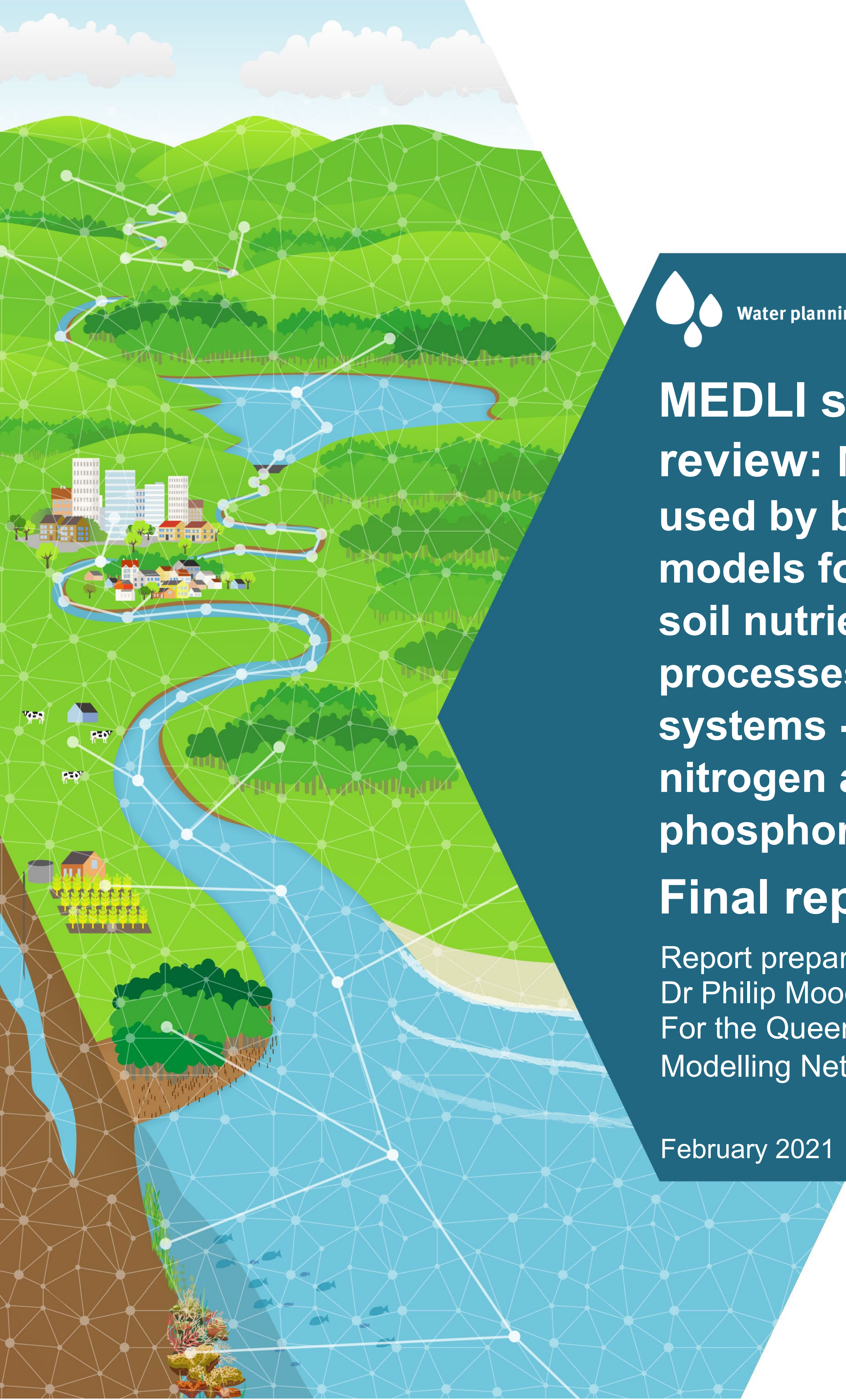
QUEENSLAND WATER MODELLING NETWORK



Water planning, integration and management

MEDLI science review: Methodologies used by biophysical models for simulating soil nutrient pools and processes in pasture systems - Carbon, nitrogen and phosphorus

Final report

Report prepared by
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For the Queensland Water
Modelling Network

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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.

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(Dr Moody passed away in June 2020)

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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, "Pond chemistry module" by Dr Mike Johns and Dr Bronwen Butler, "MEDLI Science Review: Synthesis" by Prof. Ted Gardner and "Modelling of Water and Solute Transport in MEDLI" by Prof Freeman Cook. This report was completed following the unexpected passing of Dr Phil Moody and QWMN would like to thank Prof. Ted Gardner, Phil Bloesch, Dr Max De Antoni and Alison Vieritz for their tireless contributions to this task, as well as Dr David Rowlings for his review comments. The Executive Summary was taken from the MEDLI Science Review: Synthesis" by Prof Ted Gardner.

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Executive Summary

The Nitrogen module in MEDLI uses Michaelis–Menten type equations to predict the rates of mineralization, nitrification and denitrification which are adjusted by 0-1 scaling factors to take into account reductions (from a defined maximum rate) due to suboptimal values of temperature, soil water status and pH. This is very similar to the approach used by the more sophisticated N models in say APSIM and DAIRYMOD, but the actual functions, and sometimes the maximum rates, vary between models. The paucity of validation data for irrigated situations indicate there is no compelling reason to change the functions used in MEDLI. The exception is the denitrification process where the maximum values vary over an order of magnitude, and it appears that the APSIM value (about 6 kg N/ha/day) most closely reflects field measured values in high production dairy pastures (Friedl et al. 2016). Given that denitrification is one of the two most important sinks for applied N in effluent irrigated pasture (the other is biomass uptake) it is recommended that MEDLI adopt this value. It is also recommended that a more detailed literature search on maximum denitrification rate be undertaken to confirm or modify the 6 kg/ha/day figure.

Denitrification requires a labile carbon source as well as anaerobic conditions. In MEDLI there is no allowance for the relative availability of C; rather it operates on a C presence/absence rule and is usually confined to the surface 10 cm. This is likely to limit the number of days denitrification which can occur in a year since the surface soil will reach the DUL sooner than deeper layers. Recent MEDLI modelling of effluent irrigated pasture in SEQ revealed a very large increase in denitrification if C were assumed to occur over the full rooting depth (of 60 cm). Hence it is recommended that MEDLI incorporate into its denitrification algorithm, a labile carbon scaling factor similar to that used in APSIM. And that measured labile carbon values be inputted for the whole soil profile (i.e., >> 10 cm).

Volatilization of N from soil is unlikely to be significant for effluent irrigation as the N is already applied in the hydrolysed form as NH4/NH3. APSIM does not consider this process except for a special adaption for NH3 loss from urine patches. However, volatilization losses from the spray irrigation can be substantial (e.g., c. 50% of TAN) depending on the pH (> 8) and the nozzle operating pressure (e.g., > 500kPa). There is no easy way to predict these ammonia losses except by experimental measurements using simple, acidified catch cans. But a default value of 15 to 20% would seem appropriate for lower pressure centre pivots.

Unlike more sophisticated N models such as the one used in APSIM, MEDLI does not contain a Carbon cycle module which allows for the mineralization and immobilization of N in fresh organic matter (FOM). Moody argues that having soil C dynamics driving the N processes is mechanistically correct, is intuitively logical, and could be incorporated into MEDLI reasonably easily following the APSIM or DAIRYMOD exemplars. However, as MEDLI is often applied to cut and cart pasture, the opportunity for significant residue levels after harvest is unlikely. Hence the extra complexity of a dynamic C module in MEDLI is unlikely to have a significant effect on the predicted surplus N available for leaching. The quantum of N leaching loss is one of the key assessment criteria for assessing environmental sustainability.

The P model in MEDLI is based on the Freundlich adsorption isotherm which is used to estimate the soil solution concentration at any soil depth, especially that at the bottom of the rooting depth, or at the bottom the assumed soil profile depth. The input data is both expensive to measure and difficult to find a soil chemistry laboratory, whilst the risk of P leaching to groundwater is remote except in very sandy soils whose groundwater is well connected to the receiving surface waters (e.g., WA). Its continued use in MEDLI is not recommended except for cases of special landscape vulnerability. Moody has presented an alternative model based on the ratio of Colwell-P to PBI - both easily measured, single point measurements. Similar to the Freundlich based algorithms used in MEDLI, the Moody approach calculates the soil solution P concentration that determines bioavailability to crops, and also the movement of P in runoff and drainage by diffusion and mass flow. The approach suggested by Moody seems to be simple to implement in MEDLI and is worthy of the effort to compare its output predictions with that of the existing Freundlich algorithms used in MEDLI, provided matching soil properties can be ensured. This ratio approach also underpins the risk assessment of P export from sugar cane farms in Great Barrier Reef catchments.

The major P export pathway of environmental concern is via attachment to sediment or in a dissolved form moving with the surface runoff. Given the high surface cover associated with irrigated permanent pasture, erosion is highly unlikely to be a significant factor and can be ignored for most situations of interest to MEDLI. However, for the exceptions, the sediment erosion/enrichment algorithms of HowLeaky could be adapted for use in MEDLI.

For dissolved P in runoff, there are two options. This first option is the soil solution P predicted by the new Moody algorithm (based on Colwell-P and PBI) which needs to be translated into runoff concentrations. Empirical soil solution P - Runoff dissolved P functions based on rainfall simulator results by Burkitt et al. (2010) could be a first approximation. The second option is to use the algorithms for dissolved P described in HowLeaky. It is uncertain how well validated these algorithms are, and this point should be investigated further before their incorporation into MEDLI. A good starting point would be the evaluation of the equations (including that of Moody 2011) for a range of Colwell-P/PBI values to see how the predicted DRP mg/L values compare with the values measured in runoff from irrigation paddocks, or their receiving waters. But perhaps the larger question is whether the quantum of this P export pathway is worth the modelling effort (in MEDLI), given Moody’s review reported that P losses from fertilized permanent pasture were usually < 1kg/ha/yr.

Because N tends to be at a much higher concentration (and more soluble) than P in both soil and effluent, it would be expected that dissolved level of inorganic N could be “quite high” in runoff from effluent irrigated pastures. HowLeaky suggests three options to predict this concentration, with the first option using a measured soil nitrate concentration, a mixing factor to allow for dilution by surface runoff, and another factor that allows for the change in the mixing factor as the runoff event proceeds. The algorithm was based on results from a Victorian DPI study of permanent pasture and seems easy to implement in MEDLI especially if the nitrate-N in the top 10cm can be used instead of the 0-2cm value recommended in HowLeaky. Its validation is unknown. The other two approaches are based on using the time series of fertilizer application (kg/ha), the cumulative rainfall from the last fertilizer addition to when runoff occurs, and two fitting parameters based on N runoff experiments in North Queensland. Their usefulness for incorporation into MEDLI is unlikely.

These issues are summarised below, along with their implications in Tables 9-1 (Nitrogen) and 17-1 (Phosphorus).

Table 1. Strategic overview of the issues and implications raised by this review for carbon and nitrogen, with additional insights from the Synthesis Report (Gardner 2021) (From p.45)

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Overview of N modelling	Other models such as APSIM and DairyMod are generally more complex than MEDLI and explicitly consider the soil Carbon cycle which drives the soil N cycle. There is also the opportunity to model the microbial fundamentals of N transformations rather than using equations such as Michaelis–Menten.	Uses Hydrological Simulation Program–FORTRAN (HSPF)-based algorithms where maximum rates (of denitrification etc.) are scaled by soil water status, soil temperature and pH.	Incorporate a dynamic soil carbon model into MEDLI. Compare the MEDLI algorithms for mineralisation/ immobilisation, nitrification, denitrification and volatilisation with those used in the empirical models of APSIM and DairyMod	Potentially improve our ability to model N.	High	Moderate	Needs a desktop investigation of the various options first.
N modelling validation	**There are little validation data for hard-to-measure processes such a denitrification**. Hence choosing the best parameter values to use in the reviewed models is hard to make. Moreover, these daily and sub-daily timestep models are generally poor at predicting daily N fluxes	Validation of the N cycle in MEDLI to date has been minimal except for mass balance sums, that include the measured values Applied N, Harvested N, *Change* in Soil N. The residual difference is assumed to equal the denitrification loss.	Experimental work is proposed to measure the processes/pools in the total N cycle. To be effective, this will require a wide array of instrumentation and intensive sampling in the field. **N^{15} will be a critical tool**. A network of sites/soils where effluent is being applied is implied. This approach would provide a first approximation validation of MEDLI outputs.	Intensive experimentation required.	High	Moderate	Needs a desktop investigation of the various options first. Investigation of experimental/research options available.
Carbon dynamics	MEDLI does not currently include a dynamic carbon	Carbon dynamics not considered. Presence	Model soil C dynamics in MEDLI following APSIM or DairyMod exemplars.	Difficult-to-obtain inputs needed for	High – difficult to accommodate in current version	Low importance. In effluent irrigated systems, the	Needs a desktop investigation of the various options first.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
	model to help ensure N dynamics are valid. Fluxes between the C pools drive the subsequent N fluxes that are based on the C pool sizes and their respective C/N ratios.	of C used to initiate denitrification. Mineralisation of native soil N (specified in input file) occurs irrespective of the amount of N added in effluent. Similarly, excess N cannot be sequestered in the soil organic matter store.	Having soil C dynamics driving the N processes is mechanistically correct, is intuitively logical, and could be incorporated into MEDLI reasonably easily following the APSIM or DairyMod exemplars.	implementation of a C model.	without major recoding.	incidence of high carbon, low nitrogen material is unlikely. Consequently, unlike APSIM, MEDLI does not currently need to model stubble decomposition.	
Carbon dynamics	The lack of a C:N ratio feedback means MEDLI will always mineralise its soil organic N to exhaustion. This becomes a problem for tree crops (which are increasingly being considered) where such a loss of soil organic N is rare because of return of C to the soil.	If depletion of soil organic-N is expected to be small (the usual case for effluent irrigated pasture), the kinetic rate coefficient for ammonification can be set to zero. However, kinetics of N immobilisation have been turned off in MEDLI.	Explore options from APSIM and DairyMod. Activate the immobilisation kinetics that have been turned off within MEDLI.	Require further kinetic rate coefficient inputs which are difficult to determine. Need validation data.	High	Low importance – dealt with user training and user manual explaining model limitations.	Needs a desktop investigation of the various options first.
Mineralisation/ Ammonification *Mineralisation of organic N to ammonia. Mineralisation **or***	MEDLI uses different response curves (and parameter values) for organic matter mineralisation to those used in APSIM. These differences	MEDLI uses a simple kinetic function that ignores the C:N ratio of the substrate but considers soil water &	Implement a carbon model or adjust the net mineralisation coefficient to lower value? Mineralisation rates of the slow and fast organic pools	Adjusting the net mineralisation coefficient would be the preferred alternative before implementing a new carbon model in MEDLI.	Moderate	High	Manipulate the coefficient. Establish the basis of the difference between the APSIM and MEDLI soil water content and

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
immobilisation of mineral N is determined as the balance between the release of mineral N during decomposition of the various fractions of organic matter (FOM, BIOM and HUM), and the N required by the microbial biomass.	in the response curves should be reconciled.	temperature effects using a scaling factor.	should be used rather than the statistically fitted values for individual soils. The N mineralisation rates found by Wang et al. (2004) and Allen et al. (2019) provide an independent means for validating potential ammonification/ nitrification estimates simulated by APSIM and MEDLI.				temperature modifiers for ammonification and suggest revisions to MEDLI if necessary.
N volatilisation *Gaseous ammonia loss during irrigation and from the soil.*	Volatilisation during irrigation is considered but volatilisation from soil is not included in APSIM or MEDLI. High effluent pH (> 9) high temperature, and low salinity are most likely to result in appreciable N loss by volatilisation due to NH_3-NH_4 partitioning favouring NH_3. However, most effluents are pH < 9 and commonly, evaporation from many small droplets created by spray irrigation will be the dominate loss mechanism.	The loss of ammonia gas (volatilisation) is considered to occur only during the irrigation event. The amount is currently a fixed fraction of the NH_4-N in the effluent. Volatilization loss from soils is only likely to occur in moderately alkaline soils(pH>8).	Further investigation of volatilisation during irrigation needed.	Since the pH of effluents are mostly < 9, this process is unlikely to be significant. However, the process of droplet formation in high pressure spray irrigators may cause significant volatilisation losses.	High – experimentation needed.	Important as losses of up to 50% during irrigation have been measured at Beaudesert.	"*Acidified catch-can*" experiments recommended to establish relationships to predict losses.
Nitrification *Nitrifying bacteria transforms soil ammonia into nitrates.*	APSIM and MEDLI soil water content modifiers for nitrification are different.	APSIM, DairyMod and MEDLI use Michaelis-Menten kinetics to estimate maximum nitrification rate.	Desktop study to review the response functions and revise MEDLI if necessary.	Potential contradiction between APSIM and MEDLI will persist if not addressed.	Low	High	Desktop study to review the response functions and revise MEDLI if necessary.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
		The temperature scaling factor for nitrification [as well as for ammonium adsorption/desorption, immobilisation and mineralisation] is based on a modified van't Hoff-Arrhenius equation.					
Denitrification *Reduction of nitrates (and nitrites) to gaseous products including NO, N_2O and N_2 by microbial processes that occur under anaerobic conditions. They are influenced by organic carbon content, water-filled pore space, soil temperature and soil pH.*	Simulation of denitrification differs markedly across APSIM, DairyMod and MEDLI. Whilst MEDLI & APSIM maximum denitrification rates are similar (10% & 5%), Dairy-Mod is almost 10 times smaller. This range is indicative of the difficulty in simulating this process.	A maximum denitrification rate is user specified and modified by soil water content and temperature. Default value is 0.1. i.e., 10% of the current amount of NO_3-N (mg/kg) in the soil layer of interest. MEDLI is not designed to provide estimates of the emissions of greenhouse gases (e.g., N_2O) so this aspect of denitrification is not considered further.	The denitrification rate in APSIM is a function of soil NO_3 concentration, soil pH, soil water content, temperature. and labile organic C MEDLI needs to simulate labile organic C which is part of a soil C model The depth of soil containing labile organic C is user-defined, and most users accept the MEDLI default value of 100 mm. Hence all deeper soil depths are effectively made N "inert". If labile C is available at deep depths, this assumption is incorrect. Hence, the organic layer depth needs adjusting using measured organic C data. This will require adjustment to the suite of measurement instructions given to the soil analyses laboratory.	More explicit guidance to MEDLI users needed for depth labile organic carbon layer. **N^{15} experiments to get a better handle on N loss from irrigated pastures**	Low- for more guidance to user. High for N^{15} experiments	High. **Denitrification may be a critical N loss mechanism for the viability of some high-strength effluent** irrigation schemes. Such work would benefit APSIM and other models modelling the N cycle	Undertake a review of the basis for the denitrification rate methodologies used in APSIM, DairyMod and MEDLI and suggest any revisions that might be required in the MEDLI algorithms. Also undertake a review of the historical measured denitrification rate data as well as some focused experimentation using N^{15} **as most denitrification data reported is modelled rather than measured!**

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Leaching of N solutes	Leaching of solutes is very responsive to their loading rate, soil permeability and irrigation/rainfall regime. Leaching should take into account the fraction of mobile and immobile water in soils. Both Nitrate-N and dissolved organic N (e.g., urea and amino acid molecules) are solutes that should be considered.	Leaching of solutes (Nitrate-N and Phosphate-P) moves with the transit of water down the soil profile, assuming each soil layer is a constantly stirred reactor.	The drainage algorithm (based on cascading buckets) needs improvement as per the Cook (2021) review.	Coding to include changes is anticipated to be difficult in the current version.	High	High	**The drainage algorithm (based on cascading buckets) needs improvement as per the Cook (2021) review.**
N runoff loss	Nitrogen enrichment in runoff is not modelled in MEDLI.	MEDLI does not model nitrogen loss from rainfall runoff. In the rare case where the soil profile becomes hydraulically overloaded during irrigation, effluent runoff will occur with the runoff N concentration equal to that of the effluent.	The Victorian DPI runoff algorithm used in the HowLeaky Model could be incorporated into MEDLI, depending on the peer review status of the alternative method.	Whilst not hard to implement, it will involve the addition to two model parameters which may be difficult to measure.	Moderate – but need to also consider how to incorporate enrichment ratio into the N mass balance.	Low for pastures on low slopes (e.g., 3% maximum), typically used for irrigation. With crops, usually irrigation on very low slopes to avoid runoff. N losses in rainfall runoff are generally very small (<5 kg N/ha/yr)..	It appears that the process of N enrichment is considered not sufficiently significant to be included in MEDLI but needs further review.
Ammonium-N sorption	Why is Ammonium-N sorption mentioned in the MEDLI technical manual? Leaching of ammonium-N is rare in Australian soils and not considered in MEDLI	Sorption/desorption of ammonium-N on the soil's exchange sites is not modelled in MEDLI (this code has been "turned off"). However, ammonium-N is assumed not to be transported with the deep draining flux. This simplification may	Delete all mention of Sorption of ammonium-N from MEDLI	Nil	Nil	Low	Leave code as is. De-emphasise in MEDLI technical manual

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
		not valid in paddocks overloaded with N if nitrification to nitrate-N is incomplete.					

Table 2 Strategic overview of the issues and implications raised by this review for phosphorus, with additional insights from the Synthesis Report (Gardner 2021) (From p.66)

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
P mineralisation from organic matter	MEDLI does not consider P mineralisation from organic matter. Most models such as APSIM do not consider the off-site export of P. Rather they focus on P availability and plant growth. MEDLI focuses on off-site export via leaching.	MEDLI uses a dynamic P and crop growth model to assess solution conc. and crop uptake. It does not consider mineralization of P from organic matter.	No **change** to the P mineralization process is recommended	Because of cut and cart, the return of P from organic matter is expected to be small.	Not applicable	Low	No **change** to the P mineralization process is recommended
P runoff loss	P enrichment in surface runoff from rainfall is not considered in MEDLI Export load (kg/ha/yr) often small but concentration (mg/L) can exceed ANZECC water quality standards.	MEDLI does not model phosphorus loss from rainfall runoff. In the rare case where the soil profile becomes hydraulically overloaded during irrigation, effluent runoff will occur with the runoff P	Use the Dougherty (2011) algorithm with Moody's (2011) correction to calculate soil solution & assume it equals the concentration in rainfall runoff. Use 0-10 cm soil data to calculate driving parameters (Colwell P & PBI). Alternatively, could use Dissolved Reactive	P concentration can exceed ANZECC water quality guideline values.	Moderate to high.	High	Review alternatives. Needs some working through and testing of Moody's approach.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
		concentration equal to that of the effluent.	Phosphorus runoff algorithm from HowLeaky (2018)				
P soil sorption and P leaching	Adsorption of P in MEDLI is predicted by the data-demanding Freundlich equation (requires a P sorption isotherm which is expensive to measure and offered by few laboratories). Simpler algorithms are desirable considering the relative rareness of P leaching in most Australian soils.	MEDLI uses a Freundlich equation to calculate P sorption and soil solution P available for leaching. Leaching occurs after the P storage capacity of any one soil layer is filled. Piston flow is assumed in moving the solute through the soil.	A much simpler model by Moody is suggested driven by Colwell P and the PBI. It calculates soil solution P and runoff P concentrations. The model can also predict changes in soil solution P concentration following P addition.	Removes need for P sorption isotherm data for most model applications. Freundlich approach best reserved for vulnerable sandy soils.	Moderate to high.	Moderate	Investigate adding the option of simpler Moody approach for non-sandy soils. Needs some working through and testing of Moody's approach.
P sorption by Root Mat	Stoloniferous grass can develop a large root mass which sequesters P.	Process ignored.	Calculate root mass from above ground biomass and assume 0.3% P concentration. Estimate microbial biomass from soil organic C analysis and assume a C:P ratio of 156	Mature irrigated pastures can store a very large amount of P.	Moderate	Moderate	Should be incorporated into MEDLI for species that produce stolons.

1 Carbon and Nitrogen Overview

A literature scan has identified that four comprehensive plant growth/soil water/soil nitrogen (N) models have been applied at the paddock scale to pasture systems in Australia- APSIM (Holzworth et al. 2014), DNDC (Saggar et al. 2007), WNMM (Chen et al. 2010) and DairyMod (Johnson et al. 2008). Most of these contemporary models have components and algorithms incorporated from earlier plant growth and hydrology models. For example, the lineage of APSIM has contributions from PERFECT/ CERES-Maize (Holzworth et al. 2014). DAYCENT is included with the other models because the algorithms used for soil N processes in this model have been precursors to those used in WNWM and DairyMod. Table 1-1 summarises various characteristics and kinetic principles of these models. HSPF has not been included because it is a lumped parameter model that is generally applied at sub-catchment-catchment scale and does not consider nutrient processes, but rather nutrient coupled mass balance equations describing nutrient compartments of dissolved inorganic and organic, particulate organic and sediment nutrients (Li et al., 2015). It is noted however that many of the algorithms in MEDLI have been imported from this model.

Although all models operate on a daily (or sub-daily) time step, comparisons of simulations with measured data indicate that the model outputs are most applicable over longer timeframes (weeks) and are generally poor at predicting daily fluxes for processes such as denitrification (e.g., APSIM and DairyMod: Bilotto et al. 2021; APSIM and DNDC: Vogeler et al. 2013). This is a common problem with all these models, as denitrification has only ever been validated on very sparse data.

The models can be classified as either mechanistic (viz. WNMM, DNDC and DAYCENT), or empirical (viz. APSIM and DairyMod). The way that the processes are handled in the mechanistic models can be conceptually different from the empirical model treatments; for example, in APSIM, the processes of nitrification and denitrification are described as an empirical reaction, expressed via a Michaelis–Menten type equation, whereas DNDC uses a microbial growth model (Table 1-1). Due to time constraints, their wide adoption in Australia and simpler structure, this work focused on the APSIM and DairyMod empirical models, but it may be worth exploring mechanistic ones in the future.

Despite the commonality across the models in terms of factors considered to modify process kinetics such as soil water content, temperature and pH (Fig. 1-1), the scaling modifiers used in the models for processes such as nitrification and denitrification can be different between models as described in Table 1-1. Therefore, it is not surprising that models often simulate different outputs for specific N processes from the same input data.

Table 1-1. Characteristics, process kinetic principles and process scaling modifiers used in N models that have been applied to pasture systems in Australia.

	APSIM	DNDC	WNMM	DairyMod	DAYCENT
Scale	Point	Point	Point-Catchment, spatially referenced	Point	Point
Time step	Daily	Daily/Hourly	Daily/ hourly	Daily	Daily
Plant growth model lineage	AUSIM (McCown et al., 1989)	Crop DNDC (Zhang et al., 2002) based on phenology/ LAI/ assimilate allocation/ root processes	EPIC (Williams et al., 1984)	Johnson (2008) based on phenology/ LAI/ assimilate allocation/ root processes	Developed ad-hoc
Hydrology model lineage	CERES (Jones and Kiniry, 1986)/ PERFECT (Littleboy et al., 1992)	CERES-wheat (Ritchie et al., 1988)	EPIC (Williams et al., 1984)/ PERFECT (Littleboy et al., 1992)	Richards equation/ Manning equation/ Penman-Monteith equation (Johnson et al., 2003)	Not considered
Soil C Pools with assigned C/N ratios and Scaling Modifiers (in parentheses)					
No. of pools	2 + 1 inactive + 3 fresh added org C pools	Anaerobic balloons	2 + 1 fresh added org C pool	2 + 1 inactive	Three soil organic matter pools (active, slow and passive) with different potential decomposition rates, above and belowground litter pools and a surface microbial pool which is associated with decomposing surface litter.

	APSIM	**DNDC**	**WNMM**	**DairyMod**	**DAYCENT**
Ammonification (decomposition) - Kinetics - *scaling modifiers*	First order kinetics *(soil water, temperature)*	Microbial growth model Rate based on ‘anaerobic balloons’ with carbon, ammonium and nitrate split into aerobic/ anaerobic microsites based on oxygen partial pressure; ammonifier activity estimated	First order kinetics *(soil water, temperature, pH, clay content)*	First order kinetics *(soil water, temperature)* (Johnson et al., 2008)	First order kinetics *(soil water, temperature, lignin, clay content)*
Soil N Processes and Scaling Modifiers (in parentheses)					
Nitrification - Kinetics - *scaling modifiers*	Michaelis-Menten kinetics [ammonium-N] *(soil water, temperature, pH)*	Microbial growth model Rate based on ‘anaerobic balloons’ with carbon, ammonium and nitrate split into aerobic/ anaerobic microsites based on oxygen partial pressure; nitrifier activity estimated *(texture, water filled pore space)*	First order kinetics [ammonium-N] *(soil water, temperature, pH)*	Michaelis-Menten kinetics [ammonium-N] *(soil water, temperature, labile C [surrogate for microbial activity])* (Johnson et al., 2008)	First order kinetics [ammonium-N] *(soil water, temperature, pH, texture)*
Volatilisation - Kinetics - *scaling modifiers*	Not specifically considered. Vogeler et al. (2019) added a volatilisation routine to APSIM (See Section 4.3.1)	Specific module addition (Dutta et al., 2016)	Not considered	Fixed proportion of ammonium-N	Not considered
Denitrification - Kinetics - *scaling modifiers*	Michaelis-Menten kinetics [nitrate-N] *(organic C, soil water, temperature)*	Microbial growth model. Rate based on ‘anaerobic balloons’ with carbon, ammonium and nitrate split into aerobic/ anaerobic microsites based on oxygen partial pressure; denitrifier activity estimated *(pH, temperature)*	Michaelis-Menten kinetics [nitrate-N] *(water filled pore space, temperature)*	Michaelis-Menten kinetics [nitrate-N] *(soil water, temperature, labile C [surrogate for microbial activity])* (Johnson et al., 2008)	Uses a function of nitrate-N and microbial growth model. *(soil respiration, water filled pore space, temperature, texture)*

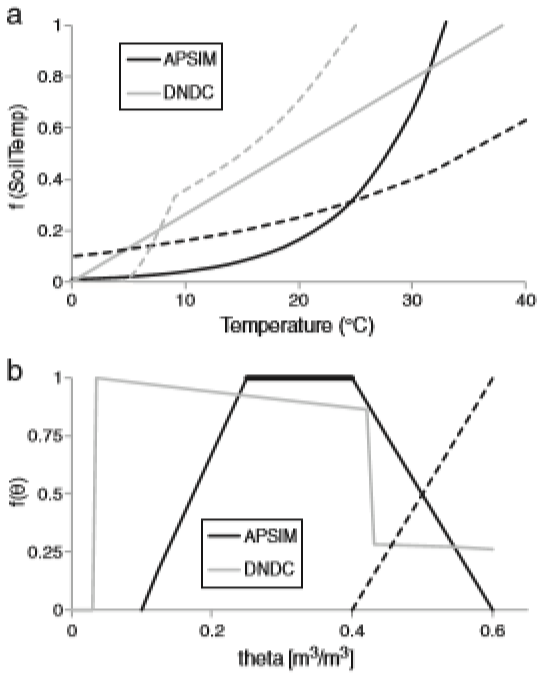


Figure 1-1. Functions used for (a) temperature and (b) soil water content as used by APSIM and DNDC for nitrification (solid lines) and denitrification (broken lines). Reproduced from Fig. 1 Vogeler et al. (2013).

1.1 Implications for MEDLI

Given the general lack of consistency in modelled N processes when models are compared, there is no compelling case to suggest that the MEDLI N process components should move from their current empirical basis to a more mechanistic basis. In any case, such a move would require substantially more input data, moving away from the MEDLI *raison d'être* of practicality. However, it would be productive to compare the MEDLI algorithms for mineralisation/immobilisation, nitrification, denitrification and volatilisation with those used in the empirical models of APSIM and DairyMod to identify differences and how these might affect outputs.

Consideration could also be given to revising MEDLI to include a carbon (C) component that would be the driver for the ammonification process (organic matter decomposition). Both APSIM and DairyMod use the rate of breakdown of at least two soil organic matter pools to inform net N mineralisation/ immobilisation. Having soil C dynamics driving the N processes is mechanistically correct, scientifically sound, and could be incorporated into MEDLI reasonably easily following the APSIM or DairyMod exemplars.

2 Measuring the Nitrogen Cycle

2.1 Pools and Processes

Modelling the N cycle requires model calibration and validation to provide a satisfactory level of confidence in scenarios simulated by the models. Figure 2-1 illustrates the N pools and N loss pathways that must be measured to provide validation data for undertaking a closed N budget in an **ungrazed** pasture over a specified time period, viz.:

- Total N inputs (organic and inorganic)
- Total N removal in harvested product
- ∆ above ground and below ground biomass N
- ∆ profile total N (organic and inorganic)
- N loss by drainage below the root zone
- N loss as ammonia gas by volatilisation
- N loss in runoff as dissolved organic and inorganic N
- N loss in sediment as particulate organic and inorganic N
- N loss by denitrification as dinitrogen and NO_x gases

Measuring these processes/pools requires a wide array of instrumentation and often presents logistical problems.

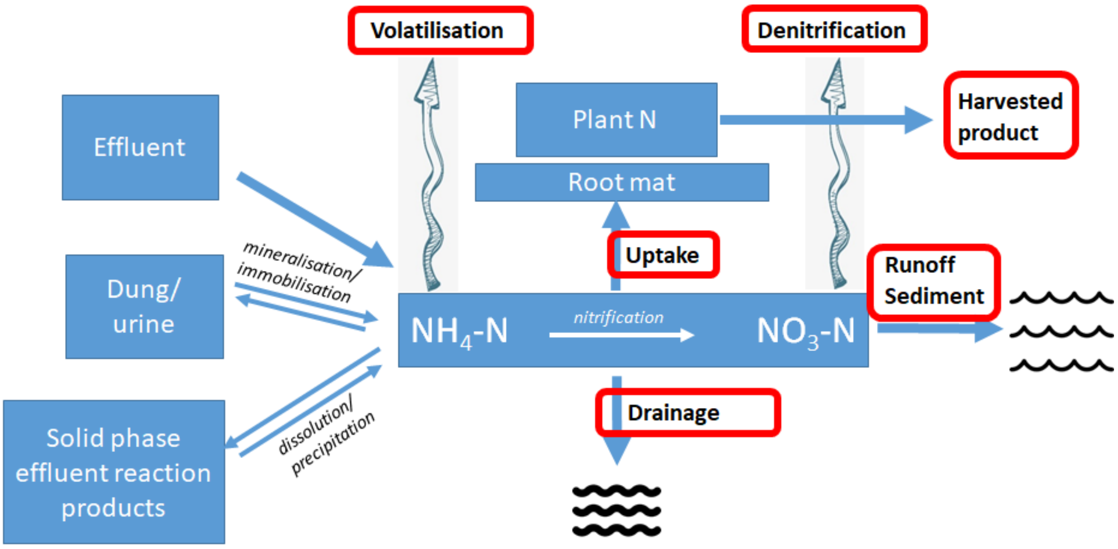


Figure 2-1. N pools and processes comprising the N cycle in a grazed or cut-and-carry system.

2.2 Model validations

Although several papers report the use of the models in Table 1-1 for simulations of pasture systems in Australia, there are few reports of validation studies. Exceptions include Bilotto et al. (2021) who compared APSIM and DairyMod validations on 2 grazed pasture sites for 1.5 years, and Johnson et al. (2008) who validated DairyMod at 3 cut-and-carry sites over 1 year. Pembleton et al. (2013) validated APSIM for production of five fodder crops grown at several dairy sites in south-eastern Australia.

2.3 Instrumentation and methodology

Table 2.1 summarises the methodology and instrumentation required to measure the pools and processes listed. Because of the intensive sampling and extensive analyses required, there are few published accounts of total N budgets derived from field data (one example being Marshall et al. (2001). Unambiguous measurement of total denitrification can only be achieved by continuous monitoring of ^{15}N labelled gases by field-based mass spectroscopy following addition of labelled material (fertiliser; plant residues; effluent) in the field (Friedl et al. 2016., Rowlings et al. 2016; Friedl et al. 2018, Warner et al., 2019). Because of these logistical difficulties, most model validation is undertaken on a particular N loss pathway such as runoff or drainage, which is site-, soil- and season-specific, and hence variable amounts of added N are unaccounted for. For example, after two growing seasons on a cracking clay soil, Robertson et al. (1997) found that 40% of the applied ^{15}N was unaccounted for in the pasture system, and 66% unaccounted for in the crop system.

Table 2-1. Methodology to measure N pools and processes

Process/Pool	Methodology
Total N inputs	Inventory; chemical analysis
Total N removal in harvested product	Harvested product inventory; chemical analysis
Above ground and below ground biomass N	Biomass sampling; chemical analysis
Profile total N	Soil profile sampling; chemical analysis
N loss by drainage below the root zone	Partial vacuum lysimeters/ drainage flux meters/ soil solution suckers/ piezometers; chemical analysis
N loss as ammonia gas by volatilisation	Micro-met towers/ gas chambers
N loss in runoff as dissolved organic and inorganic N	Flumes; chemical analysis
N loss in sediment as particulate organic and inorganic N	Flumes/ stilling chamber; chemical analysis
N loss by denitrification as dinitrogen and NO_x gases	Continuous gas sampling by mass spectrometer

2.4 Implications for MEDLI

Given the logistics, instrumentation, and expense associated with model validation, the strategy for validation of MEDLI outputs would be best served by a network of sites/soils where effluent is being applied and where a minimum dataset of measurements can be implemented. Such a strategy would provide a range of data on plant N recovery and ‘black box’ unaccounted N. This approach can lead to significant decision making based on flawed model output when a particular lost pathway needs to be targeted – i.e., strategies to reduce leaching where denitrification (N_2:N_2O) is the major pathway. Some validation of at least one pathway should be promoted. Informed by site/soil hydrology modelling, inferences could be drawn about the most likely N loss pathway/s active for each site/season, and ‘predicted’ versus ‘inferred’ matrices set up for each N loss pathway. This approach would provide a first approximation validation of MEDLI outputs. Importantly, some of these data sets are already available from the National Agricultural Nitrous Oxide Program (NANORP) project. (See http://www.n2o.net.au/about-us/, https://ecoapps.nrel.colostate.edu/global_n2o/).

3 Carbon and Nitrogen Modules in DairyMod

3.1 Overview

DairyMod is an empirical biophysical model that has modules for pasture growth and utilisation by grazing animals, water and nutrient dynamics, animal physiology and production, and a range of options for pasture management, irrigation, and fertiliser application (Johnson et al. 2008). It evolved from the SGS Pasture Model (Johnson et al. 2003).

3.2 Carbon pools and processes

DairyMod has two soil C pools with fast and slow turnovers respectively (Fig. 3-1). A third inert C pool is estimated. Fresh organic C input enters the fast pool. The fast pool includes the soil microbial biomass (MB) with a prescribed C/N ratio of 8. During organic matter (OM) decay, a user-defined proportion of the C is respired. The resulting C:N ratio (after respiration), is then compared with the C:N ratio of the MB, which determines whether there will be mineralisation or immobilisation of nutrients. During decay from the fast pool, it is further assumed that a proportion of the MB is transferred to the slow pool, which represents the movement from unprotected to protected material.

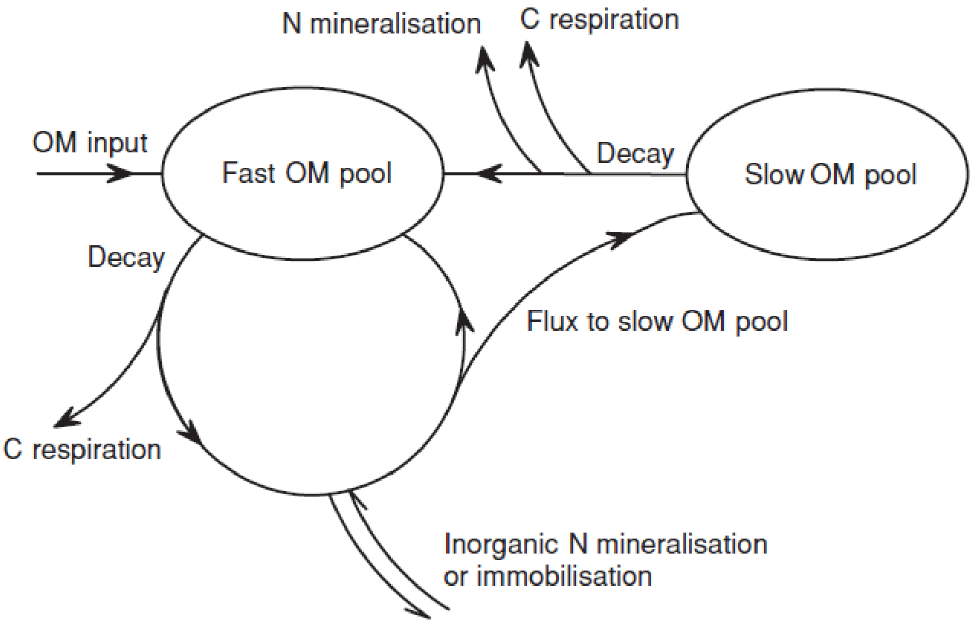


Figure 3-1. Schematic representation of the organic matter dynamics for N in the model. P and S are treated in a similar way. Reproduced from Fig. 1 Johnson et al. (2008).

OM dynamics are influenced by water and temperature and these responses are incorporated using generic functions defining an increase in the turnover rates in response to increases in both temperature and available soil water.

3.3 Nitrogen pools and processes

3.3.1 Volatilisation

Volatilisation is assessed for urine patches and recently applied urea fertilizer. For urine patches, a user-defined fixed proportion of N from daily urine inputs is assumed to be lost. For surface-applied urea, losses are assumed to occur for 2 days following application, with 50% of the applied N per day transferred to the surface soil layer. Volatilisation is suppressed when daily rainfall exceeds a user-defined amount (default value 5 mm/day).

3.3.2 Nitrification

Nitrification is described using first order kinetics with a prescribed proportion of [NH_4-N] converted to NO_3-N each day. For low [NH_4-N], the response is approximately linear and so the initial slope (Fig. 3-2) is the proportion of NH_4-N that nitrifies each day (20% with the default parameters).

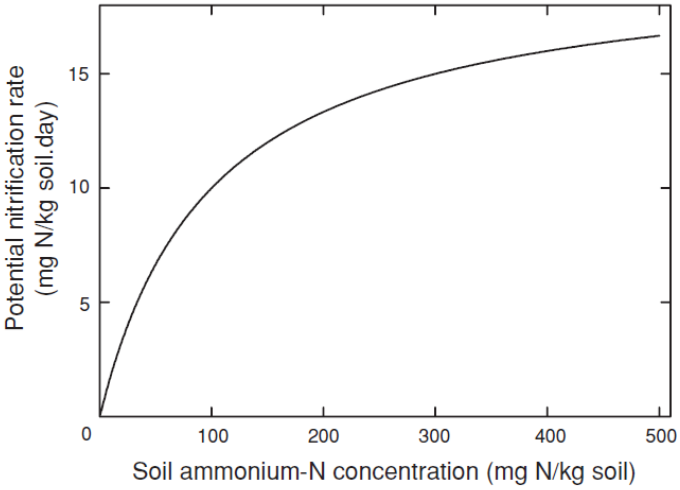


Figure 3-2. Default rate of nitrification as a function of available soil ammonium for non-limiting water, temperature and C conditions. Reproduced from Fig.3 Johnson et al. (2008).

Nitrification is also affected by soil water conditions, temperature and the soil microbial pool. Generic response functions for the influence of soil water status and temperature on soil organic matter dynamics are stated to be used but were **not defined** in either Johnson et al. (2003) or Johnson et al. (2008). The effect of soil pH on nitrification rate is not considered. Since there is no direct treatment of the soil microbial pool, it is assumed that the level of microbes in the soil is proportional to the total labile soil C (fast plus slow turnover). Hence, the level of labile C in any layer, relative to that in the top layer, is used as a scaling factor for nitrification. Thus, as soil C declines through the soil profile, so too does the rate of nitrification.

3.3.3 Denitrification

Denitrification is assumed to only occur in saturated soil; the rate is defined using first order kinetics and increases as nitrate-N (NO_3-N) increases (Fig. 3-3). The partitioning of denitrified gases into dinitrogen (N_2) and nitrous oxide (N_2O) uses a modifier based on water-filled pore space.

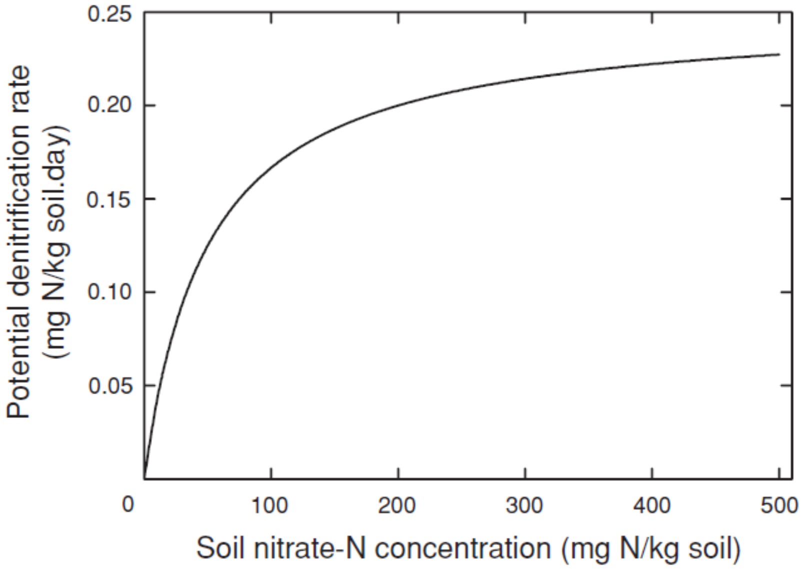


Figure 3-3. Default rate of denitrification as a function of available soil NO_3 for non-limiting soil water conditions. Reproduced from Fig. 4 Johnson et al. (2008).

Denitrification is influenced by temperature and, as a microbial process, the soil C status. Temperature effects and soil C effects use the same generic response function as for nitrification (which has not been specified).

3.3.4 Drainage

Nitrate-N loss by drainage is calculated as convective flow when soil water exceeds the drained upper limit (DUL) [(adaptation of Addiscott (1977)]. Drainage does not occur evenly but will show preferential flow according to soil pore size distribution, partitioning the water flow into mobile and immobile fractions. The effect of mixing (by dispersion or diffusion) of the solute in the mobile and immobile water must be taken into account to describe solute movement. The model assumes that the solute stored in some proportion of the immobile water can readily mix with the mobile water and so can be leached within a period of a day. The rest of the solute is assumed to mix less readily and is only equilibrated with the mobile water at the end of each day. Mixing occurs at the end of the day so that the remaining nutrients are then mixed with any fresh water that has been moved into the profile.

4 Carbon and Nitrogen Modules in APSIM

4.1 Overview

APSIM is a biophysical model comprising several modules attached to the core 'engine'. Of particular relevance to this review are the SOILWAT, SOILN, and RESIDUE modules. Much of the code in these modules has evolved from PERFECT and the CERES family of models, notably CERES-Maize.

4.2 Carbon pools and processes

APSIM uses three conceptual soil C pools – BIOM (labile C- microbial biomass and microbial by-products- rapid turnover- days); HUM (stable C- slow turnover- months-years); and INERT- not specifically identified in the C pool diagram (Fig. 4-1) but considered not to participate in the modelled mineralisation/immobilisation processes (Probert et al. 1998).

The fresh C input pool is FOM (fresh organic matter) which comprises added organic amendments and on-site vegetative residues including decomposing root material (Fig. 4-1). To account for variation in the decomposability of the organic C in FOM, it has been sub-divided into three pools of different lability (and possibly different C/N ratios- Fig. 4-1): carbohydrate-C, cellulose-C and lignin-C (Probert et al. 2005). These organic C forms need to be characterised by chemical analysis.

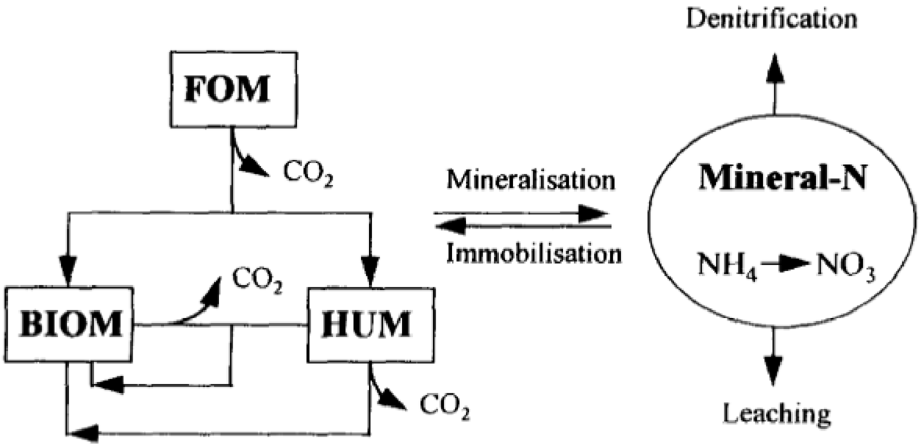


Figure 4-1. Carbon and mineral N pools in APSIM's N module. Reproduced from Fig. 3 of Probert et al. (1998).

Carbon flows between pools are assumed to follow first order kinetic behaviour, with the rate (day^{-1}) modified by soil water content and temperature using scaling factors (0-1) as shown in Figs 4-2 and 4-3.

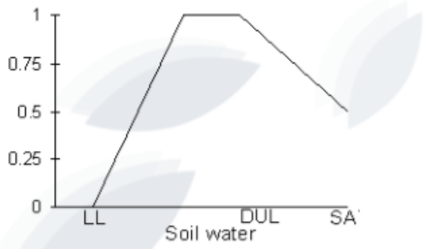


Figure 4-2. Water scaling factor affecting mineralisation rates of the various soil organic matter pools at soil water contents of Lower Limit (LL), Drained Upper Limit (DUL) and Saturation (SA). Reproduced from Fig. 2 of Probert et al. (2005).

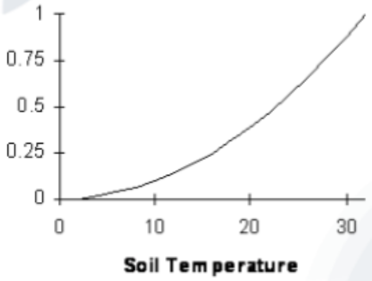


Figure 4-3. Temperature scaling factor affecting mineralisation rates of the various soil organic matter pools. Reproduced from Fig. 3 of Probert et al. (2005).

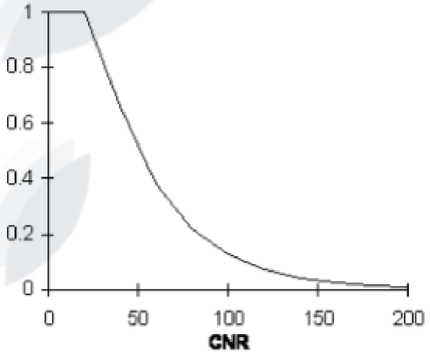
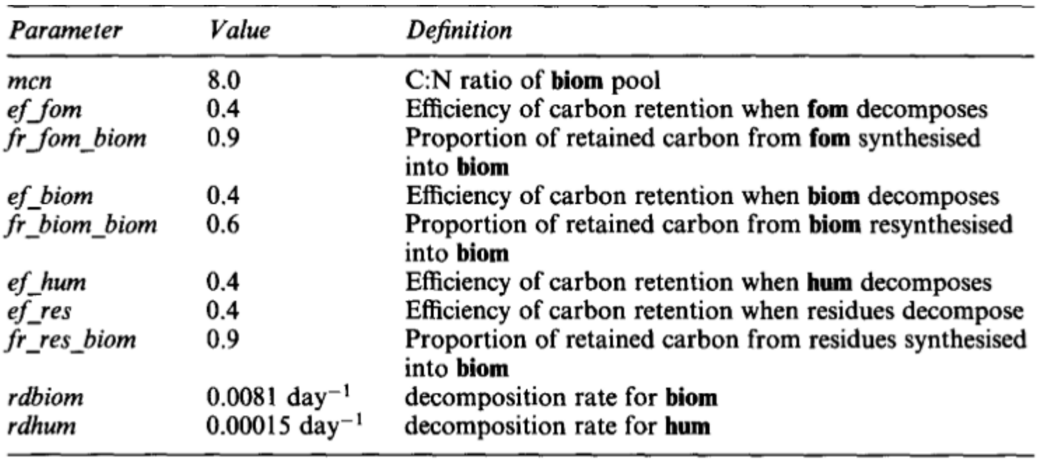


Figure 4-4. C:N ratio scaling factor affecting mineralisation rate of soil FOM pools is calculated using a modified C:N ratio that includes the mineral N in the soil layer. CNR = fom_C / (fom_N + min_N). Reproduced from Fig. 4 of Probert et al. (2005).

Fluxes between the C pools drive the consequent N fluxes that are based on the C pool sizes and their respective C/N ratios. The C/N ratio of BIOM has an assigned value, while the C/N ratio of HUM is that measured in a sample of the soil layer being considered. The FOM C/N ratio is measured and has an assigned modifier that captures the mineralisation/immobilisation characteristics (Fig. 4-4).

The flows are defined in terms of efficiency coefficients, representing the proportion of C retained in the system, and the fraction of the retained C that is synthesised into the BIOM pool (see Table 4-1 for parameter definitions and values). When BIOM decomposes, there is an internal cycling of C (microbes feeding on microbial products).

Table 4-1. The maximum decay rates of carbohydrate, cellulose and lignin pools in FOM are: rd_carb, 0.2 day-1; rd_cell, 0.05 day-1; rd_carb, 0.00095 day-1. Reproduced from Table 1 of Probert et al. (1998).



Parameter	*Value*	*Definition*
mcn	8.0	C:N ratio of **biom** pool
ef_fom	0.4	Efficiency of carbon retention when **fom** decomposes
fr_fom_biom	0.9	Proportion of retained carbon from **fom** synthesised into **biom**
ef_biom	0.4	Efficiency of carbon retention when **biom** decomposes
fr_biom_biom	0.6	Proportion of retained carbon from **biom** resynthesised into **biom**
ef_hum	0.4	Efficiency of carbon retention when **hum** decomposes
ef_res	0.4	Efficiency of carbon retention when residues decompose
fr_res_biom	0.9	Proportion of retained carbon from residues synthesised into **biom**
rdbiom	0.0081 day^{-1}	decomposition rate for **biom**
rdhum	0.00015 day^{-1}	decomposition rate for **hum**

Mineralisation or immobilisation of mineral N is determined as the balance between the release of N during decomposition of FOM, BIOM and HUM, and the N required by the microbial biomass during microbial synthesis and humification. An inadequate supply of mineral N to satisfy the immobilisation demand results in a slowing of the decomposition.

At initialisation, the proportion of soil C in each layer that is inert (fINERT) is specified and the amount of *inert-C* calculated. Thus, *inert-C* is effectively the organic C content that would result **after** a long period of decomposition without any input of fresh organic matter. As an approximation of fINERT, the TOC content of the deepest profile soil sample is assumed to be entirely INERT C and this content is subtracted from concentrations in other soil samples to calculate BIOM + HUM C.

Residue characteristics are linked to the SOILWAT module (surface cover to mitigate erosion) and the contribution of residues to the C and N pools is modified by tillage management or a ‘contact’ factor for surface retained residues (Fig. 4-5).

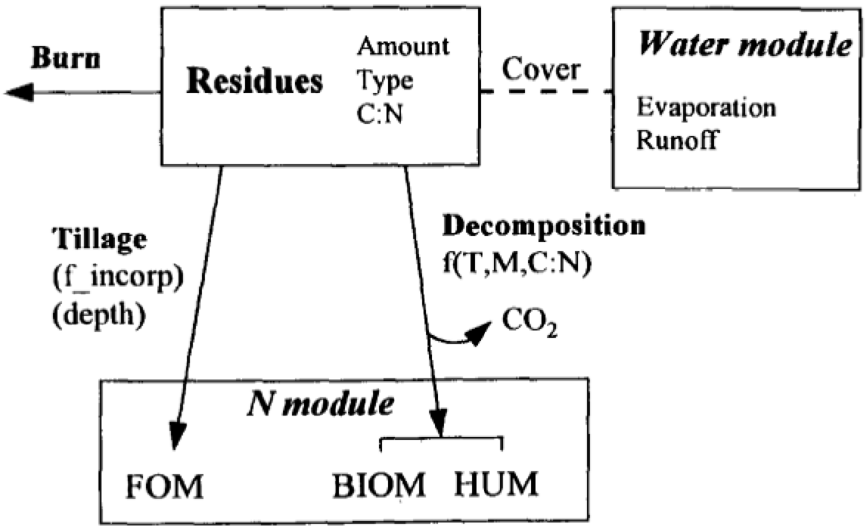


Figure 4-5. Schematic representation of the processes dealt with in the RESIDUE module. Reproduced from Fig. 4 of Probert et al. (1998).

4.3 Nitrogen pools and processes

4.3.1 Volatilisation

Volatilisation is not currently included in APSIM. However, Vogeler et al. (2019) added a volatilisation routine to APSIM when simulating the effect of irrigation management on N losses from pasture. The routine is based on the mechanistic volatilisation model of Génermont and Cellier, (1997) which considers the partitioning of ammonium-N in solution between $[NH_4^+]$ and $(NH_3)_{aq}$ and Henry's Law to estimate $(NH_3)_{gas}$.

4.3.2 Nitrification

Nitrification in the APSIM-SoilN model follows the Michaelis–Menten response to available soil ammonium, with the rate of nitrification (Rnit) given by:

$$R_{nit} = k_{max} ([NH_4]/[NH_4]+K_{NH4})\ f(T)\ f(\theta)\ f(pH)$$

where $[NH_4]$ is the ammonium-N concentration in the soil (mg/kg), k_{max} is the maximum nitrification rate (default setting of 40 mg/kg/day), K_{NH4} is the $[NH_4]$ concentration for half the maximum rate (default setting of 90 mg/kg), and $f(T)$, $f(\theta)$ and $f(pH)$ are 0 to 1 scaling functions accounting for the limitations imposed by temperature, soil water content and pH. Both $f(\theta)$ and $f(pH)$ decrease on either side of an optimum level and $f(T)$ increases exponentially up to an optimum temperature of 32°C (Figs 4-6 to 4-8).

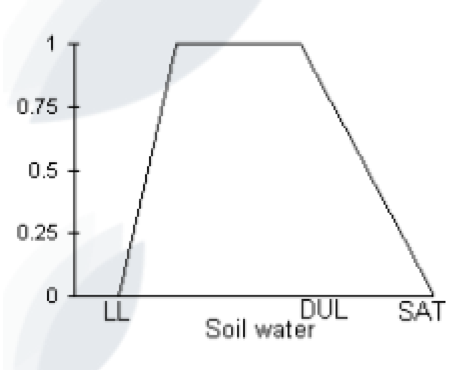


Figure 4-6. Water scaling factor affecting the nitrification rate of ammonium in each soil layer. Reproduced from Fig. 5 of Probert et al. (1998).

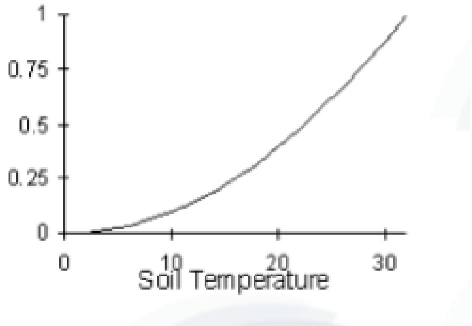


Figure 4-7. Temperature scaling factor affecting the nitrification rate of ammonium in each soil layer. Reproduced from Fig. 6 of Probert et al. (1998).

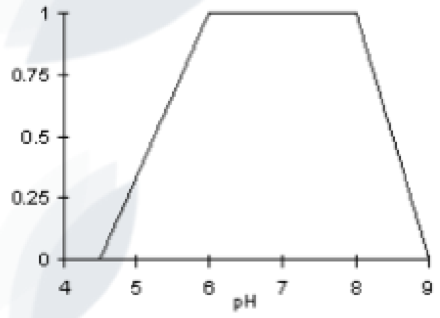


Figure 4-8. pH scaling factor affecting the nitrification rate of ammonium in each soil layer. Reproduced from Fig. 7 of Probert et al. (1998).

4.3.3 Denitrification

The denitrification rate (R_{denit}) in APSIM-SoilN is calculated by:

$R_{denit} = k_{denit} [NO_3] C_A f(T) f(\theta) f(pH)$

where k_{denit} is the denitrification coefficient, with a default value of 0.0006, [NO3] is the amount of nitrate-N in the soil (mg/kg) and C_A is the active C (mg/kg) defined by Rolston et al. (1984) as:

$C_{A,i} = 0.0031FOM + 24.5$

where FOM is the sum of the organic C (mg/kg) in the fresh organic matter soil C pools. The modifier functions for soil water content and temperature for denitrification are shown in Figs 4-9 and 4-10.

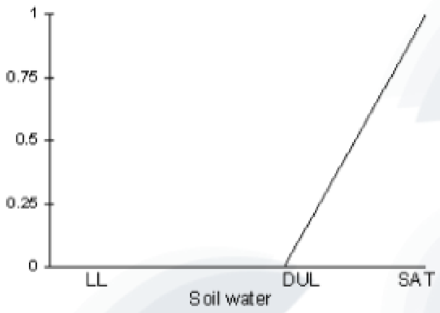


Figure 4-9. Water scaling factor affecting the denitrification of NO_3 in each soil layer. Reproduced from Fig. 8 of Probert et al. (1998).

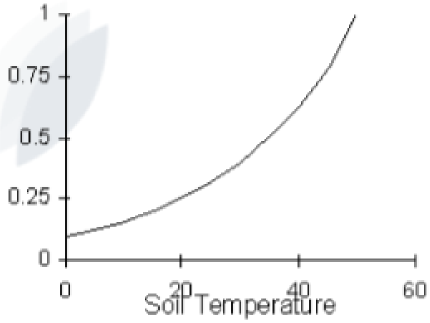


Figure 4-10. Temperature scaling factor affecting the denitrification of NO_3 in each soil layer. Reproduced from Fig. 9 of Probert et al. (1998).

APSIM does have routines for estimating the proportion of denitrified N gas as nitrous oxide (N_2O), but because of the large number of factors affecting the ratio of N_2O:N_2, it is not possible to assign a default value (which might change at sub-daily level). MEDLI is not designed to provide estimates of the emissions of greenhouse gases so nitrous oxide emission due to denitrification is not considered here.

4.3.4 Drainage

Solute (i.e., NO_3-N) transport is treated as convective flow in soil water. APSIM allows the use of either a mechanistic (e.g., Richards' equation) or simple model (e.g., capacity or 'bucket') to describe water movement. SoilWat module is the simple 'cascading' water balance model used in APSIM where water movement is described using separate algorithms for saturated flow (defined here as water content between saturation and DUL) and unsaturated flow (defined here as water content below DUL). Unsaturated flow is allowed to occur upwards or downwards between adjacent soil layers thereby accounting for the capillary flow effects at soil water contents lower than DUL. Solute flux is then associated with both saturated and unsaturated fluxes assuming complete mixing of the solution in the soil water in each layer. Solute movement is calculated as the product of water flow and the solute concentration in that water.

SWIM3 is the more detailed hydrological module using Richards' equation to describe flows under certain boundary conditions (e.g., fluctuating water tables), detailed solute fluxes (e.g., salt or NO_3 leaching), complex flow processes (e.g., sub-surface drains), or processes occurring at much smaller time and spatial scales.

5 Carbon and Nitrogen Modules in MEDLI

5.1 Carbon pools and processes

MEDLI has two N pools and therefore two C pools: a *labile pool* (here designated 'LABILE C/N' and a *non-labile pool* (here designated 'NON_LABILE C/N', with different first-order mineralisation rates: 0.0081 day^{-1} (LABILE N) and user-defined value for 'NON_LABILE N'; typically 0.00035 day^{-1}. Total organic N in the effluent is assigned as LABILE N, while soil organic N (i.e., TN minus mineral-N) is assigned as NON_LABILE N. The C/N ratio of neither of these C/N pools is considered.

5.1.1 Mineralisation (ammonification) and immobilisation

Irrespective of whether net mineralisation (ammonification) or immobilisation is occurring because of microbial oxidation of organic C, microbial activity is impacted by temperature and soil water content. The temperature effect on rate of mineralisation/immobilisation is captured by a temperature modifier based on the Arrhenius equation (Fig. 5-1).

$$TF_i = \gamma^{(T_i - 35)} \quad \text{.......................................}\text{Equation 6.13}$$

where:

TF = Arrehenius temperature correction scaling factor for soil layer i

γ = Temperature correction coefficient

T_i = Soil temperature in °C for soil layer i

Figure 5-1. Effect of temperature on the modifier for mineralisation/immobilisation rate. Reproduced from MEDLI Technical Reference (2016).

The γ value has been hard wired in MEDLI as 1.06 which is a typical value.

The relationship for estimating soil moisture effects on mineralisation/immobilisation is based on Myers *et. al*. (1982). For soil moisture between air dry and drained upper limit, the moisture correction factor is calculated by the equation in Fig. 5-2, and this factor is capped at 1.0 for soil water contents above drained upper limit as shown in Fig. 5-2.

$$MF_i = 0.054 + 0.96 \times \frac{sw_i}{fc_i} \quad \text{.......................................}\text{Equation 6.12}$$

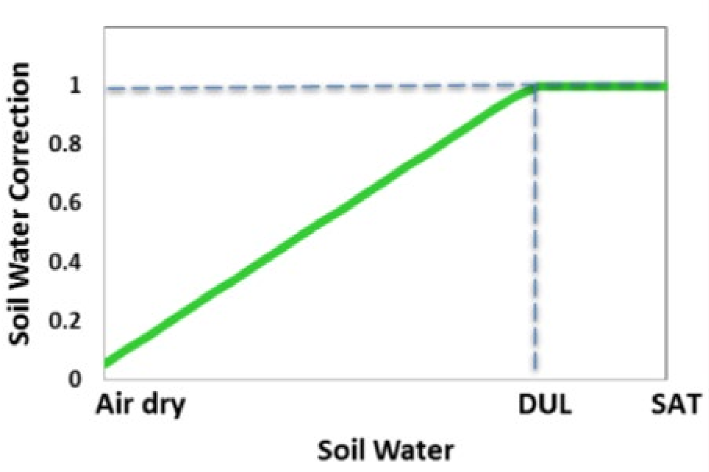


Figure 5-2. Effect of soil water content on the modifier for mineralisation/immobilisation rate. Reproduced from MEDLI technical Reference (2016).

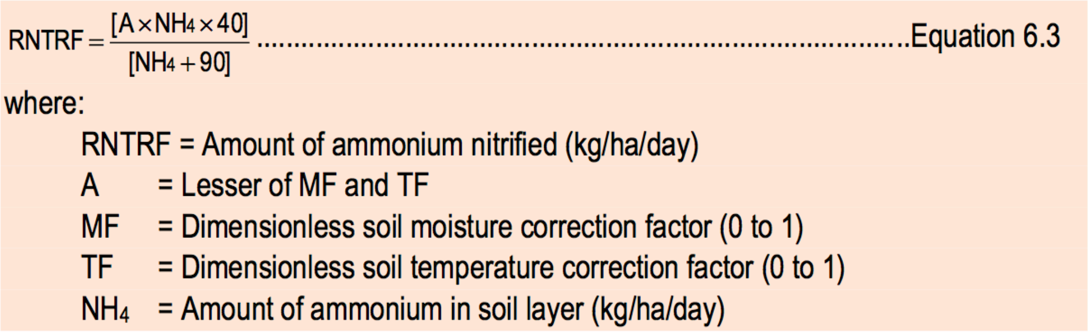
5.2 Nitrogen pools and processes

5.2.1 Volatilisation

The loss of ammonia gas due to volatilisation of ammonium-N from the source effluent is only considered to occur during the irrigation event. This loss is dependent on the type of spray nozzle, its operating pressure and the amount of NH_4 in the effluent. MEDLI computes volatilisation loss as a user specified fraction of the ammonium-N in the effluent. Typical values are 20% but, in some cases, can reach 50% in high pressure irrigators that produce “**lots” of small droplets** per litre of effluent (Natasha Smith - Gelita pers. Comm.)

5.2.2 Nitrification

The nitrification algorithm for MEDLI has been taken from the CERES-MAIZE model (Godwin and Jones, 1991). Instead of using a kinetic equation, the modelling approach is based on the potential nitrification rate computed as a Michaelis-Menten kinetics function dependent only on ammonium concentration (Fig. 5-3). Therefore, the predictions are independent of the soil type.



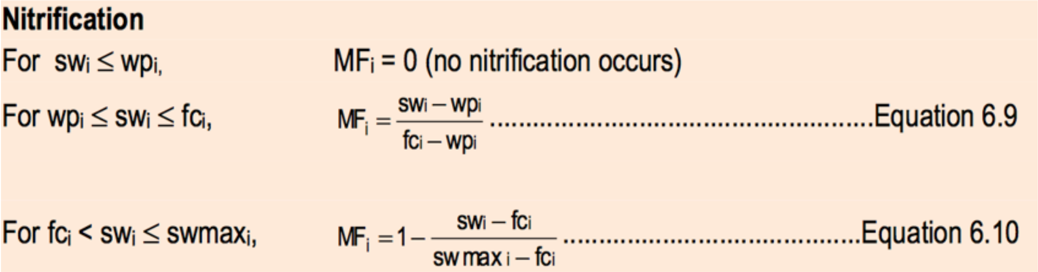
$$RNTRF = \frac{[A \times NH_4 \times 40]}{[NH_4 + 90]} \text{ ....Equation 6.3}$$

where:

RNTRF = Amount of ammonium nitrified (kg/ha/day)
A = Lesser of MF and TF
MF = Dimensionless soil moisture correction factor (0 to 1)
TF = Dimensionless soil temperature correction factor (0 to 1)
NH_4 = Amount of ammonium in soil layer (kg/ha/day)

Figure 5-3. Equation for calculating daily nitrification rate with temperature and soil water content modifiers. Reproduced from MEDLI Technical Reference (2016)

The potential nitrification rate is adjusted using scaling functions to take into account the effects of soil water content and temperature. Figure 5-4 presents the equation and plot for the soil water content effect on nitrification.



Nitrification

For $sw_i \leq wp_i$, $MF_i = 0$ (no nitrification occurs)

For $wp_i \leq sw_i \leq fc_i$, $$MF_i = \frac{sw_i - wp_i}{fc_i - wp_i} \text{ ....Equation 6.9}$$

For $fc_i < sw_i \leq swmax_i$, $$MF_i = 1 - \frac{sw_i - fc_i}{swmax_i - fc_i} \text{ ....Equation 6.10}$$

Where:

MF_i = Moisture correction scaling factor (0 to 1) for layer i
sw_i = Soil water content of layer i (mm)
$swmax_i$ = maximum soil water content (SAT) of layer i (mm)
fc_i = Drained Upper Limit (DUL) of soil layer i (mm)
wp_i = Lower Storage Limit (LSL) of soil layer i (mm)

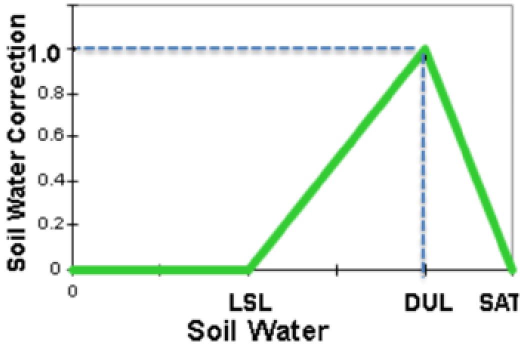
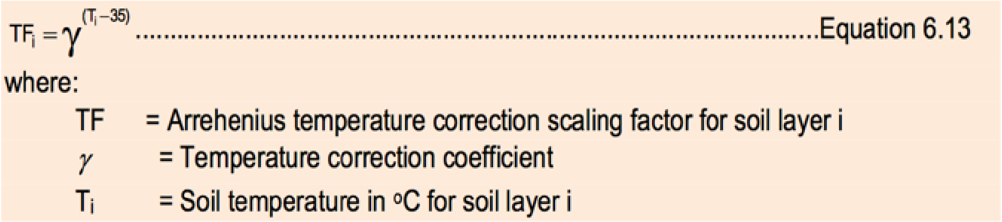


Figure 5-4. Effect of soil water content on the soil water modifier for nitrification rate. Reproduced from MEDLI Technical Reference (2016).

The temperature scaling factor for nitrification (as well as for ammonium adsorption/desorption, immobilisation and mineralisation) is based on a modified van't Hoff-Arrhenius equation (Metcalf and Eddy, 1990) (Fig. 5-5).



$TF_i = \gamma^{(T_i - 35)}$ ……………………………………………………………………………………Equation 6.13

where:

TF = Arrehenius temperature correction scaling factor for soil layer i

γ = Temperature correction coefficient

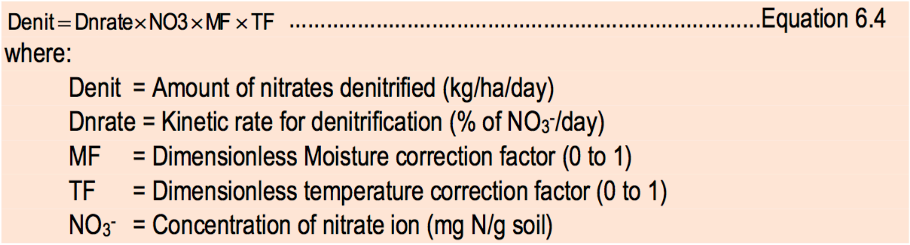
T_i = Soil temperature in °C for soil layer i

Figure 5-5. Effect of temperature on the modifier for nitrification rate. Reproduced from MEDLI Technical Reference (2016).

The γ value has been hard wired in MEDLI as 1.06 which is a typical value.

5.2.3 Denitrification

Denitrification is the reduction of nitrates (and nitrites) to gaseous products including NO, N_2O and N_2 by microbial (and less commonly, chemical) processes that occur under anaerobic conditions, and which are influenced by organic C content, water-filled pore space, soil temperature and soil pH (Otte et al. 2019). The denitrification algorithms in MEDLI are based on first order kinetics and are shown in Fig. 5-6.



$Denit = Dnrate \times NO3 \times MF \times TF$ ……………………………………………………………………Equation 6.4

where:

Denit = Amount of nitrates denitrified (kg/ha/day)

Dnrate = Kinetic rate for denitrification (% of NO_3^-/day)

MF = Dimensionless Moisture correction factor (0 to 1)

TF = Dimensionless temperature correction factor (0 to 1)

NO_3^- = Concentration of nitrate ion (mg N/g soil)

Figure 5-6. The kinetic equation for denitrification used in MEDLI to predict denitrification rate. Reproduced from MEDLI Technical Reference (2016).

Denitrification rate is positively correlated with dissolved organic C, with the **potential denitrification rate (Dnrate)** adjusted by a C scalar. For layers with labile organic C present, the scalar is set to 1, whilst for layers without labile organic C, the scalar is set to zero. MEDLI uses a default Dnrate value of 0.1, i.e., 10% of the current amount of NO_3-N (mg/kg) in the soil layer of interest

The optimum pH range for denitrification is between pH 7.0 and pH 8.0; it proceeds slowly below pH 5.5. MEDLI does not explicitly consider the pH effect, but Dnrate should be reduced if the pH_{water} of the receiving soil is lower than 5.5.

The effect of temperature on Dnrate is taken into account of by using the scaling function from the CERES-MAIZE model (Godwin and Jones, 1991) (Fig. 5-7).

$$TF_i = 0.1 \times e^{0.046 \times T_i} \quad \text{.......Equation 6.14}$$

where:

TF_i = Soil temperature correction factor (0 to 1) for soil layer i

T_i = Soil temperature in °C for soil layer i

Figure 5-7. The soil temperature modifier for denitrification. Reproduced from MEDLI Technical Reference (2016).

The effect of soil water content on denitrification is accounted for by the soil water modifier (Fig. 5-8).

Denitrification

if: $sw_i \le fc_i$ then $MF_i = 0$ (no denitrification occurs)

if: $fc_i \le sw_i \le swmax_i$, then $$MF_i = \frac{sw_i - fc_i}{swmax_i - fc_i} \quad \text{.......Equation 6.11}$$

Where:

MF_i = Moisture correction scaling factor (0 to 1) for layer i
sw_i = Soil water content of layer i (mm)
$swmax_i$ = Maximum soil water content (SAT) of layer i (mm)
fc_i = Drained Upper Limit (DUL) of soil layer i (mm)
wp_i = Lower Storage Limit (LSL) of soil layer i (mm)

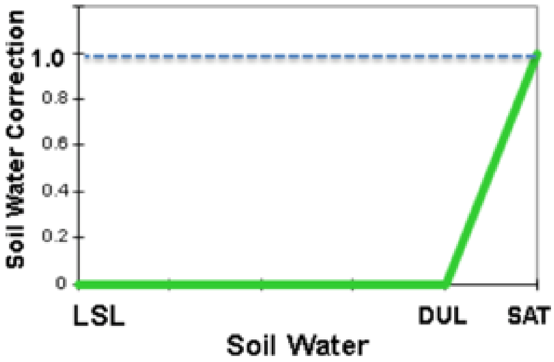


Figure 5-8. The soil water content modifier for denitrification. Reproduced from MEDLI Technical Reference (2016).

5.2.4 Drainage

Solutes such as NO_3 move with the drainage water. The amount of NO_3 leached to the next layer is based on the concentration in upper layer and total amount of water drained. All the drainable soil water is assumed to be mobile. However, ammonium and organic-N are not allowed to move with the drainage water as leaching of these positively charged ions is expected to be minimal. At each time step, water and nutrient balances are computed for each layer, and concentrations of different solutes in each layer are updated.

6 Comparisons of Parameters used by Models to Simulate Carbon and Nitrogen Pools and Processes

The algorithms and parameters that DairyMod, APSIM and MEDLI use to simulate C and N pools and processes are summarised in Table 6-1.

6.1 Carbon pools and net nitrogen mineralisation/immobilisation

APSIM has three C pools of differing turnover rates; the inert C pool is not directly involved in any processes but is required for model initiation.

The fresh organic matter pool (FOM) in APSIM is sub-divided into three sub-pools of different C lability (carbohydrate, cellulose, and lignin) that can be quantified by routine chemical analyses. Each pool and sub-pool have an allocated efficiency and decomposition rate, and when this is combined with measured (or inferred) C/N ratios, net N immobilisation or net mineralisation (ammonification) can be identified. Neither DairyMod nor MEDLI have this simple sophistication that allows flexibility in reflecting differing levels of C lability in FOM inputs.

Rather than using C decomposition rate coupled with the relevant C/N ratio to estimate ammonification/immobilisation, N mineralisation can be estimated directly by measuring the organic N content of the decomposing C pool. This approach has been taken by Allen et al. (2019), and it was found that long term N mineralisation (305 days @ 35^{o}C in a controlled laboratory incubation study) in 15 sugarcane-producing soils was correlated ($P<0.05$) with total N. However, CO_2 evolution over 3 days was the best predictor of net N mineralisation, confirming that the C cycle was the driver of net N mineralisation.

When measuring short (days) and seasonal (months) net N mineralisation in laboratory incubation studies, both Wang et al. (2004) and Allen et al. (2019) fitted a two-pool exponential N model to describe cumulative N mineralisation; ‘*active*’ for the initial (days) high rate of mineralisation and ‘*slow*’ for the slower, longer term (months) rate of mineralisation. Wang et al. (2004) found large variation between soils in the *active* and *slow* mineralisation rates and suggested that when attempting to understand factors affecting the quantum of N mineralised from the two pools, mean mineralisation rates should be used rather than the statistically fitted values for individual soils. The mean values from Wang et al. (2004) are compared with those found by Allen et al. (2019) in Table 6-1 and there is reasonable agreement between the two studies.

The N mineralisation rates found by Wang et al. (2004) and Allen et al. (2019) provide an independent means for validating estimates of potential ammonification/nitrification simulated by APSIM and MEDLI from decomposition rates and measured (or inferred) C/N ratios of the C pools. Orton et al. (2019) used the potential mineralisation rates of Allen et al. (2019) to simulate seasonal in-soil N mineralisation by taking account of long-term temperature and rainfall effects using the APSIM modifiers for soil water content and temperature on N mineralisation. It would be interesting to compare these simulations with outputs from MEDLI and APSIM. However, these comparisons would need to be ground-truthed by field measurements.

6.2 Volatilisation

For effluent-irrigated pastures, there are two opportunities for N loss by volatilisation: (i) directly from the effluent during the actual irrigation event, and (ii) from the receiving soil post-irrigation. MEDLI only considers volatilisation from effluent, whereas APSIM with added a volatilisation routine by Vogeler et al. (2019) and DairyMod only consider ammonia volatilisation from the soil after fertiliser urea and/or urine application.

Table 6-1 Comparison of parameters used to estimate C and N pools and processes.

Nutrient/Process	**Pool**	**MEDLI**	**APSIM**	**DairyMod**	**Wang et al. (2004)**	**Allen et al. (2019)**
C oxidation – max rate (expressed as a fraction of organic carbon day^{-1})	BIOM [1]		0.0081	User-defined C oxidation rate of two pools		
	HUM [1]		0.00015			
	FOM [1]		Carbohydrate-like C: 0.2 Cellulose-like C: 0.05 Lignin-like C: 0.00095			
N ammonification/ immobilisation	Labile N	0.0081 for ammonification	Uses assumed C oxidation rate and measured C/N ratio of C pools	Uses assumed C oxidation rates and assumed C/N ratios of C pools		
	Non-labile N	0.00035 for ammonification 0 for Immobilisation				
N Mineralisation (mg N kg^{-1} day^{-1})	*Active*				0.099	$0.217\underline{+}0.032$
	Slow				0.0077	$0.003\underline{+}0.0003$
Volatilisation		Empirical fraction of NH_4-N in the applied effluent.	Calculated from (NH_4-N)/$NH_{3\,aq}$ partitioning and Henry's Law	User defined		
Nitrification (mg N kg^{-1} day^{-1})		40(NH_4-N)/[(NH_4-N)+90]	40(NH_4-N)/[(NH_4-N)+90]	*ƒ*(NH_4-N); maximum 0.2*(NH_4-N)		
Denitrification (mg N/kg soil/day)		0.10 (NO_3-N)	0.0006*(NO_3-N) x [0.0031(HUM_C+FOM_C)+24.5] $\backcong$ 0.05 x (NO_3-N) ……for 2% OC and 100 mg (NO_3-N) kg^{-1}]	*f*(NO_3-N); maximum rate: 0.22 mg N kg^{-1}		

[1] BIOM pool notionally representing the more labile, soil microbial biomass and microbial products, HUM comprises the rest of the soil organic matter. FOM is the fresh organic matter which will decompose into BIOM or HUM.

In both volatilisation scenarios, the partitioning of aqueous ammonia ($NH_{3\ aq}$) follows the dissociation equation:

$$\mathrm{Kd} = \frac{[\mathrm{NH_3}]_{\mathrm{aq}} * [\mathrm{H^+}]}{[\mathrm{NH_4^+}]} \quad \text{(Eqn 6-1)}$$

where units are moles/L. This can be represented graphically as a function of solution pH (Fig. 6-1). In aqueous solution, Kd is 5.01×10^{-10}

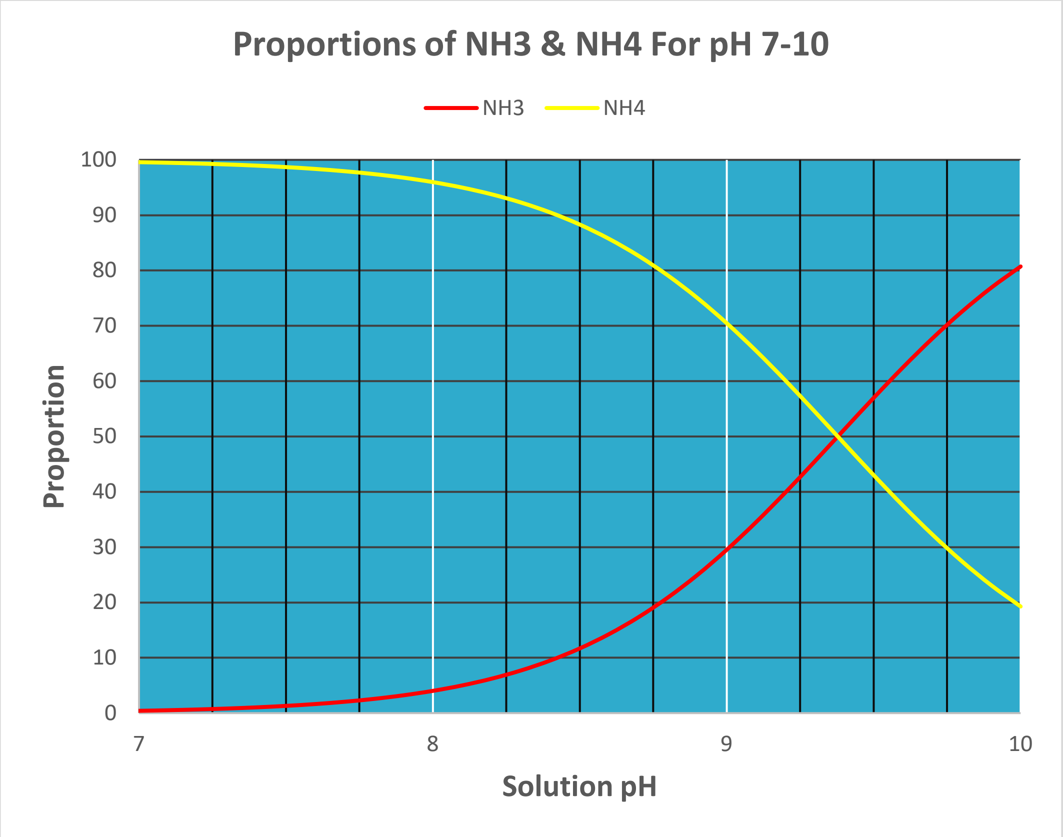


Figure 6-1. The relationship between the fraction of NH_3 and NH_4 in a TAN solution (total ammoniacal N) as a function of its pH. Note that the sum of the fractions always equals 1. (Based on equations from Emerson et al. 1975).

The equilibrium between ammonia gas and dissolved ammonia [$NH_{3\ aq}$] follows Henry's Law:

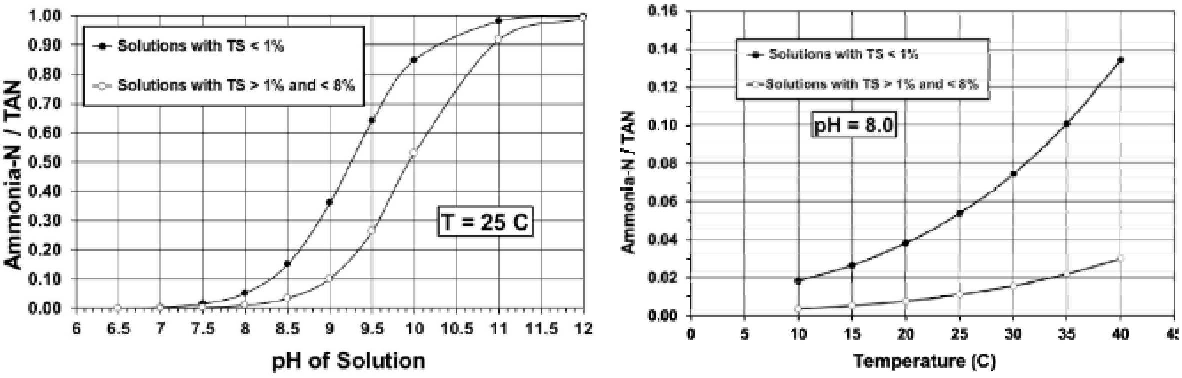
$$\mathrm{Kh} = \frac{[\mathrm{NH_3}]_{\mathrm{gas}}}{[\mathrm{NH_3}]_{\mathrm{aq}}} \quad \text{(Eqn 6-2)}$$

where units are atm/Mole; Kh in aqueous solution is 0.016 atm/M, which is little different to 0.0158 atm/M found by Liang et al. (2011) for litter slurry. Both Kd and Kh increase with temperature.

6.2.1 Volatilisation from effluent

Chastain (2019) reviewed available data from studies of spray irrigated effluent and concluded that volatilisation losses were not significant for effluent with total ammoniacal nitrogen (TAN) of 11 to 1183 ug/L, and TS 0.04-8.4%. The ratio of [$(NH_3)_{aq}$/TAN] increased as pH (and temperature) increased, and was higher for effluent <1%TS than for effluent 1-8%TS (presumably because of the EC effect on ion activity coefficients) (Fig. 6-2).

There was an exponential increase in [$(NH_3)_{aq}$/TAN] at pH>8.2 (<1%TS) or pH>8.7 (1-8%TS), and a linear increase in the ratio at >25 °C (Fig. 6-2), and these are the conditions most likely to result in appreciable N loss by volatilisation from effluent.



(a) (b)

Figure 6-2. Impact of pH (a, temperature held at 25 ◦C) and temperature (b, pH held at 8.0) on the fraction of total ammoniacal nitrogen (TAN = NH_4^+-N + NH_3-N) in ammonia form for liquid animal manure (Reproduced from Chastain 2019, Figure 1.)

At Beaudesert, Queensland, high pressure travelling irrigators (> 500kPa) were found to cause TAN losses in excess of 50 % (Natasha Smith - Gelita pers. Comm.) due to evaporation/volatilization processes from the many fine droplets created. If the pressure drops below about 300kPa, the TAN losses reduce to <25%. It is very difficult to predict the size distribution of spray droplets (but see Kincaid et al. 1996) and the loss percentage will need to be established experimentally using catch cans acidified to prevent NH_3 loss. A typical loss pattern measured using catch cans is shown in Fig. 6-3.

6.2.2 Volatilisation from receiving soil

In the absence of applied urea or urine, it is unlikely that irrigation of a soil with high pH effluent will affect soil pH; except in the case of sands, soil pH buffer capacity will likely be sufficiently high to mitigate any potential alkalising effect of the added effluent. However, if the receiving soil is moderately alkaline (pH_w>8.0) then Eqn 6-1 indicates that volatilisation is likely to occur in the presence of high NH_4-N concentration in the soil solution. It can be calculated from Eqn 6-1 that at pH 7, 0.1% of NH_4-N will be in (NH_3) aqueous form, but at pH 9, this percentage increases to 10.2%. This is well illustrated in Fig. 6-1.

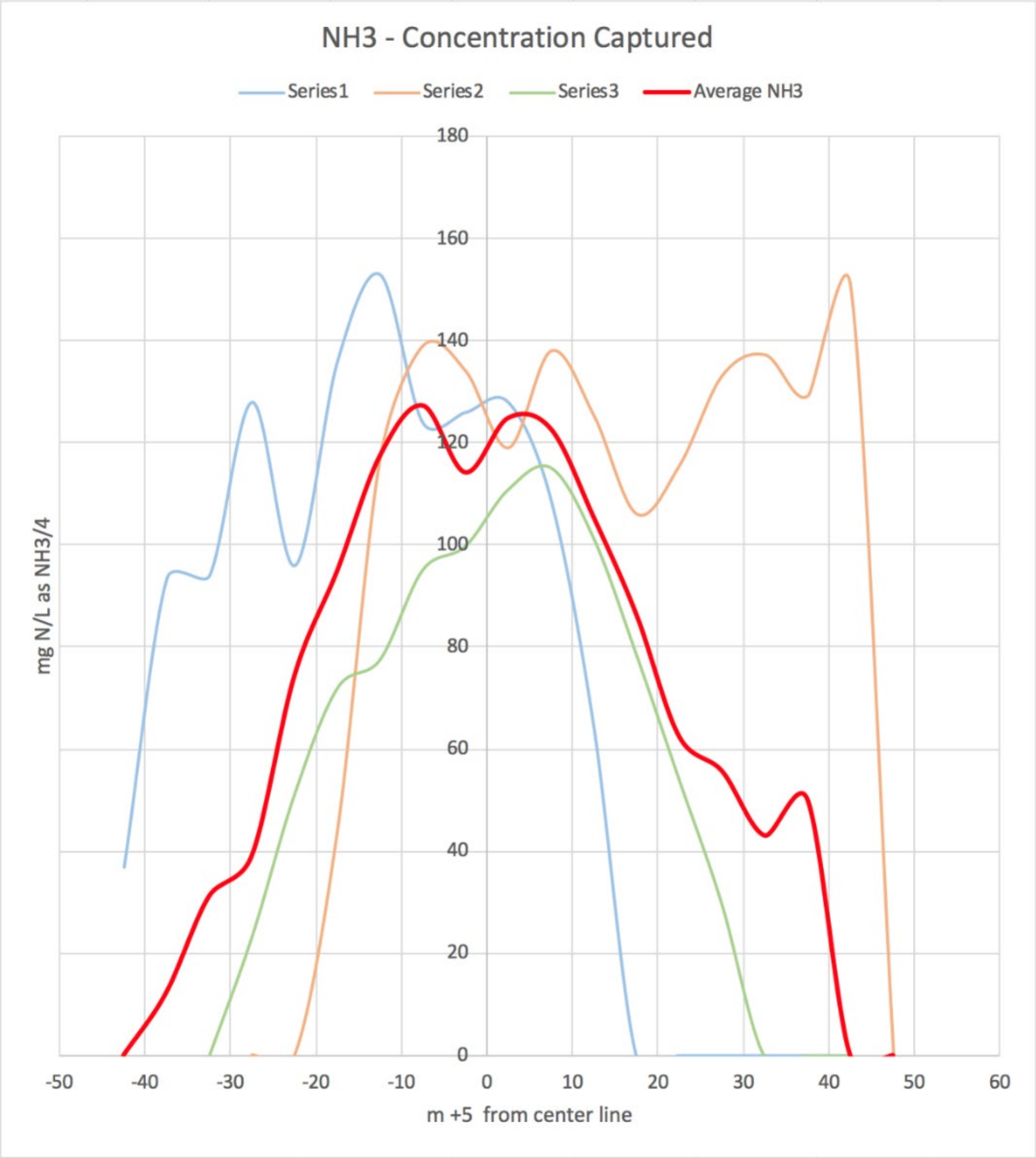


Figure 6-3. Variation in NH_4-N concentration (mg N/L) with distance (m) from the centre line of a Marani travelling irrigator. Effluent was captured in acidified catch containers. Three separate runs were undertaken with the mean results shown by the thick red line (Natasha Smith - Gelita pers. Comm., with permission).

6.3 Nitrification

APSIM, DairyMod and MEDLI use Michaelis-Menten kinetics to estimate maximum nitrification rate. The mineralisation equation used by APSIM and MEDLI (Table 6-1) is based on Godwin and Jones (1991). The equation used in DairyMod is not specified, but Fig. 3 in Johnson et al. (2008) indicates that maximum daily nitrification from 100 mg NH_4-N kg^{-1} would be 20 mg NO_3-N kg^{-1}. This agrees with the nitrification predicted by the MEDLI equation (approximately 21 mg NO_3-N kg^{-1}).

6.4 Denitrification

Denitrification in APSIM increases with (NO_3-N) and labile organic C whereas, in DairyMod, denitrification increases with increasing (NO_3-N) to a maximum value of 0.22 mg NO_3-N kg^{-1} soil. MEDLI uses a maximum denitrification value of 0.10 x (NO_3-N). The APSIM equation predicts 0.05 x (NO_3-N) denitrification for a combination of 20 mg kg^{-1} labile C and 100 mg (NO_3-N) kg^{-1}. There is an order of magnitude difference in the simulation of denitrification by the three models which is indicative of the difficulty in capturing this process correctly.

6.5 Drainage

Drainage losses of NO_3-N from fertilised pastures are dependent on N inputs, pasture growth, pasture management, rainfall/irrigation event frequency and volume, and soil and site hydrology. Because of these numerous factors, measured N loss by this pathway is highly variable. For example, in grazed dairy pastures receiving 200 kg N/ha/yr in split applications, Eckard et al. (2004) measured annual NO_3-N leaching losses of 4-15 (kg N/ha) from the control treatment, 6-22 (kg N/ha) from the urea treatment, and 4-38 (kg N/ha) from the ammonium nitrate treatment, for the lowest and highest drainage years. Pakrou and Dillon (2004) measured the effect of irrigation on N drainage losses and found that the nitrate flux leaching from the root zone in the irrigated pasture paddock was 26-33 kg N/ha/yr compared to 10-13 kg N/ha/yr in the non-irrigated paddock. In comparison, N losses in runoff are generally lower (<5 kg N/ha/yr), except under border-check flood irrigation (3-23 kg N/ha/yr) (Burkitt, 2014). Measurement of leaching flux is further challenged by the high spatial variability of water drainage through the soil.

7 Comparison of Modifiers used by Models to Account for Constraints on Carbon and Nitrogen Processes

7.1 Soil water content

APSIM, DairyMod and MEDLI have modifiers scaled from 0 to 1 to capture the effects of soil water content on organic matter (OM) mineralisation/ammonification and nitrification. The APSIM and MEDLI soil water modifiers comprise linear sections, whereas the response surface used by DairyMod was not specified in the references reviewed.

The same response curves are used by APSIM for soil water content effects on OM mineralisation and nitrification. In contrast, MEDLI uses different response curves for OM mineralisation and nitrification, and these curves are different to those of APSIM. For example, the APSIM modifier for OM mineralisation has a value of 1 from lower soil water content than DUL to DUL and then declines to saturation. However, the MEDLI modifier for OM mineralisation only reaches 1 at DUL and then remains at this value as soil water content increases to saturation. For the nitrification modifier, the MEDLI modifier surface increases linearly to DUL and then declines to SAT whereas the APSIM surface reaches a value of 1 at lower soil water content than DUL before declining at soil water content greater than DUL. These differences in the response surfaces should be reconciled.

For denitrification, APSIM and MEDLI use the same linear segments configuration for the soil water modifier, but as expected, it is different from the configurations used for OM mineralisation and nitrification. The response surface used by DairyMod for the denitrification modifier was not specified in the references reviewed.

7.2 Temperature

Arrhenius equations are used by APSIM to capture temperature effects on OM mineralisation, nitrification and denitrification. However, two different Arrhenius equations are used; one for OM mineralisation and nitrification, and another (with a wider temperature range) for denitrification. Likewise, MEDLI uses different Arrhenius equations to calculate the modifiers for nitrification and denitrification. MEDLI does not use a temperature modifier for OM mineralisation. Temperature modifiers are used for OM mineralisation, nitrification and denitrification in DairyMod, but the form of these ‘generic functions’ was not indicated in the reviewed papers.

7.3 Soil pH

APSIM has a modifier surface comprising linear segments for the effect of soil pH on nitrification. While mentioning the importance of pH as a modifier for biological processes, neither MEDLI nor DairyMod explicitly define a pH modifier.

8 Suggested Actions, including Revisions/Enhancements to MEDLI Carbon and Nitrogen Modules

8.1 OM mineralisation (ammonification)

- Enhance MEDLI mineralisation module to include characterisation of effluent organic C in terms of the three fractions of fresh organic matter used in APSIM. The biggest current limitation is that MEDLI keeps mineralising, irrespective of N status in soil. This results in mining of the native OM because there is no C:N feedback loop.
- Undertake organic C screening of effluents to assess whether there are differences in DOC lability that need to be considered in MEDLI. However, note that MEDLI deals with low OM effluents. APSIM instead must account for the much greater OM added via stubble
- Establish the basis of the difference between the APSIM and MEDLI soil water content and temperature modifiers for ammonification and suggest revisions to MEDLI if necessary.

8.2 Volatilisation

- Add a routine to MEDLI that assesses volatilisation risk of applying high NH_4-N effluent to alkaline soils. However, volatilisation losses that occur during the spray irrigation event are arguably much more important.

8.3 Nitrification

- Establish the basis of the difference between the APSIM and MEDLI soil water content modifiers for nitrification and suggest revisions to MEDLI if necessary.

8.4 Denitrification

- Undertake a review of the basis for the denitrification rate methodologies used in APSIM, DairyMod and MEDLI, and suggest any revisions that might be required in the MEDLI algorithms. Also undertake a review of the historical experimental denitrification rate data, as well as some focused experimentation using N^{15} as **most denitrification data reported is modelled rather than measured!**

8.5 Drainage

- Review data on the mobility, and likely significance, of dissolved organic N in drainage from pastures to assess whether this effluent property needs to be considered in MEDLI. Leaching algorithms that account for mobile and immobile water are described in Cook (2021).

8.6 Sorption/desorption of NH_4-N

- MEDLI includes NH_4 sorption/desorption in the User Manual, but then dismisses it by setting the modifier values to zero. These processes are only of significance in potassium-depleted soils with an appreciable content of illite and vermiculite clay minerals. Such soils are rare in Australia, and it is suggested that mention of this process is deleted from the MEDLI manual.

8.7 N in surface runoff

- When choosing which modelling approach to try in MEDLI, the algorithm with the maximum amount of physically measurable inputs and the fewest empirical matching coefficients seems preferable. Hence it is recommended that the Victorian DPI approach described in the HowLeaky technical manual (Queensland Government 2019) should be considered for further investigation. (See Gardner 2021).

9. Implications of the issues identified for nitrogen modelling

Implications of the issues identified in this report for nitrogen modelling are summarised in Table 9.1.

Table 9-1. Strategic overview of the issues and implications to MEDLI raised by this review for carbon and nitrogen, with additional insights from the Synthesis Report (Gardner 2021).

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Overview of N modelling	Other models such as APSIM and DairyMod are generally more complex than MEDLI and explicitly consider the soil Carbon cycle which drives the soil N cycle. There is also the opportunity to model the microbial fundamentals of N transformations rather than using equations such as Michaelis–Menten.	Uses Hydrological Simulation Program–FORTRAN (HSPF)-based algorithms where maximum rates (of denitrification etc.) are scaled by soil water status, soil temperature and pH.	Incorporate a dynamic soil carbon model into MEDLI. Compare the MEDLI algorithms for mineralisation/ immobilisation, nitrification, denitrification and volatilisation with those used in the empirical models of APSIM and DairyMod	Potentially improve our ability to model N.	High	Moderate	Needs a desktop investigation of the various options first.
N modelling validation	**There are little validation data for hard-to-measure processes such a denitrification**. Hence choosing the best parameter values to use in the reviewed models is hard to make. Moreover, these daily and sub-daily timestep models are generally poor at predicting daily N fluxes	Validation of the N cycle in MEDLI to date has been minimal except for mass balance sums, that include the measured values Applied N, Harvested N, *Change* in Soil N. The residual difference is assumed to equal the denitrification loss.	Experimental work is proposed to measure the processes/pools in the total N cycle. To be effective, this will require a wide array of instrumentation and intensive sampling in the field. **N^{15} will be a critical tool**. A network of sites/soils where effluent is being applied is implied. This approach would provide a first approximation validation of MEDLI outputs.	Intensive experimentation required.	High	Moderate	Needs a desktop investigation of the various options first. Investigation of experimental/research options available.
Carbon dynamics	MEDLI does not currently include a dynamic carbon model to help ensure N dynamics are valid.	Carbon dynamics not considered. Presence of C used to initiate denitrification.	Model soil C dynamics in MEDLI following APSIM or DairyMod exemplars. Having soil C dynamics driving the N processes is	Difficult-to-obtain inputs needed for implementation of a C model.	High – difficult to accommodate in current version without major recoding.	Low importance. In effluent irrigated systems, the incidence of high carbon, low	Needs a desktop investigation of the various options first.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
	Fluxes between the C pools drive the subsequent N fluxes that are based on the C pool sizes and their respective C/N ratios.	Mineralisation of native soil N (specified in input file) occurs irrespective of the amount of N added in effluent. Similarly, excess N cannot be sequestered in the soil organic matter store.	mechanistically correct, is intuitively logical, and could be incorporated into MEDLI reasonably easily following the APSIM or DairyMod exemplars.			nitrogen material is unlikely. Consequently, unlike APSIM, MEDLI does not currently need to model stubble decomposition.	
Carbon dynamics	The lack of a C:N ratio feedback means MEDLI will always mineralise its soil organic N to exhaustion. This becomes a problem for tree crops (which are increasingly being considered) where such a loss of soil organic N is rare because of return of C to the soil.	If depletion of soil organic-N is expected to be small (the usual case for effluent irrigated pasture), the kinetic rate coefficient for ammonification can be set to zero. However, kinetics of N immobilisation have been turned off in MEDLI.	Explore options from APSIM and DairyMod. Activate the immobilisation kinetics that have been turned off within MEDLI.	Require further kinetic rate coefficient inputs which are difficult to determine. Need validation data.	High	Low importance – dealt with user training and user manual explaining model limitations.	Needs a desktop investigation of the various options first.
Mineralisation/ Ammonification *Mineralisation of organic N to ammonia. Mineralisation **or** immobilisation of mineral N is*	MEDLI uses different response curves (and parameter values) for organic matter mineralisation to those used in APSIM. These differences in the response curves should be reconciled.	MEDLI uses a simple kinetic function that ignores the C:N ratio of the substrate but considers soil water & temperature effects using a scaling factor.	Implement a carbon model or adjust the net mineralisation coefficient to lower value? Mineralisation rates of the slow and fast organic pools should be used rather than	Adjusting the net mineralisation coefficient would be the preferred alternative before implementing a new carbon model in MEDLI.	Moderate	High	Manipulate the coefficient. Establish the basis of the difference between the APSIM and MEDLI soil water content and temperature modifiers for ammonification and

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
determined as the balance between the release of mineral N during decomposition of the various fractions of organic matter (FOM, BIOM and HUM), and the N required by the microbial biomass.			the statistically fitted values for individual soils. The N mineralisation rates found by Wang et al. (2004) and Allen et al. (2019) provide an independent means for validating potential ammonification/ nitrification estimates simulated by APSIM and MEDLI.				suggest revisions to MEDLI if necessary.
N volatilisation *Gaseous ammonia loss during irrigation and from the soil.*	Volatilisation during irrigation is considered but volatilisation from soil is not included in APSIM or MEDLI. High effluent pH (> 9) high temperature, and low salinity are most likely to result in appreciable N loss by volatilisation due to NH_3-NH_4 partitioning favouring NH_3. However, most effluents are pH < 9 and commonly, evaporation from many small droplets created by spray irrigation will be the dominate loss mechanism.	The loss of ammonia gas (volatilisation) is considered to occur only during the irrigation event. The amount is currently a fixed fraction of the NH_4-N in the effluent. Volatilization loss from soils is only likely to occur in moderately alkaline soils(pH>8).	Further investigation of volatilisation during irrigation needed.	Since the pH of effluents are mostly < 9, this process is unlikely to be significant. However, the process of droplet formation in high pressure spray irrigators may cause significant volatilisation losses.	High – experimentation needed.	Important as losses of up to 50% during irrigation have been measured at Beaudesert.	"*Acidified catch-can*" experiments recommended to establish relationships to predict losses.
Nitrification *Nitrifying bacteria transforms soil ammonia into nitrates.*	APSIM and MEDLI soil water content modifiers for nitrification are different.	APSIM, DairyMod and MEDLI use Michaelis-Menten kinetics to estimate maximum nitrification rate.	Desktop study to review the response functions and revise MEDLI if necessary.	Potential contradiction between APSIM and MEDLI will persist if not addressed.	Low	High	Desktop study to review the response functions and revise MEDLI if necessary.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
		The temperature scaling factor for nitrification [as well as for ammonium adsorption/desorption, immobilisation and mineralisation] is based on a modified van't Hoff-Arrhenius equation.					
Denitrification *Reduction of nitrates (and nitrites) to gaseous products including NO, N_2O and N_2 by microbial processes that occur under anaerobic conditions. They are influenced by organic carbon content, water-filled pore space, soil temperature and soil pH.*	Simulation of denitrification differs markedly across APSIM, DairyMod and MEDLI. Whilst MEDLI & APSIM maximum denitrification rates are similar (10% & 5%), Dairy-Mod is almost 10 times smaller. This range is indicative of the difficulty in simulating this process.	A maximum denitrification rate is user specified and modified by soil water content and temperature. Default value is 0.1. i.e., 10% of the current amount of NO_3-N (mg/kg) in the soil layer of interest. MEDLI is not designed to provide estimates of the emissions of greenhouse gases (e.g., N_2O) so this aspect of denitrification is not considered further.	The denitrification rate in APSIM is a function of soil NO_3 concentration, soil pH, soil water content, temperature. and labile organic C MEDLI needs to simulate labile organic C which is part of a soil C model The depth of soil containing labile organic C is user-defined, and most users accept the MEDLI default value of 100 mm. Hence all deeper soil depths are effectively made N "inert". If labile C is available at deep depths, this assumption is incorrect. Hence, the organic layer depth needs adjusting using measured organic C data. This will require adjustment to the suite of measurement instructions given to the soil analyses laboratory.	More explicit guidance to MEDLI users needed for depth labile organic carbon layer. **N^{15} experiments to get a better handle on N loss from irrigated pastures**	Low- for more guidance to user. High for N^{15} experiments	High. **Denitrification may be a critical N loss mechanism for the viability of some high-strength effluent** irrigation schemes. Such work would benefit APSIM and other models modelling the N cycle	Undertake a review of the basis for the denitrification rate methodologies used in APSIM, DairyMod and MEDLI and suggest any revisions that might be required in the MEDLI algorithms. Also undertake a review of the historical measured denitrification rate data as well as some focused experimentation using N^{15} **as most denitrification data reported is modelled rather than measured!**

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
Leaching of N solutes	Leaching of solutes is very responsive to their loading rate, soil permeability and irrigation/rainfall regime. Leaching should take into account the fraction of mobile and immobile water in soils. Both Nitrate-N and dissolved organic N (e.g., urea and amino acid molecules) are solutes that should be considered.	Leaching of solutes (Nitrate-N and Phosphate-P) moves with the transit of water down the soil profile, assuming each soil layer is a constantly stirred reactor.	The drainage algorithm (based on cascading buckets) needs improvement as per the Cook (2021) review.	Coding to include changes is anticipated to be difficult in the current version.	High	High	**The drainage algorithm (based on cascading buckets) needs improvement as per the Cook (2021) review.**
N runoff loss	Nitrogen enrichment in runoff is not modelled in MEDLI.	MEDLI does not model nitrogen loss from rainfall runoff. In the rare case where the soil profile becomes hydraulically overloaded during irrigation, effluent runoff will occur with the runoff N concentration equal to that of the effluent.	The Victorian DPI runoff algorithm used in the HowLeaky Model could be incorporated into MEDLI, depending on the peer review status of the alternative method.	Whilst not hard to implement, it will involve the addition to two model parameters which may be difficult to measure.	Moderate – but need to also consider how to incorporate enrichment ratio into the N mass balance.	Low for pastures on low slopes (e.g., 3% maximum), typically used for irrigation. With crops, usually irrigation on very low slopes to avoid runoff. N losses in rainfall runoff are generally very small (<5 kg N/ha/yr)..	It appears that the process of N enrichment is considered not sufficiently significant to be included in MEDLI but needs further review.
Ammonium-N sorption	Why is Ammonium-N sorption mentioned in the MEDLI technical manual? Leaching of ammonium-N is rare in Australian soils and not considered in MEDLI	Sorption/desorption of ammonium-N on the soil's exchange sites is not modelled in MEDLI (this code has been "turned off"). However, ammonium-N is assumed not to be transported with the deep draining flux. This simplification may	Delete all mention of Sorption of ammonium-N from MEDLI	Nil	Nil	Low	Leave code as is. De-emphasise in MEDLI technical manual

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
		not valid in paddocks overloaded with N if nitrification to nitrate-N is incomplete.					

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11. Phosphorus Overview

Of the models reviewed in the C and N component of this project (viz. APSIM, DNDC, WNMM, DairyMod and DAYCENT) a literature scan indicates that only the phosphorus (P) modules of APSIM and DairyMod have been applied to Australian conditions. This review will focus on these Australian models due to the high sorptivity of Australian weathered soils. The focus of the APSIM and DairyMod P components is primarily on assessing the adequacy of soil P for crop growth; unlike MEDLI, there is no focus on assessing the potential environmental risk of oversupply of bioavailable P, and in this respect, MEDLI is unique.

This review of P modelling will therefore concentrate on the modules in APSIM, DairyMod and MEDLI.

11.1. Models of phosphorus sorption

Phosphorus sorption by soils has been represented by three different equations- Langmuir, Temkin, and Freundlich (Fitter and Sutton, 1975). These equations assume different characteristics of P sorption:

- Langmuir: monolayer or bi-layer with a constant energy of adsorption and defined maximum amounts of P sorption.
- Temkin: linearly decreasing energy of adsorption as the amount of P sorbed increases, and no defined maximum amount of P sorption.
- Freundlich: the energy of P sorption decreases exponentially as the amount of P sorbed increases; no defined maximum amount of P sorption.

While it is conceptually convenient to define a P sorption maximum with a single bonding energy (viz. Langmuir equation) and assume that once this ‘bucket’ is full in a particular soil layer, surplus P will move into the next soil layer, this concept does not reflect reality. Phosphorus sorption continues at all solution P concentrations, albeit becoming a smaller proportion of freshly added P as solution P increases. In addition, the hysteresis effect during desorption decreases as solution P concentration increases and effectively disappears (i.e., P sorption is completely reversible) at high solution P concentrations (Barrow and Debnath, 2014). Only the Freundlich equation mathematically represents this behaviour. The basic form of the Freundlich equation is:

$$\mathrm{Ps} = a\, \mathrm{P}_{\mathrm{sol'n}}^{\,b} \qquad \text{(Eqn 10-1)}$$

Where Ps is the amount of sorbed P (mg/kg soil), and $\mathrm{P}_{\mathrm{sol'n}}$ is P concentration in the soil (or equilibrating) solution (mg/L). The two curve-fitting coefficients, *a* and *b*, do not have specific physico-chemical meaning, but the product (*a* b)* has been termed the **Buffer Index** (Barrow and Debnath, 2014) and has been used to characterise soil P buffer capacity.

11.2. Partitioning added phosphorus between solution and sorbed phases

Partitioning P between solution and sorbed phases is a requisite output for any P model because it is the solution phase P concentration that determines bioavailability to crops, and also the movement of P in runoff and drainage, and by diffusion and mass flow. This partitioning is possible when the Freundlich *a* and *b* coefficients are measured (or inferred from data libraries), but this requires a multiple point P sorption curve to be determined using graded amounts of added P in a soil testing laboratory. To simplify and expedite this procedure, a single **P buffer index (PBI)** was developed (Burkitt et al., 2001; Burkitt et al. 2002):

$$\mathrm{PBI}_{\mathrm{Colwell}} = (\mathrm{P_s} + \text{Colwell-P})/c^{0.41} \qquad \text{(Eqn 10-2)}$$

where $\mathrm{P_s}$ is the amount of P sorbed (mg P/kg) from a single addition of 1000 mg P/kg, and *c* is the resulting solution P concentration (mg P/L). and Colwell-P is in mg P/kg soil

Based on the fundamental principle that soil P buffer capacity is the slope of the (linearized) P sorption curve (viz. *y* axis: sorbed P *vs x* axis: solution P), Moody (2011) developed a simple estimate of solution P concentration from the ratio of Colwell-P to $\mathrm{PBI}_{\mathrm{Colwell}}$ (Colwell-P:$\mathrm{PBI}_{\mathrm{Colwell}}$).

The Colwell-P soil test is used as an indicator of initial Ps (before any P additions), and PBI is used as an indicator of soil P buffer capacity. Therefore, two simple and commercially available soil tests can be used to estimate the soil solution P concentration in a soil. Note that it is a necessary condition when calculating PBI that the soil's Colwell-P value is added to the freshly sorbed P from the single P addition made in the PBI method. This correction is required to take account of the effect of previously sorbed P on the solution P concentration resulting from a fresh P addition.

Validation of the use of (Colwell-P:PBI$_{\text{Colwell}}$) to estimate soil solution P concentration is shown in Fig. 10.1, where soil solution P concentrations at drained upper limit for two independent data sets for a wide range of Australian soils (Moody et al., 1988: Moody unpubl. data) are plotted against (Colwell-P:PBI$_{\text{Colwell}}$). Runoff P concentrations from rainfall simulator plots (Dougherty et al., 2011b) are also presented in the plot. Note the curvilinear nature of the relationship for the laboratory studies, but the linear relationship for runoff data. The curvilinear response is indicative of the multilayer P sorption process. The linear response apparent between (Colwell-P:PBI$_{\text{Colwell}}$) and runoff-P concentration may be caused by the short opportunity time for interaction between runoff and the vegetated soil surface (Dougherty et al. 2008a).

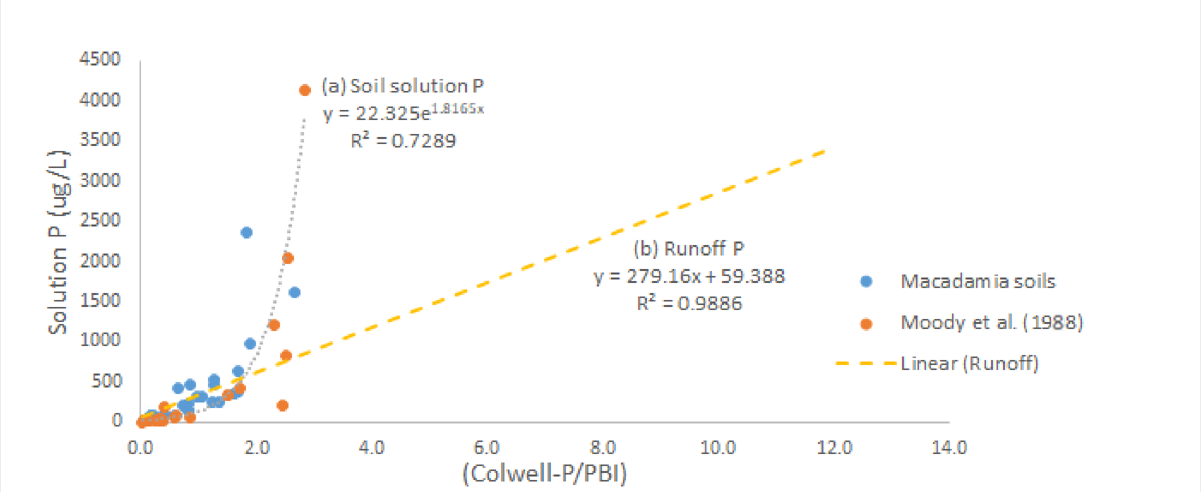

Figure 10-1. Plot of (a) soil solution P concentration and (b) runoff P concentration versus the (Colwell-P:PBI) index. Data for (a) from Moody (unpubl. data for macadamia soils) and Moody et al. (1988). Data for (b) from Dougherty et al. (2011b).

These differences in response shape essentially disappear at solution P concentrations less than about 2000 ug P/L as shown in Fig. 10-2.

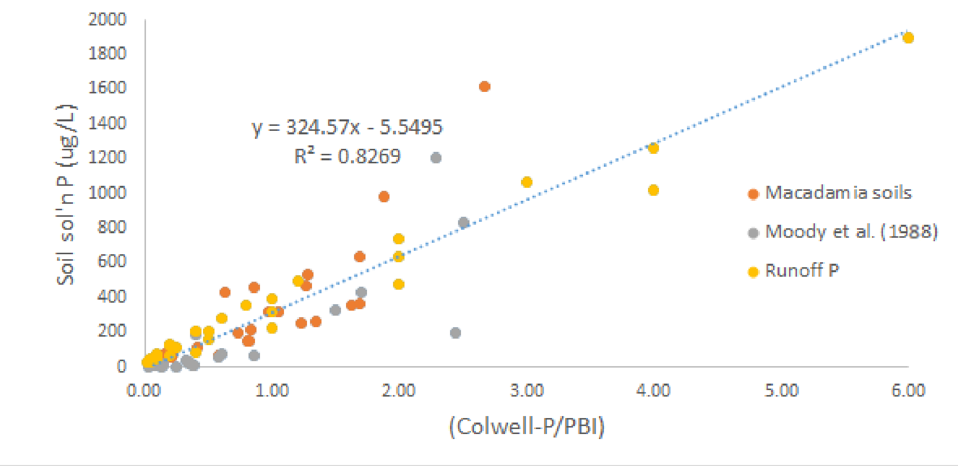

*Figure 10-2. Plot of soil solution P concentration versus the (Colwell-P:PBI) index for solution P concentrations less than 2000 ug P/L. Data from Moody (unpubl. data for macadamia soils), Moody et al. (1988), and **runoff P** from Dougherty et al. (2011b).*

Measuring initial Colwell-P and $PBI_{Colwell}$ of the receiving soil *prior* to fresh P addition (or effluent application) allows an estimate of the current soil solution P concentration. However, the P module must be able to predict changes in soil solution P concentration *following* P addition without undertaking additional soil analyses. This requires partitioning of the added P into the solution ($P_{sol'n}$) and sorbed (Ps) phases. Figure 10-3 shows the relationship between the Extractability[1] of added P and PBI for a diverse range of soils. As PBI increases, P Extractability decreases as proportionally more of the added P partitions into the sorbed phase.

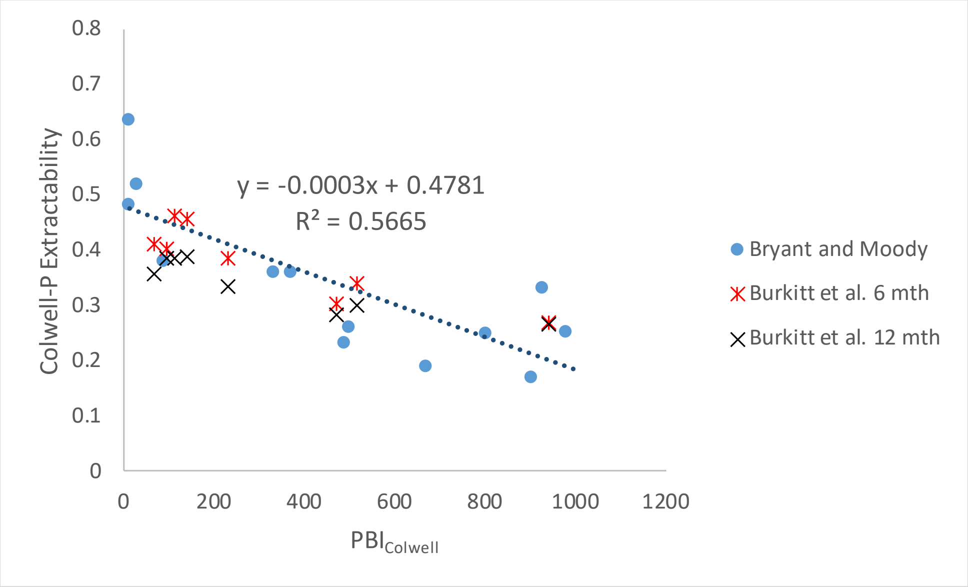

Figure 10-3. Effect of PBI on the extractability of freshly added P. Data on 8 soils from Burkitt et al. (2001) and 15 soils from Bryant and Moody (unpubl. data).

In summary, two commercially available soil tests, namely Colwell-P and $PBI_{Colwell}$, can be used to partition added P between sorbed and solution phases, thereby providing the solution P value for input into the next soil layer of the reactive leaching model.

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[1] Extractability = Change in Colwell-P/unit applied P

12. Phosphorus Module in DairyMod

12.1. Principle

In DairyMod, the relationship between adsorbed and solution P pools is described by the single surface Langmuir equation (Johnson et al., 2008). As described in Johnson et al. (2008), this equation is used because it is mathematically convenient, and it is possible to derive an analytical expression for the solution and sorbed P components in terms of quantities of P. The equation form is approximately linear at low P concentrations and approaches an asymptote at high P concentrations. These characteristics are reflected in the model parameters, which are interpretable in relation to sorption characteristics.

12.2. Limitation

As described in Section 10.1, neither the single nor the double surface Langmuir equation describe the multi-layer sorption of P adequately, and consequently, the validity of any simulated results can be questioned. For this reason, it is concluded that the DairyMod P module has little or nothing to offer the MEDLI P module.

13. Phosphorus Module in APSIM

13.1. Principles

The pools and processes informing the APSIM P module are shown in Fig. 12-1, and those of relevance to effluent disposal onto land are circled in red. The 'labile-P' pool is assumed to be in equilibrium with another pool that simulates P concentration in the soil solution. The partitioning of added P into the labile and solution pools is described by the *a* and *b* coefficients of the Freundlich sorption equation. As described in Section 10.1, neither coefficient has a physico-chemical basis, but it is often assumed (including in APSIM) that *a* is directly linked to the P buffering capacity of the soil, and *b* serves as a variable to adjust the sorption isotherm.

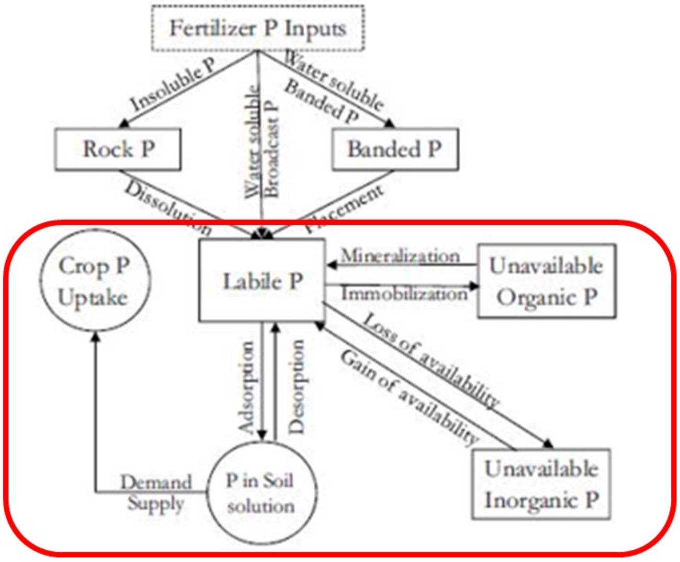

Figure 12-1. Pools and processes in the APSIM P module.

While some models with P modules such as EPIC (Sharpley et al., 1984) use soil P tests and other specific soil properties as surrogate measures of 'labile-P', APSIM does not specify such relationships to describe the magnitude of labile P. Probert (2004) argues this pool is better aligned with a soil P budget approach (accounting for P inputs and removals) than a mechanistic approach to soil P processes.

No action is required from the user to set the value of the 'unavailable inorganic-P' pool in the APSIM P module. There is an assumption that, at steady state, the 'unavailable inorganic-P' pool is 10 times larger than the 'labile-P' pool (Probert, 2004). While the APSIM P module attributes change in P availability between the 'labile-P' pool and the 'unavailable inorganic-P' pool to temperature and soil moisture effects, these are not specifically defined nor have guidelines been documented for allocating appropriate availability factors.

The 'organic-P' pool is linked to the Soil N and Surface Organic Matter modules that assume these pools also contain P. The two modules calculate the mineralisation of P from, and the immobilisation of P into, the soil organic matter. Other than setting the Soil N and Surface Organic Matter module parameters, no other parameterisation is required by the user (Wang et al., 2014). Note however, the occurrence of mineralisation/immobilisation of P depends on the organic matter decomposition rate and the C:P ratio that is set by the user.

13.2. Limitations

From the description in Section 12.1, it is apparent that parameterising the various P pools and processes in the APSIM module lacks mechanistic principles, and only generalised guidance is provided in model documentation. Although a sorption curve could be used to provide the Freundlich parameters (as currently occurs in MEDLI) such an approach is often not feasible, and the user is subsequently left with a ‘trial-and-error’ approach until a suitable combination of these parameters is found to provide a satisfactory fit to data. Likewise, there is a lack of guidance on the ‘labile-P’ / ‘unavailable inorganic-P’ pool sizes, and rates of change in availability. It is concluded from this overall assessment that the APSIM P module has little to offer in terms of informing or revising the P module in MEDLI.

14. Phosphorus Module in MEDLI

14.1. Principles of current module

The current P module in MEDLI uses algorithms that are based on those of HSPF (Johnson et al., 1984). The algorithms are used to:

- Partition incoming effluent P into solution P ($P_{sol'n}$) and sorbed P (Ps).
- Route $P_{sol'n}$ between soil layers and then partition the incoming P into solution P ($P_{sol'n}$) and sorbed P (Ps) in each layer.
- Estimate the quantity of desorbed P (P_{des}) in a soil layer when $P_{sol'n}$ decreases due to plant uptake or dilution by irrigation/rainfall.
- Adjust $P_{sol'n}$ and Ps in the soil layer as a consequence of the P desorption.

These calculations are based on *a* and *b* coefficients of the Freundlich equation (see Eqn 10-1 above) in adsorption or desorption form. The current input data comprise:

- Soil-specific adsorption Freundlich *a* and *b* coefficients, ideally calculated from the P sorption curve of the receiving soil, or user-selected from the MEDLI data library.
- The soil-specific *desorption* Freundlich *b* coefficient is unknown unless soil-specific desorption curves have been carried out using successive extractions in dilute salt solutions, or by using anion exchange resins/strips as sinks for solution P. However, because of the paucity of measured desorption data, the value of the desorption *b* coefficient is generally set by the user to slightly less than the adsorption *b* coefficient.

14.2. Assumptions and limitations of current module

The following assumptions and limitations apply to the current MEDLI P module:

- Dissolved organic P input is treated as inorganic P; consequently, no modelling of organic P mineralisation is required.
- Effects of soil solution pH, EC and temperature on P sorption/ desorption are not considered.
- ‘Slow fixation’ of sorbed P into less available forms (i.e., lower extractability over time) is not considered.

15. Suggested Revision of the Phosphorus Module in MEDLI

15.1. Principles

The P pools and processes in the suggested revision of the P module are shown in Fig. 14-1.

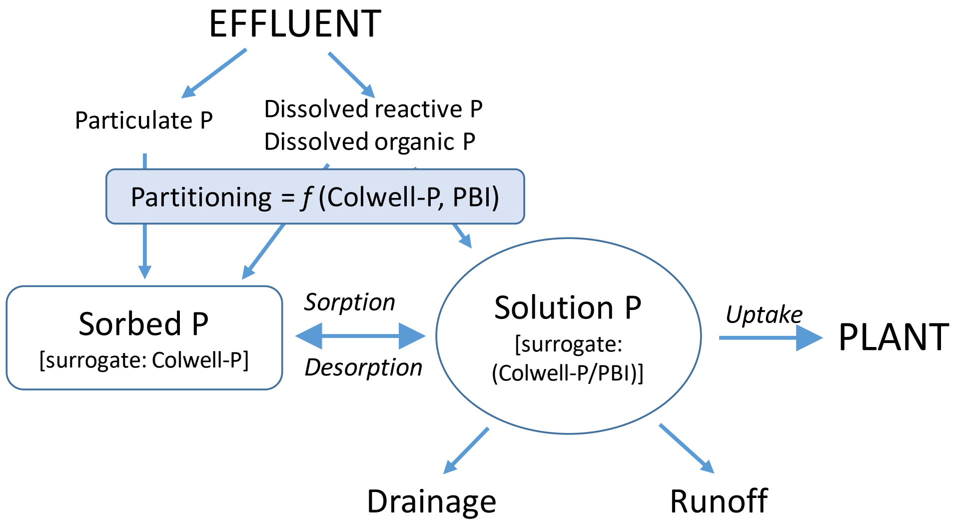

Figure 14-1. Phosphorus pools and processes and the relevant surrogate measurements and algorithms.

The flowchart comprises the following assumptions and predictive relationships:

- Colwell-P is assumed to be an estimate of sorbed P (**Ps**) (Barrow, 2000).
- Partitioning of incoming effluent P into solution P ($P_{sol'n}$) and freshly sorbed P (Ps) is based on the linear regression equation of Fig. 10-3[2]:

$$Ps = \text{Effluent P} \times \text{Extractability} = \text{Effluent P} \times (0.60 - 0.0005PBI_{Colwell}) \qquad \text{(Eqn 14-1)}$$

where units of Ps and Effluent P are mg P/kg soil and $PBI_{Colwell}$ refers to the PBI of the receiving soil layer.

- Solution P ($P_{sol'n}$) immediately following effluent application is estimated from the equation:

$$0.34429 \ \ln(P_{sol'n}) = [(Ps+Colwell\text{-}P)/PBI_{Colwell}] + 0.95 \qquad \text{(Eqn 14-2)}$$

where Ps is the freshly sorbed P from Eqn 14-1 and Colwell-P and $PBI_{Colwell}$ refer to the values of the receiving soil prior to effluent application.

- Solution P ($P_{sol'n}$) following P desorption is re-estimated using the following modification of Eqn 14-2, but with P_{des} comprising the quantity of desorbed P, Colwell-P comprising the estimated Colwell-P status of the soil prior to desorption [i.e., (Ps+Colwell-P) from Eqn 14-2, and with $PBI_{Colwell}$ being the value for the soil prior to effluent application.

$$0.34429 \ LN(P_{sol'n}) = [(Colwell\text{-}P - P_{des})/PBI_{Colwell}] + 0.95 \qquad \text{(Eqn 14-3)}$$

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[2] Note, for unresolved reasons, the equation for extractability used here differs slightly from that in shown in Figure 10-3 which is $0.48-0.0003PBI_{Colwell}$

15.2. Input parameters

The following input parameters are required:

- Receiving soil layers: Colwell-P (Method 9B: Rayment and Lyons, 2011) and $\mathrm{PBI}_{\mathrm{Colwell}}$ (Method 9I: Rayment and Lyons, 2011).
- Dissolved reactive P (DRP), dissolved organic P concentrations in the incoming effluent.

15.3. Assumptions and limitations

- No account is taken of ‘slow fixation’. However, it has been shown that there is little difference in P extractability 6 and 12 months after application (Burkitt et al., 2001) (Fig. 10-3), so this is considered to be a reasonable assumption.
- Dissolved organic P in the incoming effluent is treated as DRP from the viewpoint of P sorption reactions. This assumption is supported by the results of Gerritse et al. (1982) who concluded that the mobility (i.e., partitioning into solution and sorbed phases) of dissolved organic P from ‘animal waste’ slurries was best described by considering all added P as DRP.

16. Implications of a Revised Phosphorus Module in MEDLI on Estimates of Phosphorus Losses in Drainage and Runoff

16.1. Overview

There have been several Australian studies of the parameters governing off-site P movement in runoff and drainage from fertilised pastures. These studies have used rainfall simulator plots, instrumented small plots, or instrumented irrigation bays and drains to measure off-site P movement at paddock scale. Pathways and P pools associated with runoff and drainage are shown in Fig. 15-1.

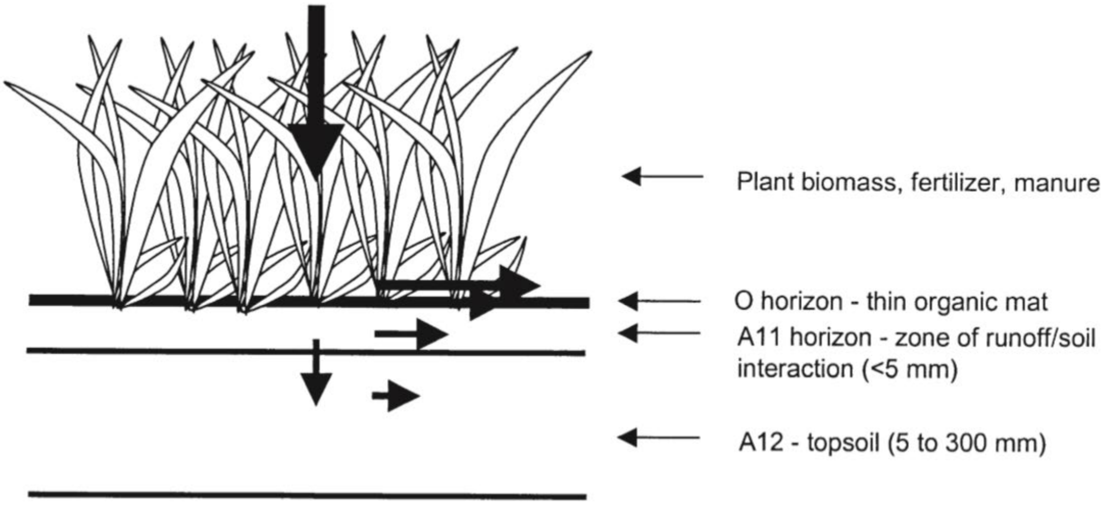

Figure 15-1. Schematic representation of the soil–plant system. Surface runoff travels primarily in the top several millimetres of soil (A11 horizon), the thin organic mat (O horizon, which may or may not be present), and in a layer above these. Arrows denote typical characteristics of water movement. Longer arrows indicate greater velocities, and thicker arrows indicating greater volumes of water moving along the indicated pathway. Reproduced from Fig. 3 in Dougherty et al., 2004.

16.2. Factors affecting P in runoff

Dougherty et al. (2008b) measured P in runoff from Victorian grazed dairy pasture plots (0.125 ha) broadcast-fertilised with P at rates ranging from 0 to 80 kg P/ha /yr over 3.5 years. Runoff P concentration was correlated with P rate (+), P rate × number of applications (+), P rate × time since fertiliser application (-), dung P (+), time since grazing (-), and pasture biomass (-). These results were captured by a three-component concept model of P in runoff: a *baseline or systemic component* corresponding to grazing a pasture on a soil of basal soil P status; a *fertility component* that comprises the effect of fertiliser P in raising soil P status above the baseline; and an *incidental component* that comprises P that is poorly equilibrated with soil P when runoff occurs. Annualised runoff P loads (dominated by DRP) increased from 0.4 kg P/ha/yr from nil applied P, to 1.1 kg P/ha/yr for an input of 80 kg P/ha/yr.

Greenhill et al. (1983) also measured P loss by runoff from pastures receiving up to 80 kg P/ha/yr at three sites on differing slopes and reported a maximum loss of 0.05 kg P/ha/yr. ANZECC (1992) guidelines for water quality suggest indicative environmentally acceptable total P concentrations of 10-100 ug/L in rivers and streams, and 5-50 ug/L in other water bodies. While absolute amounts from both these studies were very low (less than 1% of fertiliser P input), the reported runoff concentrations often exceeded the ANZECC water quality guidelines several-fold. Even the baseline runoff concentration from the nil applied P treatment of Dougherty et al. (2008a) exceeded the water quality standard. It is therefore imperative that dilution of the runoff from fertilised pastures occurs before it enters a watercourse, and thus the water quality impacts of the drainage system from paddock to farm boundary come into play.

Barlow et al. (2003) found surface drain conditions (bare earth vs. grazed pasture) and management (weed growth and herbicide application) affected the P concentration, and to a lesser extent, the form of P at end of drain. For example, at 160 m down gradient, P concentration had increased by 4.4 mg P/L in the pasture-lined drain and *decreased* by 1.2 mg P/L down an earthen drain. Dissolved reactive P (DRP) comprised at least 80% of the total P in the runoff.

At a larger scale of several hectares, Nash et al. (2000) reported that total P export in runoff from dryland paddocks was negatively correlated with days since fertilising ($P<0.001$), but only weakly correlated with days since grazing. Adjusting P application in relation to timing of runoff events appeared to be the main strategy for mitigating P runoff losses. Bayesian modelling at catchment scale (Burkitt et al., 2011) arrived at a similar conclusion, but also highlighted that less frequent P applications during periods when the risk of runoff is high, was an effective management strategy for reducing P loss. We note that MEDLI must address the application of P at every effluent irrigation event!

16.2.1. Soil-specific factors affecting P in runoff

Dougherty et al. (2011b) demonstrated a highly significant curvilinear relationship between runoff DRP concentration, which was described by a multiple regression equation comprising Colwell-P, and the product of Colwell-P and PBI. However, their use of the product of Colwell-P and PBI is conceptually incorrect, as Moody (2011) showed that the ratio (Colwell-P:PBI) is the appropriate conceptual surrogate for soil solution P concentration. By substitution of a range of Colwell-P and PBI values into the equation on p. 527 of Dougherty et al. (2011b), the equation then becomes:

$$\text{Solution P} = 0.279^{*}\ (\text{Colwell-P}/\text{PBI}_{\text{Colwell}}) + 0.059 \qquad \text{(Eqn 15-1)}$$

where Colwell-P and $\text{PBI}_{\text{Colwell}}$ are the values of the source soil.

The impact of extractable P (i.e., Colwell P) and P buffer capacity on solution P concentration was verified by laboratory incubation and extraction studies of soils receiving freshly applied P (Dougherty et al., 2011a).

Dougherty et al. (2008a) cautioned extrapolating small plot run off concentrations to larger scale; they suggested that the lack of equilibration time between soil surface and runoff, short flow path, and high velocity contributed to the generally lower P runoff concentrations compared to paddock scale data.

Implications for MEDLI

Implementation of the Equation 15-1 should be considered to estimate dissolved reactive P export in surface runoff from a given soil with measured Colwell-P and PBI measurements.

16.2.2. Root mat effect on soil P budget

Perennial grass pastures such as kikuyu (*Pennisetum clandestinum*) develop a high organic C root thatch (or ‘mat’) of dense root and plant residue material that resembles a peat layer. This layer can be several centimetres deep and is not normally included in surface soil samples. When studying the effect of prolonged irrigation of effluent onto a Duplex soil, Menzies et al., (1999) measured the P stores in this root mat and the soil profile. They found large amounts of organic P in both the root mat and the surface soil (0-10 cm). The P stored in the effluent-treated soil was much higher than the unirrigated soil and occurred primarily in the organic form. It is therefore suggested that the organic P store in the root mat and surface soil is primarily within the cells of the microbial biomass; as such, it is not accounted for in P sorption capacity measurements that are used to estimate allowable P loading, nor in the partitioning of added effluent P between sorbed and solution phases.

Implications for MEDLI

It is suggested that the MEDLI P module requires inclusion of additive algorithms for estimating P sequestration in the following pools:

- root material, possibly calculated as a proportion of above-ground biomass, and with an assumed P concentration of 0.3% P.
- microbial biomass in the root mat, possibly calculated by direct total P analysis of a root mat sample and estimation of root mat weight.
- microbial biomass in the surface soil (0-10 cm), estimated by organic C analysis and assuming the C:P ratio of the surface soil plus microbial biomass is 156 [after Griffiths et al. (2012)].

16.2.3. Soil sampling depth effect on P in runoff

Although the interactive zone between soil and runoff water is generally assumed to be 1-2 cm in depth, the soil sampling depth for fertility assessment of pastures in Queensland is 0-10 cm. Hart and Cornish (2010) investigated the relationship between dissolved P in surface runoff and soil-test P measured at different sample depths (0–2 and 0–10 cm). Small-plot rainfall simulations at 14 of the sites found highly significant linear relationships between runoff DRP concentrations and extractable P for soils split into high and low-moderate P buffer capacities. The results suggest that agronomic (0–10 cm) soil P testing in pastoral soils is sufficient for estimating the potential for losses of P in runoff and that there is no need to collect shallow soil samples especially for this purpose.

17. Implications of the issues identified for phosphorus modelling

The issues and implications for MEDLI identified in this report for phosphorus modelling are summarised in Table 17-1.

Table 17-1. Strategic overview of the issues and implications for MEDLI raised by this review for phosphorus, with additional insights from the Synthesis Report (Gardner 2021).

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
P mineralisation from organic matter	MEDLI does not consider P mineralisation from organic matter. Most models such as APSIM do not consider the off-site export of P. Rather they focus on P availability and plant growth. MEDLI focuses on off-site export via leaching.	MEDLI uses a dynamic P and crop growth model to assess solution conc. and crop uptake. It does not consider mineralization of P from organic matter.	No **change** to the P mineralization process is recommended	Because of cut and cart, the return of P from organic matter is expected to be small.	Not applicable	Low	No **change** to the P mineralization process is recommended
P runoff loss	P enrichment in surface runoff from rainfall is not considered in MEDLI Export load (kg/ha/yr) often small but concentration (mg/L) can exceed ANZECC water quality standards.	MEDLI does not model phosphorus loss from rainfall runoff. In the rare case where the soil profile becomes hydraulically overloaded during irrigation, effluent runoff will occur with the runoff P concentration equal to that of the effluent.	Use the Dougherty (2011) algorithm with Moody's (2011) correction to calculate soil solution & assume it equals the concentration in rainfall runoff. Use 0-10 cm soil data to calculate driving parameters (Colwell P & PBI). Alternatively, could use Dissolved Reactive Phosphorus runoff algorithm from HowLeaky (2018)	P concentration can exceed ANZECC water quality guideline values.	Moderate to high.	High	Review alternatives. Needs some working through and testing of Moody's approach.
P soil sorption and P leaching	Adsorption of P in MEDLI is predicted by the data-demanding Freundlich equation (requires a P sorption isotherm which is expensive to measure and offered by few laboratories). Simpler algorithms are desirable considering the relative rareness of P leaching in most Australian soils.	MEDLI uses a Freundlich equation to calculate P sorption and soil solution P available for leaching. Leaching occurs after the P storage capacity of any one soil layer is filled. Piston flow is assumed in moving the solute through the soil.	A much simpler model by Moody is suggested driven by Colwell P and the PBI. It calculates soil solution P and runoff P concentrations. The model can also predict changes in soil solution P concentration following P addition.	Removes need for P sorption isotherm data for most model applications. Freundlich approach best reserved for vulnerable sandy soils.	Moderate to high.	Moderate	Investigate adding the option of simpler Moody approach for non-sandy soils. Needs some working through and testing of Moody's approach.

Model Process	Issue(s) identified	Current handling	Proposed alternative(s)	Implications	Degree of difficulty	Importance	Recommendation
P sorption by Root Mat	Stoloniferous grass can develop a large root mass which sequesters P.	Process ignored.	Calculate root mass from above ground biomass and assume 0.3% P concentration. Estimate microbial biomass from soil organic C analysis and assume a C:P ratio of 156	Mature irrigated pastures can store a very large amount of P.	Moderate	Moderate	Should be incorporated into MEDLI for species that produce stolons.

18. References for Phosphorus

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