,i}$  = phosphate concentration out and in (mg/l)
- A = assimilated phosphate (mg/l)
- VSS = volatile suspended solids (mg/l)
- G = 0.17, VSS growth rate ( $d^{-1}$ )
- VPC = 0.0275, biomass P/C ratio (based on generalised cell formulae of algae and bacteria)
- t = average hydraulic retention time of pond (d).
- $K_{sp}$  = solubility products of the respective precipitation reactions.

The VSS concentration in the pond was estimated as a product of VSS in the influent and an exponential VSS settling function but could equally be estimated from TSS levels. It should be noted that the pond data set used to estimate model parameters is the same as that used to validate the model, which is not good modelling practice and probably accounts for the good degree of fit observed.

To provide an indication of the quantum of P removal given by the model, Table 1 presents outcomes using the equation set on arbitrarily selected initial P concentrations and HRT and a pond VSS concentration of 100 mg/l (mid-range of typical algal levels in ponds (Powell et al, 2007) and ignoring precipitation contributions. In the absence of anything better, the results are not without merit for estimating effluent phosphate concentrations, even without adjustments for Australian conditions.

Table 3: Solution of Vijay & Yuan equation ignoring precipitation

Initial P (mg/l)	HRT, t (day)	A (mg/l)	$P_o$ (mg/l)	P removal (%)
12	10	4.67	8.2	32
12	20	9.35	7.1	41
30	10	4.67	20.4	32
30	20	9.35	17.7	41

## 5.4. Recommendations for Phosphorus Modelling in MEDLI

In summary, while mechanisms promoting P removal in WSP are reasonably understood, in practice P removals in WSP are highly variable and the contributions of the different mechanisms to removal hard to determine. In short, there has been little effort made to model P removal in ponds, despite the acknowledged importance of phosphorus discharges in receiving environments.

As outlined in Section 5.1, the current MEDLI approach to estimate P removal in ponds is simple and brutal. All P removal (by biological, chemical and physical mechanisms) is credited to the first (anaerobic) pond through use of Fr\_P – a net settling fraction. The default value is 90%, a value which substantially over-estimates P removal for STP WSP and agro-industrial ponds.

As with nitrogen, the challenge is how to improve estimations for varying systems. Existing QWMN models offer little benefit since phosphorus transformation and losses are either not included, or the models are not appropriate to WSPs.

Our recommendations are:

1. P removal. The Vijay & Yuan model offers a relatively elegant, simple and reasonable equation set for use in the pond chemistry module. This model looks particularly suited for STP WSPs of any type. Table 1 indicates that for HRTs of 10 – 20 days the model (admittedly ignoring precipitation reactions) returns P removals within the usual range reported for WSPs (20 – 50%). It would be important to test the variable ranges to ensure that only appropriate value ranges can be used so as to avoid excessive P removals. In addition, a maximum P removal of perhaps 50% through pond activity alone could be instituted into the software. This would be a considerable improvement to the existing MEDLI approach.

The Vijay & Yuan model is challenged by the lack of validation against real WSP data and especially pond data sets not used for parameter estimation. It might be useful to commission a small study to test the model against Australian or Queensland STP WSP data sets for phosphorus removal to get a better understanding of its performance prior to use in MEDLI. This might include an allowance for adjusting the “G” factor for temperature in the manner used by many existing kinetic models in wastewater design.

2. Pond pH. The Vijay & Yuan model was designed for operation between pH 8-10. Many ponds operate at lower pH for much of the time and it can be expected that this will impact the type and quantum of P removal through precipitation reactions, which have a marked dependence on pH across the usual range observed in ponds. For example, a WSP operating at pH 7 might have much less P precipitation than one at pH 8.

In this respect, it is noticeable that precipitation reactions due to other cations are ignored – such as calcium and magnesium, despite evidence that precipitation due to struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) for example can be significant especially in effluents rich in the component ionic forms.

This is a strong reason to consider an inclusion of a basic ionic model in MEDLI (per recommendation 4 in Section 4.4. This would be helpful in estimating pH conditions and the propensity for the major precipitation reactions (removing phosphorus) and precipitate dissolution (resolubilisation). This in turn allows MEDLI to predict the partitioning of phosphate especially between soluble forms and sediment forms such as insoluble chemical precipitates and settled microbial phosphate.

3. Sedimentation. The substitution of the Vijay & Yuan model would eliminate the requirement for a settling fraction. MEDLI would assume that the removed P is removed as sediment to the base of the pond. This seems acceptable given the preference of phosphorus for the solid state and its absence from any form of loss by gaseous emission.
4. Applicability. As stated in 1 above, in our view, the model needs to focus improvements in phosphorus estimation for STP WSP systems where traditional ponds remain in widespread use and where the need for intensive or mechanically aerated pond systems is unnecessary for treatment. In contrast, and as for nitrogen, current practice for medium to large agro-industrial wastewater plants (e.g., meat processing, dairy processing etc) treating high phosphorus load (and concentration) wastewaters is to adopt intensive BNR and/or chemical precipitation systems to arrive at the required compliance P level. The use of MEDLI for the latter typically focusses on irrigation of an effluent of known phosphorus concentration (usually a function of compliance limits and available irrigation area and wet weather storage volume) which can be input as the effluent composition from the final pond.

## 6. Anaerobic Pond Module

### 6.1. Current MEDLI Anaerobic Pond equations and assumptions

The anaerobic module in section 3.2.2.5 of the MEDLI Technical Reference calculates the sludge deposition to inform on desludging frequency. Equation 3.19 calculates the additional daily sludge added to the anaerobic pond based on the mass of solids entering and the fraction settled. Equation 3.20 calculates the fraction of nutrients in the settled sludge and is based on the assumption that the mass of nutrient is a constant fraction of the total solids loading.

There are a number of weaknesses in the current MEDLI anaerobic pond module, namely:

- Major
  - Equation 3.19 - Sludge accumulation rate proportionality constant of 0.003 m<sup>3</sup>/kg TS and 0.004m<sup>3</sup>/kg TS for piggeries and cattle wastewater should be reviewed and values for other wastewater types considered.
  - The mass of nutrient is NOT a constant fraction of the total solids loading in non-piggery wastewater therefore Equation 3.20 does not apply to the majority of wastewater streams.
  - Facultative and maturation (non-anaerobic) ponds will also have sludge accumulation from influent suspended solids and death of algal cells grown within the pond.
- Minor
  - Only the first pond is anaerobic. Pond type allocation better based on aerial organic loading rate.
  - The assumption that anaerobic ponds require residence time of 40d. Most meat processing anaerobic ponds operate on residence times of less than 15 days.
  - Minimum anaerobic treatment volume should be based on organic loading rate (including soluble organic) not volatile solids.
  - Desludging protocol is missing the message “Do not remove all sludge as it plays an integral role in the overall pond treatment performance” although in practice it is impossible to remove all the sludge from such ponds.

The literature review below considers the major weaknesses only.

### 6.2. Anaerobic Pond and Sludge Deposition Literature Review

Anaerobic sludge accumulation rates reported in literature vary significantly. The range will be due to varying feed wastewater composition and different pond conditions that affect solids digestion. In practice sludge deposition depends on a large number of variables including climate (wind), pond geometry, depth and age, inlet & outlet structures and placement, the presence of mixing equipment and baffles and solids content, type and size distribution in the influent. Most values in the literature are from sewage treatment systems which is relatively constant in composition world-wide and even then, considerable variation in sludge deposition rates is reported. The situation for industrial wastewater is even more complex and data is negligible and often unreliable.

Settled sludge degrades as pond temperature increases (Shilton, 2005) with the settled sludge layer depth typically following a sinusoidal pattern with high values in winter and low values in summer (Papadopoulos et al., 2003). Some recent reported anaerobic sludge accumulation rates are:

- Mara and Pearson 1998 (as cited in Shilton, 2005) suggest a “slightly conservative value” of 0.1 m<sup>3</sup>/EP.yr.
- Piggery sludge accumulation rates in anaerobic pond measured at 0.0012 m<sup>3</sup>/ kg TS which is lower than current NRCS and ASABE standards (Hamilton, 2010) used in the MEDLI pond models.
- Anaerobic pond sludge accumulation ranges from 1.5 to 46.4 cm/yr. (Shilton, 2005)



Saqqar & Pescod (1995) developed a model to describe the volume of sludge accumulated in a primary anaerobic pond as a function of TSS and BOD in the raw (sewage) wastewater and an “accumulated sludge coefficient” that they calculated as 0.6. The MEDLI Technical Reference sludge accumulation equation 3.19 needs to be reviewed to broaden the relevance to a range of wastewater streams.

Sludge accumulation is also reported in facultative and maturation ponds. Recent reported values for sludge accumulation are:

- Facultative ponds sludge accumulation rates from 0.06 to 4.86 cm/yr. (Shilton, 2005).
- Polishing ponds sludge accumulation rate of 70g/m<sup>3</sup> of wastewater with half from settled influent solids and half settled algae (Cavalcanti et al., 2002).
- Maturation pond sludge accumulation of 0.04m<sup>3</sup>/EP wet or 0.01m<sup>3</sup>/EP dry treating sewage (Ashworth & Skinner, 2011).

Cavalcanti et al. (2002) considered the rate of sludge accumulation in polishing ponds as so low that desludging is not required over the useful life of the pond.

Pond sludge composition depends on the source of settled solids. Algae nutrient content varies from 0.6 to 16% (average 8%) nitrogen and 0.16 to 5.0% (average 2%) phosphorus (Hemens and Mason, 1968 cited in Shilton, 2005). Precipitated phosphates will increase the phosphate portion. A polishing pond sludge was reported to have 3.9% N and 1.1% P of the total solids mass (Cavalcanti, et al., 2002).

The above values can potentially be used to provide some guidance to MEDLI users, particularly in the case of STPs. For industrial wastewater systems, provision of reliable sludge deposition rates remains elusive.

### 6.3. Anaerobic Nutrient Modelling Options

The MEDLI nitrogen removal model only considers ammonia volatilization as a function of pond area and an empirical constant factor,  $b_i$ , of 9.6 cm/wk. In light of recent research this appears to misrepresent actual nitrogen removal processes in wastewater ponds.

Camargo Valero & Mara (2010) propose that commonly accepted empirical models such as Pano and Middlebrooks may still be valid but are not necessarily due to ammonia volatilization as originally assumed. The Pano and Middlebrooks nitrogen removal equation estimates nitrogen concentrations from ponds as a function of inlet nitrogen concentration, surface area, flowrate, water temperature and pH (Ashworth & Skinner, 2011). This model may be useful for nitrogen removal modelling for anaerobic ponds in MEDLI since many of the same nitrogen removing processes remain valid except for nitrification (zero oxygen environment) and algal uptake since typically the high turbidity of anaerobic pond contents limits light availability. Where there is either natural crusting or a synthetic cover, nitrogen removal will be very limited, although there is a very significant conversion of organic nitrogen to ammonia.

Phosphorus removal modelling in anaerobic ponds is largely non-existent and will be affected by similar biological and physicochemical mechanisms as for WSPs. Our experience indicates that conversion of biologically available organic phosphorus to soluble phosphate is rapid and almost stoichiometrically complete in active anaerobic ponds. In such a case, the Vijay & Yuan (2017) approach offers a tantalising but unproven application to anaerobic systems.

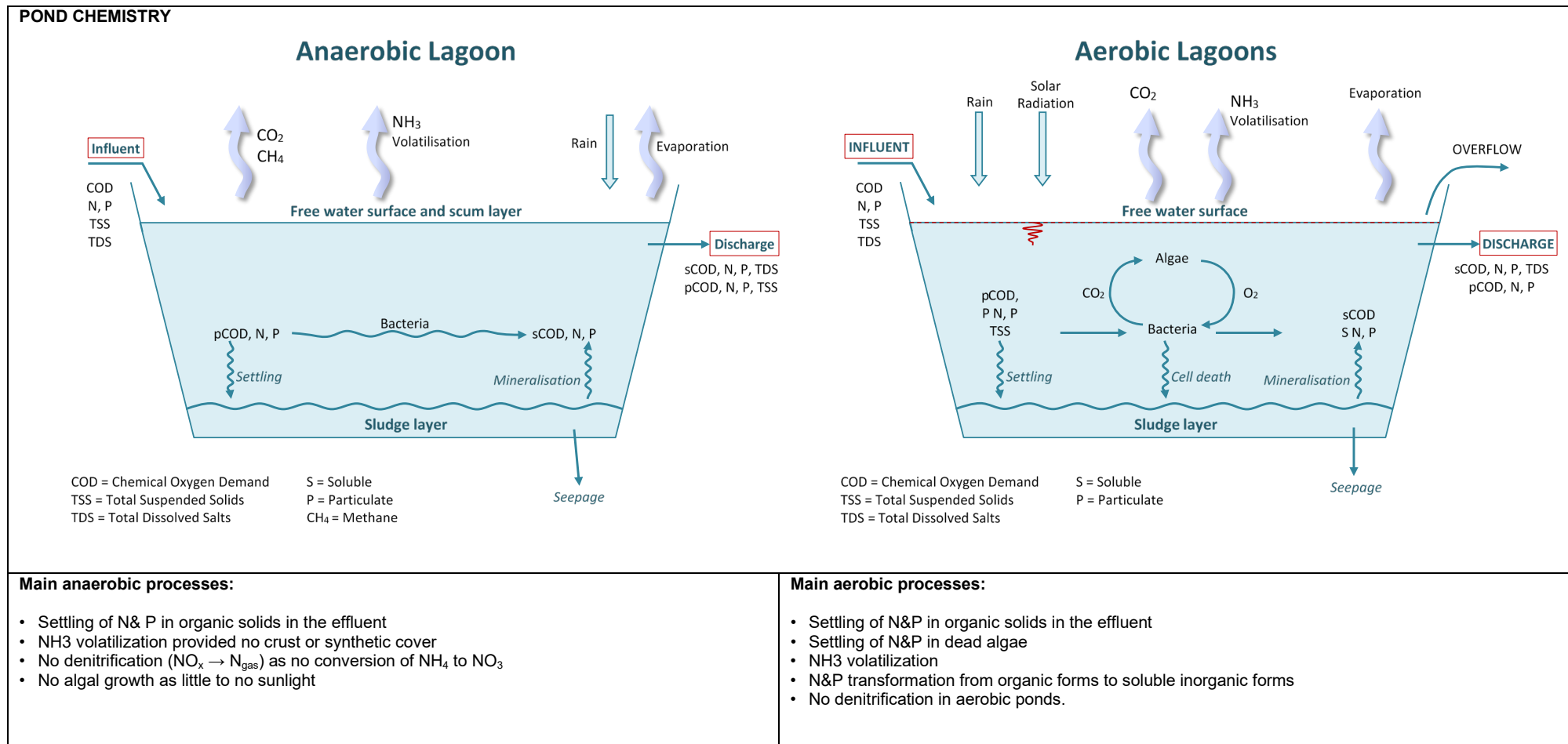
## 7. Implications of the issues raised

Implications of the issues identified in this report are summarised in Tables 4 (Pond hydrology) and 5 (Pond Chemistry).

Table 4: Strategic overview of the issues and implications raised by this review – Pond Hydrology.

POND HYDROLOGY							
Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Pond geometry	Limited to trapezoidal-shaped ponds.	A “MEDLI-helper” spreadsheet is provided to allow users to enter in their own pond depth – water surface area – water volume data points and retrieve the trapezoidal inputs that best match their pond geometry.	Allow calculation of equivalent surface area and volume for irregular shaped ponds within MEDLI.	Addressing this issue to allow for user specification of pond geometry (e.g., for round, rectangular, trapezoidal, or irregular ponds) will improve relevance to many users.	Low to moderate.	High. This has been raised by users frequently	Implement a module to generate the depth– water surface area – water volume relationship for each pond that can be directly used for all pond calculations. This relationship would be derived from user input for round, rectangular, trapezoidal, or irregular ponds.
Pond evaporation	Check the assumed default Pan factors used for ponds. E.g., anaerobic, facultative/wet weather, and anaerobic ponds with a crust.	Evaporation takes place from all ponds if no crust or synthetic cover. A Pan evaporation factor is used to derive pond water evaporation from daily Class A Pan. The default Pan evaporation factor is 0.7 for anaerobic and facultative ponds.	Consider the WATHNET, IQQM or MIKE models that may have pan evaporation factors for ponds and eWater Source – Water Quality may have nutrient removal estimates.  Check for a more correct Pan factor or replace with Penman equation or similar.	Errors in evaporation prediction carry over into errors of pond overflow prediction.	low	high	Investigate alternatives as listed.

Table 5: Strategic overview of the issues and implications raised by this review – Pond Chemistry.



Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Pond treatment	MEDLI's pond treatment trains do not reflect the treatment trains now used by medium to large agro-industrial wastewater generators. Engineered pre-treatment systems have replaced the need for anaerobic ponds. More efficient to input the water <b>quality</b> characteristics of the irrigation pond.	The pond treatment trains currently offered are (1) "anaerobic pond first followed optionally by up to three "facultative/wet weather storage" ponds; (2) Up to four "facultative/wet weather storage" ponds. The last pond is always the irrigation pond.  Apart from calibrating MEDLI's predicted irrigation water quality by adjusting the wastestream inputs in MEDLI., there is no easy way of "turning off" pond treatment and inputting the irrigation water quality characteristics directly.	Add a new option to allow the direct input of water quality characteristics of the last pond used for irrigation. This will turn off pond treatment algorithms but allow pond hydrology modelling to continue.	This new feature will allow MEDLI's simple pond chemistry algorithms to be bypassed in favour of irrigation water quality. <b>This will have potentially large impacts on all post-irrigation processes including nutrient loading on the irrigation area and plant growth.</b>  <b>This option will need the user to measure the irrigation water quality.</b>	Low	High	Add a new option to allow the direct input of water quality characteristics of the last pond used for irrigation.  Retain the option to use the MEDLI pond chemistry algorithms but investigate the recommendations N and P transformations as listed below in the future. E.g., the Pano and Middlebrooks model
Minimum pond treatment volume for odour control of anaerobic ponds	Minimum anaerobic treatment volume should be based on BOD.	Volatile Solids Loading Rate used to estimate malodour potential	Use mean BOD data for raw influent  Use a table of BOD loading vs Malodour generation to estimate minimum pond treatment volume.	An accurate estimate of minimum pond treatment volume will impact on rate of desludging and to a lesser extent, the pond hydrology.  Will need user to input BOD data.	Moderate	High for high strength waste streams (e.g., meat rendering plant, abattoir), low for low strength waste streams e.g., conventional STP.	Investigate adding the option for high strength wastestream.
Sludge generation and accumulation	MEDLI assumes only the anaerobic pond has settlement of solids. N&P are removed with the solids.  MEDLI ignores sludge accumulation from algal growth.	(1) Sludge accumulation is based on a simple user-specified sludge accumulation rate applied to total solids concentration of the influent. It only occurs in (the first) anaerobic pond.  (2) The sludge accumulation rate is based on experimental piggery and cattle data.	(1) Allow sludge accumulation to occur in all ponds, especially those with algal growth.  (2) Review literature to identify the likely sludge accumulation rates. Implement to all ponds considered in MEDLI.  (3) May be simpler to input final water quality leaving irrigation pond if available.	More user inputs needed to specify sludge accumulation rate across all ponds, and desludging protocols.  Modelling sludge will impact on pond water quality predictions and hence irrigation water quality (i.e., N and P).	Moderate coding task but need data and algorithms for sludge accumulation from algal growth / death.	Low to moderate particularly as alternatives exists to simply bypass the pond chemistry.	Input the final water quality as recommended in Pond Treatment row.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Nitrogen sedimentation in ponds	<p>(1) Recent work suggests uptake by algae and bacteria followed by biomass sedimentation is a major mechanism of N removal in <b>aerobic</b> ponds</p> <p>(2) The default value for TN settling in anaerobic ponds is based on piggery data.</p>	<p>Settling of organic N only occurs in anaerobic ponds.</p> <p>A two-compartment model is used – one for “soluble” TN; the second for the solid TN fraction. This accumulates as sludge in the anaerobic pond. A settling fraction of 23.5% is used based on piggery data.</p>	<p>(1) Predicting N uptake by algal growth remains an intractable issue. The existing sludge settling approach used in MEDLI seems warranted provided the value is not overstated (as occurs now).</p> <p>The settling fraction concept could be applied to all ponds, with its value decreasing down the pond series.</p> <p>(2) Review recent studies to evaluate sludge accumulation rates for different effluents.</p> <p>(3) May be simpler to input final water quality leaving irrigation pond if available.</p>	<p>Applying the settling fraction to all ponds causes sludge accumulation in all ponds. This would necessitate including sludge volume in the pond volume calculations as done currently for the anaerobic pond.</p> <p>N sedimentation impacts on the pond water TN concentration and hence irrigation water quality.</p>	Moderate	High if there were no alternative to bypass the pond chemistry.	Input the final water quality as recommended in Pond Treatment row.
Nitrogen transformation to ammonia in ponds	<p>Volatilisation of NH<sub>3</sub> is very limited in anaerobic ponds with a natural crust or a synthetic cover. However significant conversion of organic nitrogen to ammonia still occurs. MEDLI's volatilization approach is based on TN concentration.</p>	<p>Ammonia volatilisation occurs from all ponds according to a user-defined “N transfer” coefficient applied to pond TN concentration.</p> <p>The user can adjust the default value of 0.014 <b>m/day</b> towards zero if the pond has a crust or synthetic cover.</p>	<p>Biokinetic models for nitrogen transformations (e.g., Ho et al. 2019 and Senzia et al. 2002) allow discrimination between the various N removal mechanisms but are not recommended due to their complexity and lack of validation.</p> <p>The Pano and Middlebrooks model is recommended to replace the NH<sub>3</sub> volatilisation equations in MEDLI.</p>	<p>N transformation will impact on the TN concentration and hence irrigation water quality and TN for irrigation.</p>	Moderate	High if there were no alternative to bypass the pond chemistry.	Input the final water quality as recommended in Pond Treatment row.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Phosphorus sedimentation in ponds	MEDLI's default value of 90% removal is likely to over predict P removal in anaerobic ponds. Total phosphorus removal in aerobic ponds is driven by precipitation reactions and algal growth & settling. Phosphorus may also be re-released from sediments during warmer months. Contributions from the different removal mechanisms are hard to determine.	Settling of P in organic solids in the effluent only occurs in anaerobic ponds.  A two-compartment model is used – one for “soluble” TP fraction; the second for the solid TP fraction. A default value of 90% of solid TP is assumed to settle as pond sludge. This (number based on piggery data).	1) The phosphorus settling fraction could be replaced by the Vijay & Yuan model (2017) which appears suited for STP treatment ponds of any type. A temperature correction for some of the model coefficients is required as the model was developed in Canada.  2) Suggest implementing a maximum total P removal cap of 50%.	The Vijay & Yuan model lacks validation against real WSP data. A small local validation study may be warranted before use in MEDLI. The study would also provide an opportunity to quantify values for the temperature modifier.  P sedimentation impacts on the pond water P concentration and hence irrigation water quality.	1) Moderate  2) Low	1) Moderate if there were no alternative to bypass the pond chemistry.  2) High	1) Investigate the Vijay & Yuan model.  2) Set maximum total P removal cap of 50%.
Phosphorus transformation in ponds	Conversion of biologically available organic phosphorus to soluble phosphate is rapid and almost stoichiometrically complete in active anaerobic ponds.	Not considered in MEDLI	The Vijay & Yuan (2017) approach offers an encouraging but unproven approach for P transformation and losses in anaerobic systems.	P transformation will impact on the P concentration and hence irrigation water quality.	Moderate	Moderate if there were no alternative to bypass the pond chemistry.	Investigate the Vijay & Yuan model.
Pond pH	Pond pH is currently ignored in MEDLI. This is an issue if alternative models are considered such as Vijay & Yuan model.  This model was designed to operate between pH 8-10. Many ponds operate at lower pH. It can be expected this will impact P removal via precipitation reactions.	Pond pH is ignored	Implement a basic ionic model such as that used by Gehring et al. (2010) to estimate pH effects on precipitation (removing phosphorus) and dissolution (re-solubilisation) reactions.	Significant additional measurable data will be required to implement this model.  Pond pH will impact on the P concentration and hence irrigation water quality.	Moderate to high	High if the Vijay & Yuan model was implemented and simply inputting average pond pH is insufficient for this model.	Investigate the Vijay & Yuan model.

## 8. References

- Ashworth, J., & Skinner, M. (2011). *Waste Stabilisation Pond Design Manual*. Northern Territory, Australia: Power and Water Corporation.
- Bastos, B., Rios, E., & Sanchez, I. (2018). Further contributions to the understanding of nitrogen removal in waste stabilization ponds. *Water Science and Technology*, 77(11), 2635-2641.
- Bastos, R., Rios, E., Dornelas, F., Assuncao, F., & Nascimento, L. (2007). Ammonia and phosphorus removal in polishing ponds: a case study in Southeast Brazil. *Water Science and Technology*, 55(11), 65-71.
- Camargo Valero, M., & Mara, D. (2007). Nitrogen removal in maturation ponds: tracer experiments and 15N-labelled ammonia. *Water Science and Technology*, 81-85.
- Camargo Valero, M., & Mara, D. (2010). Ammonia volatilisation in waste stabilisation ponds: a cascade of misinterpretations. *Water Science and Technology*, 61(3), 555-561.
- Camargo Valero, M., & Mara, D. a. (2009). Nitrogen removal in maturation WSP ponds via biological uptake and sedimentation of dead biomass. *8th IWA Specialist Group Conference on Waste Stabilization Ponds*. Belo Horizonte/MG Brazil.
- Camargo Valero, M., Read, L., Mara, D., Newton, R., Curtis, T., & Davenport, R. (2009). Nitrification-denitrification in WSP: a mechanism for permanent nitrogen removal in maturation ponds. *8th IWA Specialise Group Conference on Waste Stabilization Ponds*. Belo Horizonte/MG Brazil.
- Cavalcanti, P., van-Haandel, A., & Lettinga, G. (2002). Sludge accumulation in polishing ponds treating anaerobically digested wastewater. *Water Science and Technology*, 45(1), 75-81.
- de-Assuncao, F., & von-Sperling, M. (2012). Importance of the ammonia volatilization rates in shallow maturation ponds treating UASB reactor effluent. *Water Science and Technology*, 66(6), 1239-1246.
- Gehring, T., Silva, J., Kehi, O., Castilhos, A., Costa, R., Uhlenhut, F., . . . Wichern, M. (2010). Modelling waste stabilization ponds with an extended version of ASM3. *Water Science and Technology*, 61, 713-720.
- Gomez, E., Paing, J., Casellas, C., & Picot, B. (2000). Characterisation of phosphorus in sediments from waste stabilization ponds. *Water Science and Technology*, 42(10-11), 257-264.
- Gujer, W., Henze, M., Mino, T., & van Loosdrecht, M. (1999). Activated sludge model. *Water Science and Technology*, 39(1), 183-193.
- Hamilton, D. (2010). Sludge accumulation in two anaerobic/facultative lagoons treating swine manure from breeding farms in Oklahoma. *Transactions of the ASABE*, 53(2), 529-536.
- Ho, L. T., van Echelpoel, W., & Goethals, P. L. (2017). Design of waste stabilization pond systems: A review. *Water Research*, 123, 236-248.
- Ho, L., Alvarado, A., Larriva, J., & Pompeu, C. G. (2019). An integrated mechanistic modeling of a facultative pond: Parameter estimation and uncertainty analysis. *Water Research*, 151, 170-182.
- Mayo, A., & Abbas, M. (2014). Removal mechanisms of nitrogen in waste stabilization ponds. *Physics and Chemistry of the Earth*, 72-75, 77-82.
- Pano, A., & Middlebrooks, E. (1982). Ammonia nitrogen removal in facultative wastewater stabilization ponds. *Water Pollution Control Federation*, 54(4), 344-351.
- Papadopoulos, A., Parisopoulos, G., Papadopoulos, F., & Karteris, A. (2003). Sludge accumulation pattern in an anaerobic pond under Mediterranean climatic conditions. *Water Research*, 37, 634-644.



- Picot, B., Paing, J., Sambuco, J., Costa, R., & Rambaud, A. (2003). Biogas production, sludge accumulation and mass balance of carbon in anaerobic ponds. *Water Science and Technology*, 48(2), 243-250.
- Powell, N., Shilton, A., Pratt, S., Christi, Y., & Grigg, N. (2007). Factors affecting biological phosphorus removal in waste stabilisation ponds: statistical analysis. Bangkok, Thailand: IWA 7th International IWA Conference on Waste Stabilization Ponds.
- Reichert, P., Borchardt, D., Henze, M., Rauch, W. S., Somlyódy, L., & Vanrolleghem, P. (2001). River water quality model No1 (RWMQM1)II. Biochemical process equations. *Water Science and Technology*, 43(5), 11-30.
- Rodrigues, V., Mac-Conell, E., Dias, D., von-Sperling, M., de-Araujo, J., & Vassel, J. (2017). Nitrogen removal in a shallow maturation pond with sludge accumulated during 10 years of operation in Brazil. *Water Science and Technology*, 76(2), 268-277.
- Saltelli, A. (2019). A short comment on statistical versus mathematical modelling. *Nature Communications*, doi.org/10.1038/s41467-019-11865-8, 1-3.
- Saqqar, M., & Pescod, M. (1995). Modelling sludge accumulation in anaerobic wastewater stabilization ponds. *Water Science and Technology*, 31(12), 185-190.
- Senzia, M., Mayo, A., Mbwette, T., Katima, J., & Jorgensen, S. (2002). Modelling nitrogen transformation and removal in primary facultative ponds. *Ecological Modelling*, 154, 207-215.
- Shilton, A. (2005). *Pond Treatment Technology*. London: IWA Publishing.
- Silva, S., de-Oliveira, R., Soares, J., Mara, D., & Pearson, H. (1995). Nitrogen Removal in Pond Systems with different Configurations and Geometries. *Water Science and Technology*, 31(12), 321-330.
- Soares, S., & Bernardes, R. (2001). Reaction coefficient (K) evaluation for full-scale facultative pond systems. *Bioresource Technology*, 78, 99-102.
- Stratton, F. (1696). Nitrogen losses from alkaline water impoundments. *Jour. San. Eng. Div. Amer. Soc. Civil Engr.*, SA2(April).
- Stratton, F. (1968). Ammonia nitrogen losses for streams. *Jour. San. Eng. Div. Amer. Soc. Civil Engr.*, SA6(Dec).
- Vendramelli, R., Vijay, S., & Yuan, Q. (2016). Phosphorus removal mechanisms in a facultative wastewater stabilization pond. *Water Air Soil Pollut*, 227(417).
- Vijay, S., & Yuan, Q. (2017). Simplified empirical model for phosphorus removal in a facultative wastewater lagoon. *Journal of Environmental Management*, 201, 1-5.
- Zimmo, O., van-der-Steen, N., & Gijzen, H. (2003). Comparison of ammonia volatilisation rates in algae and duckweed-based waste stabilization ponds treating domestic wastewater. *Water Research*, 37, 4587-4594.