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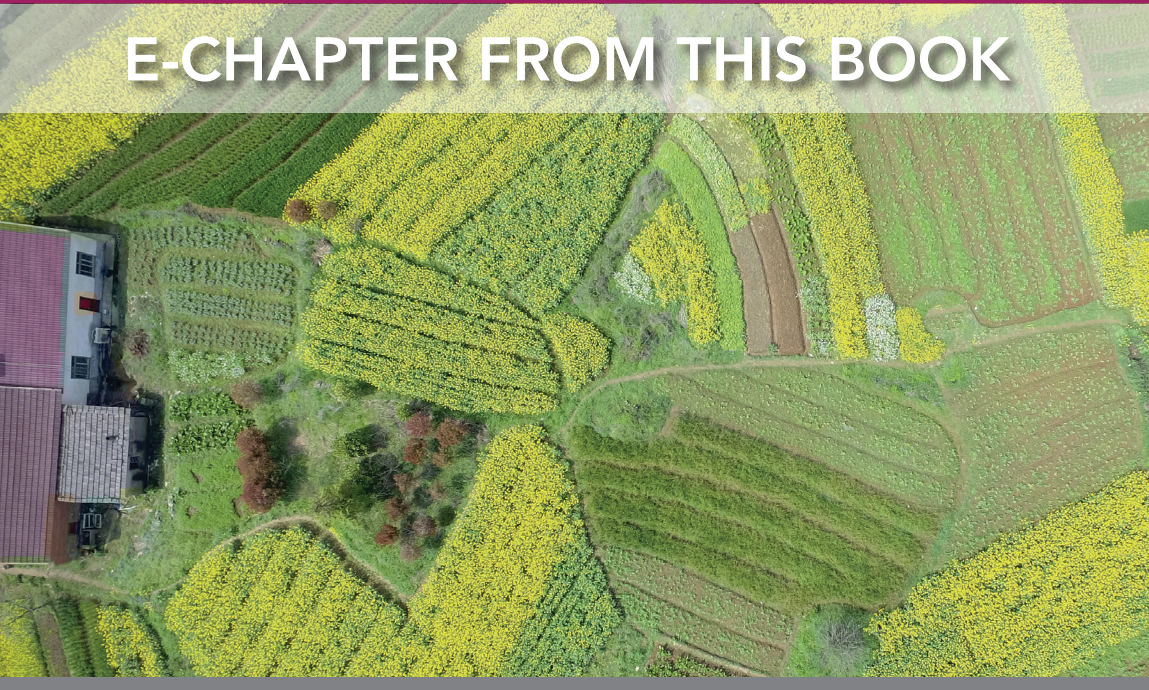

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Improving modeling of nutrient cycles in crop cultivation

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1 Introduction

Agricultural productivity depends on crops receiving adequate amounts of essential nutrients from the atmosphere, soils, and/or supplied fertilizers and manures. Through the biogeochemical cycling of nutrients, fertile soils supply the following essential nutrients to plants: nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg), iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), boron (B), molybdenum (Mo), cobalt (Co), and nickel (Ni). Deficiency of any of these nutrients results in lower productivity. In Europe, North America, and many parts of Asia, the agricultural practice of depleting soil nutrient reserves (nutrient mining) for farming ceased several decades ago. Unfortunately, nutrient mining continues in many developing countries, particularly in Sub-Saharan Africa. The impact of such practices can be seen in Sub-Saharan Africa's low rate of productivity (FAO, 2019). Mineral fertilizers are applied to soils to supplement plants' nutrient needs for adequate production. In addition to replenishing soil nutrients and increasing crop production, fertilizers facilitate the adoption of improved seed varieties, which have significantly increased yield potential; however, improved seed varieties also have higher nutrient requirements. Varieties are currently being bred to improve the nutritional quality of harvested crops. The potential of these

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improved varieties cannot be realized unless they are grown under optimum conditions, particularly under balanced plant nutrition. For the inherently nutrient-poor or degraded soils of the tropics, fertilizer use increases the production of both biomass and yields. This additional biomass will supplement the supply and maintenance of soil organic matter (SOM) and its positive effects on soil properties and nutrient use efficiency. An important component of modeling the nutrient cycle is the role and management of fertilizers in improving crop productivity and their impact on the environment via different loss processes. Fertilizers will remain a critical component of food production, as they are responsible for at least half of the global food production (Erisman et al., 2008).

The organic matter in soils can also provide an important source of nutrients for plants. As the organic matter decomposes, nutrients are released in inorganic forms, which may be available for plant uptake, depending on the pH and other chemical properties of the soil. SOM also improves the efficiency of applied fertilizers by improving the soil's water-holding capacity and nutrient retention. Agricultural systems that sustain SOM decomposition over many years must provide annual additions of organic matter to the soil, for example, from crop residues or the addition of manure, in order to offset the decomposition rates. In the tropics, organic matter decomposition often occurs faster than organic inputs are added to the soil, and organic matter depletion and degraded soils are the result.

In addition to the more prevalent nutrient deficiencies and low nutrient-retention capacities in the highly weathered soils of the tropics, high rainfall and temperatures further aggravate the soil nutrient status, leading to higher nutrient losses. Hence, crop simulation models that simulate the nutrient cycle must integrate various processes into the soil-crop-atmosphere continuum that determines crop growth and production and nutrient dynamics. Modeling the nutrient cycle also requires more input data and data that are less readily available. The tropical regions that can gain the most from nutrient modeling are, unfortunately, data poor. This also implies that soil nutrient models do not get tested and evaluated as much as crop growth models.

This chapter describes nutrient cycle modeling for N, P, and K and is not meant to be a review of existing nutrient models. A number of the nitrogen models have been reviewed by Nieder and Benbi (2008) and the P models by Barber (1995), Claassen and Steingrobe (1999), and Tinker and Nye (2000). Most of these models were designed to predict the effects of N and P on crop growth response. However, potassium models, most adapted from Barber and Cushman (1981), were concerned with calculating crop K uptake. Given the importance of N in global food production and its impact on the environment, the major emphasis has been on N modeling.

2 Modeling nitrogen dynamics

An estimated 59.0 million tons of N fertilizers were applied to cereals in 2014–2015. This represents 57.6% of the world's N fertilizer consumption, with 19.3%, 18.5%, and 15.2% of global N consumption going to maize, wheat, and rice, respectively (Heffer et al., 2017). Future projections of the human population, agricultural intensification, biofuel crops, and meat consumption demand an ever-increasing global production of nitrogen fertilizers. Together with human-driven increases in crop biological nitrogen fixation, the Haber-Bosch process of converting nitrogen gas into ammonia and N fertilizers has more than doubled the global production of reactive nitrogen compared to pre-industrial levels (Galloway et al., 2008). However, Springmann et al. (2018) argue that the use of N fertilizers for food production surpassed the safe planetary boundary in 2010, so an additional 50–52% increase in N fertilizer use, as expected by 2050, will have an even greater negative impact on the environment. N fertilizers primarily impact greenhouse gas (GHG) emissions, specifically nitrous oxide (N_2O) emissions, and contribute 1.2% toward global agricultural GHG emissions (Angle et al., 2017). Thus, to operate within a safe planetary boundary and continue to meet the increasing food demands, nitrogen use efficiency (NUE) needs to increase from the current 30–50% (Ladha et al., 2005) to 75–80%.

N modeling can play a crucial role in achieving the above-mentioned needs through efficient N fertilizer management and effective recycling of reactive N. It is not surprising that more than 50 soil N balance models exist. These models focus on various facets of the N transformation process, ranging from process-based to site-specific calibrated to empirical models (Shaffer et al., 2001). The more widely used models that are capable of process-based simulations of soil carbon (C) and N dynamics are DSSAT (Godwin and Singh, 1998), APSIM (Keating et al., 2003), DAYCENT (Kelly et al., 2000), DNDC (Li et al., 1994), DRAINMOD-Forest (Tian et al., 2012), EPIC (Williams et al., 1989), GECROS (Biernath et al., 2011), SUCROS (Stenger et al., 1999), FASSET (Berntsen et al., 2003), InfoCrop (Aggarwal et al., 2006), MAIZSIM (Kim et al., 2012), MONICA (Nendel et al., 2011), NFLOOD (Reddy et al., 1990), APSIM-Oryza (Gaydon et al., 2012), PlantSys (Jongschaap, 2007), RIWER (Jing et al., 2010), RICEWNB (Antonopoulos, 2010), RZWQM (Ahuja et al., 2000), and SALUS (Basso et al., 2010). Other models that simulate crop N response but do not simulate soil C dynamics are CropSys (Stockle et al. 2003), HERMES (Kersebaum, 2007), Sirius (Jamieson et al., 1998), and STICS (Brisson et al., 2003). Additional information on the current status of modeling C and N dynamics in soils is available in the review chapter by Nieder and Benbi (2008).

2.1 Soil carbon modeling

Most soil C cycle models have a 'system boundary' drawn around the soil column; the state variables are the soil C stored in each soil layer. These are compartmentalized into SOM and fresh organic matter (FOM). The application of organic matter amendments, senescence of roots and other plant matter, and any crop residues that are not removed from the field at harvest all help increase FOM in the soil system. FOM is reduced by decomposition, which moves C into SOM pools and releases CO_2 into the atmosphere. SOM is also reduced by decomposition accompanied by the equivalent release of CO_2 into the atmosphere. However, a tillage event can redistribute and mix the organic matter within the soil profile (Fig. 1). Major differences in soil C modeling are associated with the number of SOM pools, their relative size, and the decomposition rates. The data requirement and the lack of available data for soil C modeling increase with the increasing number of soil C pools. Various methods for measuring and estimating soil C pools are available (Basso et al., 2011). Basic soil C model inputs, in terms of initializing soil C pools, are FOM from previous crop residues (aboveground and roots); additional external organic amendments that are transported into the field (animal manures, green manure, etc.); and soil organic C content, total N content, and C:N ratio for each soil layer.

For any given FOM or SOM pool, mineralization or decomposition of the organic matter results in a net release of nutrients (N, P, and S) and a release of CO_2 into the atmosphere. Immobilization is also associated with the decay of residues and occurs when nutrients such as N, P, and S are incorporated into microorganisms and temporarily rendered unavailable to crops. FOM decay is driven by the C:N ratio of the residue; the proportion of carbohydrates, cellulose, and lignin; and, in some cases, the polyphenolic content. In general,

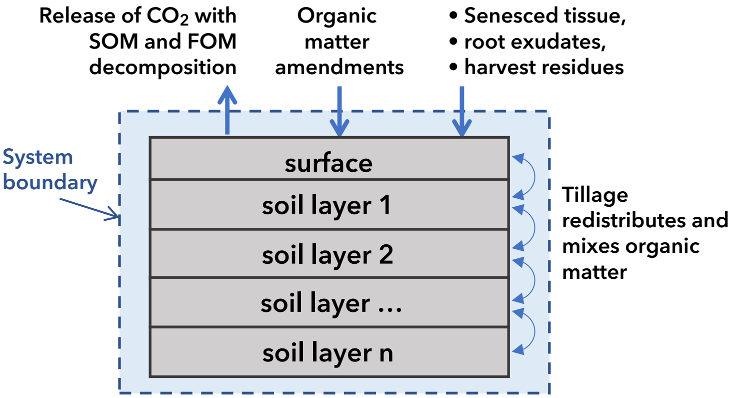


Figure 1 Components of soil C balance routine.

FOM with a low C:N ratio has a higher decomposition rate. However, pigeon pea residue, in spite of its lower C:N ratio compared to maize residue, has a lower mineralization rate due to its high polyphenol content, which acts as an anti-metabolite to the microorganisms (Singh et al., 2001). The soil's mineral N content through the 'temporary' immobilization of N lowers the C:N ratio of FOM in a given soil layer, which in turn allows decomposition to continue. Other factors that influence organic matter breakdown are soil temperature and soil moisture. The decomposition rate of FOM increases by up to 3% per °C increase under ideal soil moisture and C:N ratios (Godwin and Singh, 1998). Generally, the rate of decomposition of organic matter pools increases linearly from air-dry soil to field capacity moisture content soil; however, above the saturated soil moisture content, the decay rate declines to a relative rate of 35–50%. For any given environmental condition, as illustrated by the simulated response in Fig. 2, SOM pools play a critical role in dictating the decomposition rate and the role soils play as a CO_2 sink or source. More stable forms of SOM decompose more slowly. SOM breakdown has a positive impact on crop growth by releasing nutrients such as N, P, and S, but it also has a negative impact due to the emission of CO_2 into the atmosphere.

As expected, under anaerobic (oxygen-depleted) conditions with lower SOM breakdown, organic C storage is an important component of the global C cycle in flooded/wetland soils, and their management impacts global warming and ozone depletion (Whiting, 1994). Microbial biomass makes up a significant

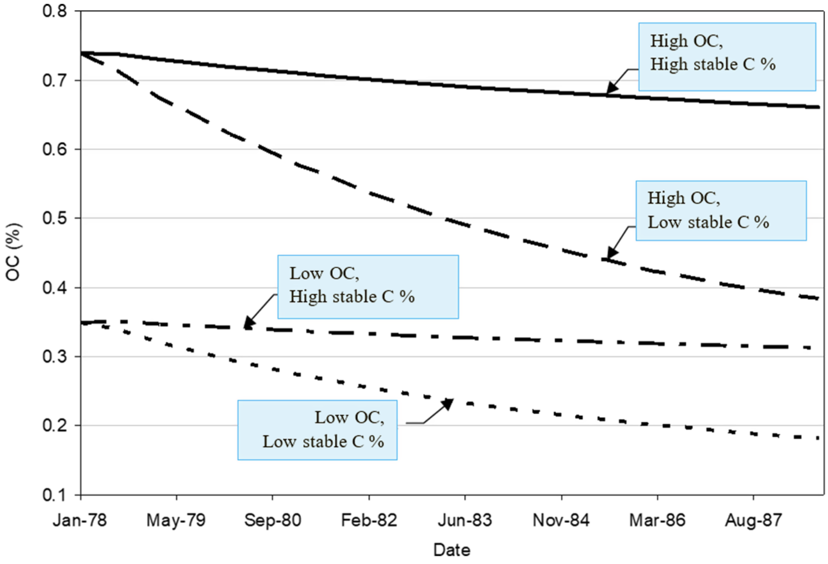


Figure 2 Effects of total organic C and stable C on the decomposition of organic matter (expressed as OC%).

amount of C in wetlands. Under anaerobic conditions, SOM mineralization results in the release of nutrients and the emission of CO_2 and methane (CH_4) (Matthews et al., 2000). Long-term microbial activity that is sustainable occurs under anaerobic conditions in which the microbial respiration is supported by electron acceptors with a lower reduction potential, such as sulfates (SO_4^{2-}) and bicarbonates (HCO_3^-). Methanogenesis and sulfate reduction are dominant processes for anaerobic decomposition in wetlands and coastal ecosystems. In addition to the reduction of CO_2/HCO_3^-, methane formation occurs due to the reduction of acetates. Soluble C substrates also facilitate heterotrophic denitrification of nitrates (NO_3^-) to nitrous oxide (N_2O) and nitrogen gas (N_2).

2.2 Soil and floodwater nitrogen (N) transformations

2.2.1 Ammonium-N

The mineralization and immobilization processes are described using the above C pools and partitioning, with some models explicitly taking into account the role of microbes. Most soil N dynamic models express the mineralization rate (RM_i) as Michaelis-Menten kinetics:

$$RM_i = (\mu_{max} C_i)/(k_s + C_i) \tag{1}$$

where C_i is the carbon content of pool i, μ_{max} is the maximum mineralization rate, and k_s is half the saturation content. For models using first-order kinetics, $(\mu_{max})/(k_s + C_i)$ is simplified to k_1, the first-order rate coefficients:

$$RM_i = k_1 C_i \tag{2}$$

For zero-order kinetics, the equation can further be simplified where the mineralization rate is dependent only on k_0, zero-order rate coefficient:

$$RM_i = k_0 \tag{3}$$

As discussed in the previous section, the amount of N mineralized is dependent on the C:N ratios of the pools in each layer, soil temperature, and soil moisture/water-filled pore space (oxygen supply). Simpler models generally have a predefined C:N ratio. Thus, the mineralization rate under anaerobic conditions is slower. Ammonium-N (NH_4-N) is the mineralized product:

$$\text{SOM pools} \underset{\text{immobilization}}{\overset{\text{mineralization}}{\rightleftarrows}} NH_4\text{-N} \tag{4}$$

The transport of NH_4-N across soil layers and floodwater (when present) is via diffusion. The diffusion of NH_4-N across soil layers driven by concentration gradients is described by Fick's law and can be in either the upward or downward direction for a given soil layer. Diffusion of NH_4-N is also influenced by the cation exchange capacity of a soil and the soil buffering power of NH_4-N. NH_4-N may reside in the soil solution (exchangeable or plant-available NH_4-N) or be adsorbed into clay particles. Some models also simulate adsorbed NH_4-N in clay particles (Li et al., 1994). NH_4-N adsorption and desorption are complex and site-specific processes, and the measurement method to discriminate between native (non-available) and recently adsorbed (plant-available) NH_4-N needs further research.

Under anaerobic conditions, N remains in the form of NH_4-N for uptake by the rice crop. N partitioning between NH_4-N and NH_3-N and its susceptibility to volatilization loss are regulated by the soil and floodwater properties, such as temperature, pH (Fig. 3), and wind speed. For soils with a pH < 8, ammonia volatilization loss should be negligible; however, when urea is applied as N fertilizer, its hydrolysis can result in a soil pH > 9 surrounding the urea granules. Under flooded conditions, floodwater pH is one of the key regulators of NH_3 volatilization (Godwin and Singh, 1998). The trend of floodwater pH peaking during the day due to the consumption of CO_2 by algal photosynthetic activity and declining at night with the release of CO_2 is captured by CERES-Rice and APSIM-ORYZA (Gaydon et al., 2012). Thus, NH_4-N concentration and volatilization loss are also regulated by floodwater depth. While most N model components operate on a daily time-step, some processes such as changes in floodwater pH and ammonia volatilization loss are modeled at sub-daily to hourly time-steps.

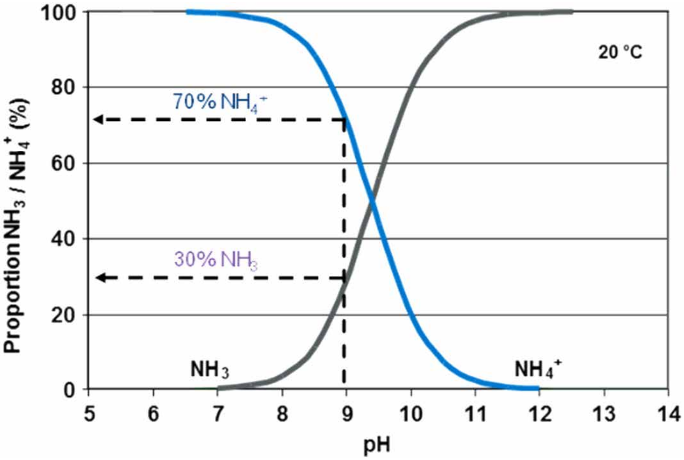
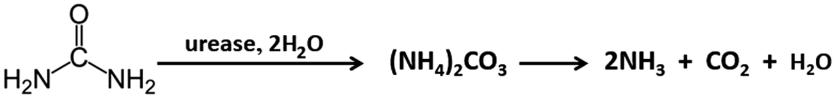


Figure 3 Changes in the proportion of NH_3-N/NH_4-N due to pH. Source: based on Denmead et al. (1982).

2.2.2 Urea-N

Urea is the most widely used N fertilizer, with a worldwide production rate of 170 million tons in 2017. It is popular due to its high N content (46.4%), easy handling (non-flammable and non-explosive properties), and low price per unit of N. Urea-N hydrolysis to NH_4-N catalyzed by urease enzymes leads to increased soil pH and favorable conditions for volatilization (Eq. (5)). Hence, it is not surprising that volatilization is a major N loss mechanism in agriculture. In rice fields, 20–50% of applied N could be lost through NH_3-N volatilization caused by the combined effects of urea hydrolysis and algal activity in floodwater with a pH > 9.



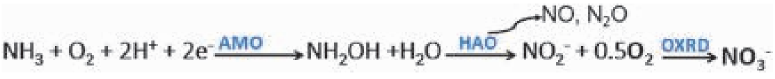
(5)

Incorporating urea into the soil column can reduce volatilization loss compared to surface broadcast application. The practice of urea application followed by irrigation for dryland crops is also an effective way to minimize ammonia volatilization loss. Under lowland (flooded) rice field conditions, 50–60% of applied urea still enters the floodwater, despite incorporation into the soil (Vlek and Craswell, 1981), with the potential for volatilization loss. Thus, model simulations may substantially deviate from reality if the model assumes that none of the urea incorporated into the soil diffuses into the floodwater. On the other hand, urea deep placement (UDP) is highly effective in preventing diffusion of urea-N and ammonium-N into the floodwater, resulting in negligible ammonia volatilization loss, as evident from Fig. 4 (IFDC, 2017).

Urease inhibitors such as N-(n-butyl) thiophosphoric triamide (NBTPT), N-(n-butyl) phosphoric triamide (NBPT), phenyl phosphoryldiamidate (PPDA), and boric acid temporarily inhibit or slow urea hydrolysis and can significantly lower NH_3-N and NH_4-N concentration and the increase in soil and floodwater pH, thereby reducing ammonia volatilization loss (Fig. 4).

2.2.3 Nitrification and denitrification

Nitrification is the oxidation of ammonium to nitrite and then to nitrate under aerobic conditions facilitated by various nitrifying organisms. Very few models consider the growth and death of nitrifiers and denitrifiers and, thus, simulate nitrification and denitrification processes using Michaelis-Menten kinetics or first-order kinetics (Godwin and Singh, 1998; Li et al., 2004).



$$NH_3 + O_2 + 2H^+ + 2e^- \xrightarrow{\text{AMO}} NH_2OH + H_2O \xrightarrow{\text{HAO}} \overset{\text{NO, } N_2O}{NO_2^-} + 0.5O_2 \xrightarrow{\text{OXRD}} NO_3^- \quad (6)$$

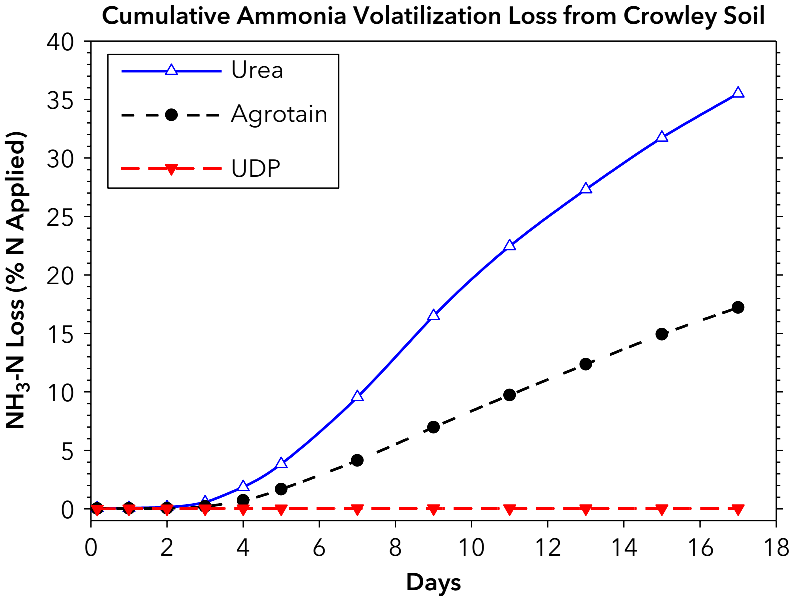


Figure 4 Effect of urea deep placement (UDP) and urease inhibitor – NBTPT (Agrotain®) compared to the broadcast application of urea on volatilization loss.

The conversion of NH_3-N/NH_4-N to hydroxyl amine (NH_2OH) as an oxidation-reduction process by *Nitrosomonas* sp. is catalyzed by monooxygenase enzyme (AMO), followed by conversion to nitrite (NO_2^-) in the presence of hydroxylamine oxidoreductase enzyme (HAO). The final step is carried out by *Nitrobacter* in the presence of nitrite oxidoreductase enzyme, converting nitrite to nitrate-N (NO_3-N). The rate coefficients of the kinetics can be constant or regulated processes limited by additional factors, such as pH, water-filled pore space, soil temperature, and a lag effect to accommodate unfavorable conditions and wetting and drying episodes. These are generally described by index-factors, ranging from zero (no activity) to unity (most active). In most models, nitrification ceases within 24 h under flooded conditions. Nitrification in the 'oxidized' soil layer under flooded conditions is insignificant and ignored by most N models. The high greenhouse warming potential of N_2O at 265 CO_2 equivalent (Myhre et al., 2013) makes nitrification process in the oxidized layer and/or its subsequent denitrification an important contributor of N_2O emission.

The denitrification process involves the reduction of NO_3-N to N_2 and N_2O gases in soils and flooded conditions where anaerobic conditions persist. Modeling of the denitrification process is empirical at best, given the spatial and temporal variability of anaerobic conditions, soil temperature, complexity of C substrates, and the presence of electron acceptors such as NO_3^-, Fe^{3+}, SO_4^{2-}, and HCO_3^- in the soil. In process-based models, the SOM modules simulate soil C in FOM, in humic matter (SOM), and as CO_2 released as a byproduct of the decomposition. These variables are then used for further calculations of denitrification and N-gas losses. The mathematical simulation can be expressed as zero-order, first-order, or Michaelis-Menten kinetics. A generalized first-order denitrification rate coefficient (k_{denit}), as used in RZWQM (Ma and Shaffer, 2001), can be expressed as:

$$k_{denit} = k_d T_{denit} [N_{wet} + MF_{denit} \left(t - N_{wet}\right) \tag{7}$$

where k_d is rate constant, T_{denit} is the effect of soil temperature on denitrification, MF_{denit} is the soil moisture factor's effect on denitrification based on water-filled pore space, N_{wet} is the number of wet days with rainfall or irrigation, and t is time in days. The first-order denitrification rate coefficient can be modified by soil-soluble carbon fraction (Rolston et al., 1980), which is an energy source for some denitrifiers. Denitrification loss from any given soil layer is then determined as a function of k_{denit} and the NO_3-N content.

In soil N models that simulate N_2O emission, denitrified N is further partitioned between N_2 and N_2O where the ratio of N_2:N_2O ($R_{N_2:N_2O}$) is dictated by functions involving soil nitrate ($F_r(NO_3)$), soil CO_2 or respiration rate ($F_r(CO_2)$), and water-filled pore space and the number of previous wet days ($F_r(WFP)$):

$$R_{N_2:N_2O} = \text{minimum}\left[F_r\left(NO_3\right),\ F_r\left(CO_2\right)\right]\ F_r\left(WFP\right) \tag{8}$$

In addition to the denitrification of NO_3-N, N_2O production and emission can occur during the nitrification process (Eq. (6)). N_2O emission from agricultural fields is one of the major GHG emissions. As with ammonia volatilization loss, losses due to N_2O emissions and NO_3-N leaching losses can be managed and reduced with the use of nitrification inhibitors. Inhibitors such as dicyandiamide (DCD), 3,4-dimethylpyrazole phosphate (DMPP), nitrapyrin, and acetylene have been very effective in reducing N losses, particularly N_2O emissions and nitrate leaching (Linquist et al., 2013; Abalos et al., 2014; Feng et al., 2016).

2.2.4 Movement of N

The transport of dissolved urea-N and NO_3-N across soil layers and floodwater occurs via mass flow (percolation). N transport simulation is dependent on the associated soil water balance modules. The movement of urea-N and NO_3-N and the diffusion of NH_4-N are represented at a complexity that varies between models. As discussed, the diffusion of NH_4-N across soil layers is driven by concentration gradients of NH_4-N, cation exchange capacity of the soil, and the soil buffering power of NH_4-N. Mass flow in most upland N models is, generally, the movement of dissolved urea and nitrate (with water) from one soil layer to the layer below. The implicit assumption in the model is that all urea-N or nitrate-N present in a particular layer is uniformly and instantaneously in solution in all of the water in that layer. This assumption will not hold for macropore water movement, for example, soils with large cracks. If needed, the DSSAT models use a nitrate retention function to model NO_3-N leaching in soils with variably charged surfaces and anion-retention capacities. The retention capacity for nitrate-N is estimated for subsoils as a function of delta pH (pH in KCl minus pH in water) and SOM content (Singh et al., 2002).

A major application of soil N models is their ability to predict N leaching losses, since maximizing crop responses to N management should not occur at the expense of high N leaching losses (McGechan and Wu, 2001; Hansen et al., 2001; Basso et al., 2016; Pathak, 2004; Gaydon et al., 2017). The long-term sustainability of both food security and the environment has set new goals for N management.

2.2.5 Enhanced efficiency N fertilizers

Enhanced efficiency N fertilizers with urease inhibitors, nitrification inhibitors, and controlled-release coatings improve NUE by reducing N losses and improving the synchrony of N release with crop N demand (Fig. 5) (Trenkel,

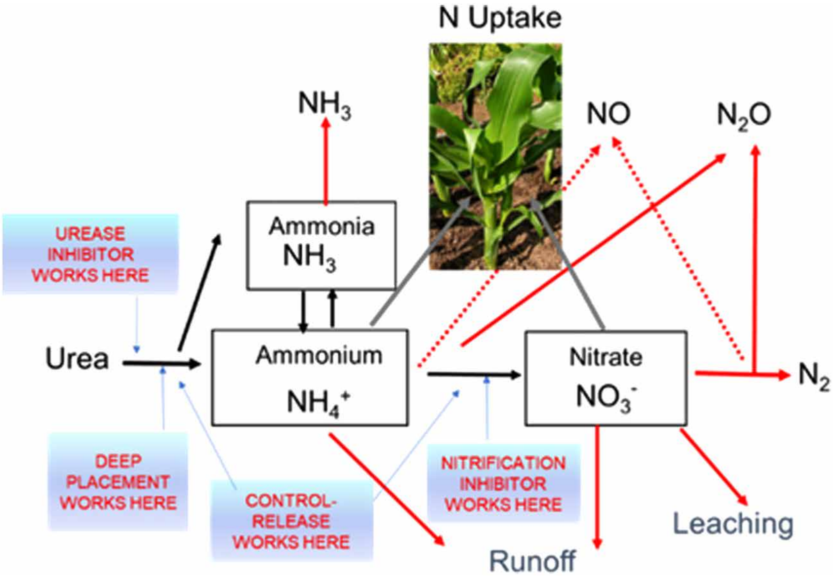


Figure 5 Role of inhibitors, control-release coatings, and urea deep placement on the N transformation process.

2010). UDP reduces N losses and improves plant N availability by preventing the diffusion of N into floodwater. With an increasing emphasis in improving NUE, the European Union has stipulated that, after 2020, urea cannot be sold without the incorporation of urease- and nitrification-inhibitor compounds. The endorsement of the international code of conduct for the sustainable use and management of fertilizers, which aims to guarantee an effective and efficient use of fertilizers, also highlights the global importance of fertilizers in food production and food security and their impact on the environment (FAO, 2019, http://www.fao.org/3/mz476en/mz476en.pdf).

The above-mentioned changes in N management and N fertilizers demand that the existing N models incorporate the effects of inhibitors, controlled-release coatings, and slow-release N fertilizers on soil and plant N dynamics. This will help improve the synchrony between soil and fertilizer N supply and crop N demand and reduce N losses.

2.3 Crop nitrogen (N) modeling

Optimal N management involves synchronizing the timing of soil N supply via mineralization and fertilization (as discussed earlier) with crop N demand to promote optimum N uptake. Crop N uptake is influenced by environmental and crop factors. As discussed in previous sections, N supply is influenced by environmental factors such as the soil temperature, soil moisture, soil pH, and management of N fertilizers and organic amendments. Root morphology, root architecture, and root length density regulate the N supply to crops. All of these factors interact with each other, to influence not just N supply, but also N demand by crops. Modeling N uptake provides a process-based approach to deal with these complex interactions. In process-based models developed to simulate crop yield, the soil and floodwater N model is coupled with the crop growth and phenology model to simulate crop N uptake. Thus, the prediction of crop N uptake depends directly on a model's ability to correctly simulate crop duration, growth stages, crop growth, root distribution, soil water balance, and soil and floodwater dynamics. Hence, input errors, simulation errors, and assumptions from other sub-models would significantly influence the performance of crop N models. Models that were developed to estimate the overall N balances, in general, use a simpler approximation of N uptake (Chowdary et al., 2004; Liang et al., 2007). N uptake has also been described by Michaelis-Menten kinetics where the maximum rate of N uptake is limited by an index-factor for leaf area index (LAI), root distribution, and temperature (Antonopoulos, 2010). Crop N demand can be estimated from a logistic growth curve in simpler models. Ma et al. (2008) provide a comprehensive review of a wide range of plant N uptake models for cereals, legumes, oilseeds, and tuber crops.

2.3.1 Nitrogen (N) supply

In most process-based models, the supply of soil N to plant roots is determined by plant available N (NH_4-N and NO_3-N), rate of water transpiration, and the diffusion of soil N to root surfaces (Shaffer et al., 2001). In the DSSAT model, the potential N supply from the soil profile (N_supply), which is the sum of nitrate and ammonium supplied from all soil layers, integrates the effect of rooting density, NH_4-N and NO_3-N concentrations, and soil water (Godwin and Singh, 1998). When N_supply for any given day is higher than crop N demand (N_demand), the ratio of N_demand to N_supply (less than 1) is used to reduce the N supply proportionally from each soil layer for NH_4-N and NO_3-N. The above normally occurs when plants are young (lower N demand) or after the application of N fertilizers (higher N supply). In legumes, when N_supply is less than N_demand, carbohydrates are metabolized to meet the crop N demand via N-fixation as dictated by nodule mass and species-defined nitrogenase activity (Boote et al., 2008). The N-fixation rate is influenced by temperature, soil water deficit, soil aeration (water logging), and plant reproductive age. For all crops, when N_supply (soil and/or N-fixation) is less than N_demand, vegetative tissues are grown at lower N concentrations. If such conditions persist, N deficiency symptoms arise. In most models, N deficiency results in LAI reduction, reduced photosynthesis (growth and yield reduction), and accelerated senescence. Prolonged N deficiency can also affect crop development (delayed vegetative development or accelerated maturity).

2.3.2 Nitrogen (N) demand

Crop N demand differs with the growth stage of a crop, as dictated by the growth of given organs (leaf blades, stalks, stems, ears/panicles/pods, and grains) and their critical tissue N concentration. As shown in Fig. 6, N uptake for hybrid maize changes over the duration of growth, with extremely high N demand from the tassel initiation (V6-8) to anthesis (R1) growth stages. For maximum use efficiency, the N supply from soils and fertilizers must match the crop N demand. N demand in most models is driven by the plant growth rate, growth stage, and tissue N status as a function of the growth stage (Godwin and Singh, 1998; Probert et al., 1998; Ahuja et al., 2000; Williams, 1995). Models differ in terms of N partitioning, ranging from a single plant N pool to shoot, root, and grain N pools to more complex models with leaf, roots, stem, ears (pods), and grain N pools.

The N status is generally expressed as the N concentration (weight basis) and content per unit area, for example, leaf N. A daily attempt is made to keep leaf, stem, root, and so on tissue N concentrations at a pre-defined critical

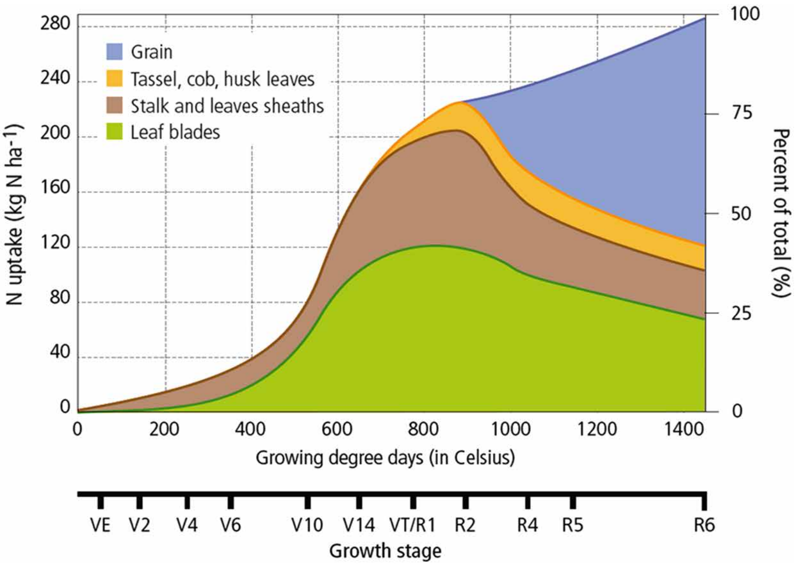


Figure 6 Nutrient uptake pattern of modern hybrid maize. Source: adapted from Bender et al. (2013).

concentration ($N_{critical}$). $N_{critical}$ is the lowest concentration at which maximum (non-stressed) growth occurs. As tissue N concentrations (N_{actual}) fall below $N_{critical}$ and growth processes are affected, while $N_{actual} > N_{critical}$ leads to luxury N consumption. The DSSAT N model also uses a minimum tissue N concentration (N_{min}), below which all growth ceases. $N_{critical}$ and N_{min} are crop specific and differ with growth stages, as illustrated for rice in Fig. 7. An index for N deficiency for a given organ on any given day (NFAC) can be determined based on the actual tissue N concentration compared to the pre-defined concentrations:

$$\mathrm{NFAC} = 1.0 - \left[\left(N_{critical} - N_{actual}\right) / \left(N_{critical} - N_{min}\right)\right] \tag{9}$$

Since all plant growth processes are affected differently by N stress, several N stress indices have been estimated based on NFAC. These indices model the effect of N stress on leaf expansion, plant height, photosynthesis, senescence, crop development, and so on. For example, N stress can shorten the duration of grain-filling, which can further reduce grain yield (Singh et al., 1999).

Total crop N demand is driven by the N demand for new growth and the demand to overcome any deficiency in the existing biomass (organs). New growth N demand (New_N_demand) is determined from potential new growth (Potential_growth) and $N_{critical}$:

$$\mathrm{New\_N\_demand} = \mathrm{Potential\_growth} * N_{critical} \tag{10}$$

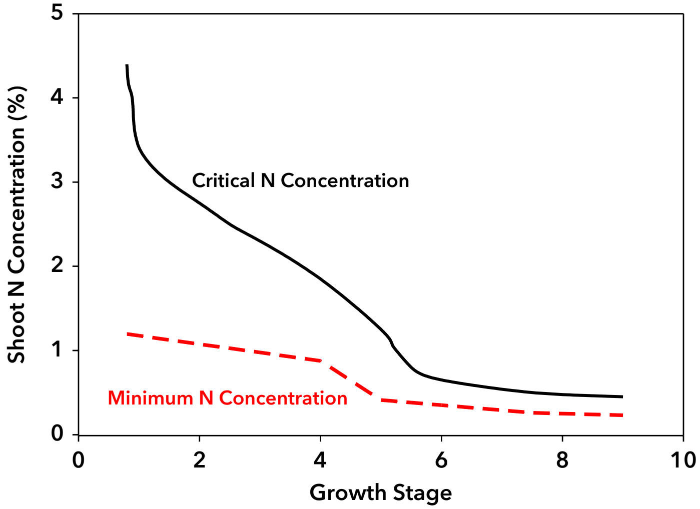


Figure 7 Changes in critical and minimum shoot N concentration in rice at given growth stages.

When New_N_demand is not met by N supply (N_supply) from soil and/or N-fixation, then mobilization of N can occur from older organs. Priority for use of mobilized N is grains > ears (shells) > vegetative organs. If New_N_demand is not met, potential growth will be reduced for that day while maintaining N concentration at $N_{critical}$. The N demand to overcome deficiency in any existing organ (DNDEM) is calculated for each organ as:

$$\mathrm{DNDEM} = \mathrm{Mass}_{organ} * \left(N_{critical} - N_{actual}\right) \qquad (11)$$

Total crop N demand (N_demand) is a summation of all deficiency demands from various plant organs and new growth demand. Based on N_demand and N_supply, N uptake from each layer can be adjusted when N_supply > N_demand. However, when N_supply < N_demand, N deficiency exists, and a nitrogen stress effect is simulated.

3 Modeling phosphorus dynamics

Phosphorus is one of the most limiting nutrients for crop growth in tropical soils. Its availability to plants is strongly dictated by soil properties, environmental factors such as temperature and rainfall, and management. Management of P inputs and rationalizing P fertilizer recommendations are crucial for improving P use efficiency – which is currently at less than 20–30% for initial P application – and reducing the risk of P losses to water bodies. Total P fertilizer consumption in 2014–2015 was 20.2 million tons; 44% of all global P application occurred on cereals and 16% on oilseed crops (soybean, oil palm, etc.) (Heffer et al., 2017). Unlike N fertilizers, P is a nonrenewable resource that is dependent on a finite supply of phosphate rock (van Kauwenbergh, 2010; Cordell et al., 2009). P fertilizer recommendations based on extractable soil P are highly dependent on the method of extraction. These methods have been developed for specific soil types based on soil pH levels and the presence of calcium carbonate, iron (Fe), or aluminum (Al) oxides. Since P has a strong residual effect that is soil dependent, long-term experiments are required to understand and predict the depletion and build-up of soil P pools through continuous cultivation and fertilization (Johnston, 1997). Since increased P loads in water bodies can have detrimental effects on aquatic life, various P dynamics models are in use for simulating P transport and exchange in watersheds, aquatic sediments, wetlands, stormwater treatments, aquaponics, and so on (Basu et al., 2018; Dahl and Pers, 2004; Sinclair et al., 2016; Walker and Kadlec, 2011; Wang et al., 2003). Since soils are often the main source of agricultural P loss through runoff, the modeling of soil P processes, the dynamics within and among soil P pools, and the effect of abiotic and biotic factors on soil P pool size and their transformation will contribute toward both watershed applications and plant P nutrition. Dynamics of plant-available soil P can be modeled using the mass conservation approach (Morel et al., 2014). Process-based simulation models, such as APEX (Gassman et al., 2010), AnnAGNPS (Yuan et al., 2011), DSSAT (Dzotsi et al., 2010), and APSIM (Keating et al., 2003) can assess agricultural P loss, soil P dynamics, and plant P response.

3.1 Modeling soil phosphorus (P) processes

Quantifying soil P content and distribution among chemical forms requires soil P models to capture the complex effects and interactions of soil, environment, time, and management factors. In intensified agriculture, soil inorganic P (P_i) dominates the soil P dynamics; however, in low-input tropical agroecosystems, organic P (P_o) can constitute more than 35% of the total P in tropical soils (Abekoe and Tiessen, 1998). Hence, simulating the soil P dynamics that accounts for both P_i and P_o pools is important. Although plant roots absorb water-soluble P as orthophosphate ions P_i, $H_2PO_4^-$, and HPO_4^{2-}, almost 99% of absorbed P_i is derived from the soil solid phase (Morel et al., 2014). Several processes, including the diffusion of P_i at the solid-to-solution interface, the dissolution of phosphate minerals by acidification, soil buffering capacity, the mineralization of organic P compounds, and soil temperature and moisture, govern the P_i release from soil constituents to the soil solution.

Mineralization of P_o from various SOM pools follows a similar process as N mineralization, with the C:P ratio dictating whether mineralization or immobilization of P occurs for a given SOM pool and soil layer. The net P

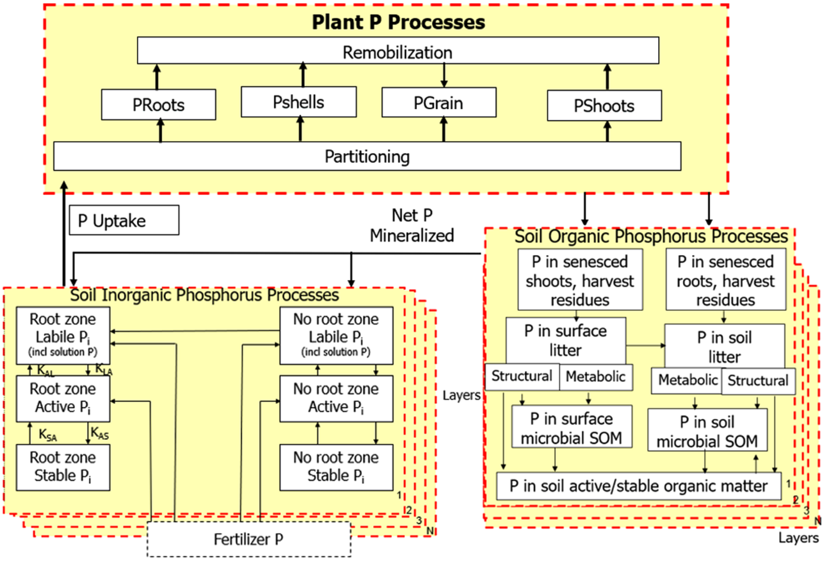


Figure 8 Generic soil and plant P model. The 'no-root-zone' pools are distant, for example, away from the effective P-absorbing radius of roots, but this pool shrinks as root length density increases.

mineralization for a given soil layer is determined from the difference of P mineralized and immobilized from different SOM pools; it is then added to the respective P_i labile pool layer (Fig. 8). The size and the dynamics of P in the inorganic and organic pools directly influence the concentration of P in the soil solution. The initialization of soil P model, both P_i and P_o pools, is perhaps the most critical input requirement because such data are rarely readily available or, if available, different extraction procedures are used. The choice of chemical extraction methods for soil P determination is dictated by soil properties. Empirical functions based on Jones et al. (1984), Sharpley et al. (1984, 1989), Singh (1985), and Vadas and White (2010) have been used to initialize P_i and P_o so that different extraction methods can be correlated to resin-extractable P. The fractionation of P_i in different pools (solution, labile, active, and stable) can be determined from the extraction of soil P with a concoction of different chemical extracts (Hedley et al., 1982). However, the fractionation procedure is complex and such data are scarce. Empirical functions based on the type of soil (calcareous, highly weathered, slightly weathered, volcanic) and its physical and chemical properties, including clay and organic matter content, have been used to derive solution, labile, active, and stable P_i pools, their respective transformation rate constants, and the proportion of sorbed and dissolved P (Fig. 8). The soil solution P pool thus captures the differences due to the above-mentioned four soil categories and the effect of soil water factor (SWF), texture (F_Texture), and organic carbon (F_OC) within each soil category:

$$\text{Soil Solution P}\left(\text{mg/kg}\right) = \text{P}_{\text{i}}\text{Labile} \times \text{PFraction} \times \text{F\_OC} \times \text{Min}\left(\text{F\_Texture, SWF}\right) \tag{12}$$

where PFraction is 0.05 for calcareous soils, 0.02 for slightly weathered soils, 0.015 for highly weathered soils, and 0.008 for volcanic soils (Dzotsi et al., 2010).

The solution P pool is subject to (i) uptake by plants, (ii) fixation by soil colloids, (iii) additions of P fertilizer, and (iv) mineralization from P_o. Since P mobility due to diffusion is restricted, P available for plant uptake is dependent on the simulation of the root 'zone'. Leaching and runoff P losses are generally modeled based on solution and labile P_i pools. A fraction (20–40%) of P leached from the top layer can be lost as runoff, while the remainder is added to the labile P_i pool in the second layer (Vadas et al., 2012). Depending on the complexity of P models, P leaching loss is simulated as a fraction from each layer or all from the bottom-most layer. P leaching losses are of concern in sandy soils.

In agricultural soils, the labile P_i pool size, particularly for the top 0–20 cm layers (depending on the tillage practice), is highly dependent on P fertilizer application. Most P models assume P fertilizers are water soluble and are immediately added to the labile and solution P_i pools. However, given the low P fertilizer use efficiency, potential leaching losses on sandy soils and conversion of applied P fertilizers to less-available active and stable P_i pools emphasize the need to explore opportunities for the direct application of phosphate rocks and other less-soluble P fertilizers (Smalberger et al., 2006).

3.2 Modeling crop phosphorus (P) processes

The supply of soil P for crop P uptake is highly dependent on the presence of roots; therefore, labile P_i, including solution P, should be within the vicinity (1–5 mm) of the roots. Unlike N, which is highly mobile, P supply is highly restricted to nearby roots. The magnitude of 'root zone' and 'non-root zone' P is modeled for each layer to determine the available P for root uptake (Fig. 8). As the root length volume per soil layer increases, the proportion of 'root zone' P pool is expected to increase and 100% of the soil volume may come in contact with the roots (Fig. 9). The potential P supply from a layer is determined as a function of labile P_i concentration and the effective root length volume (root length volume × root-fraction).

Modeling crop P demand is similar to crop N (as discussed previously). Daily demand (P_demand) is calculated for each plant part as the amount of P required to bring P concentration from the actual (P_{actual}) in each of the

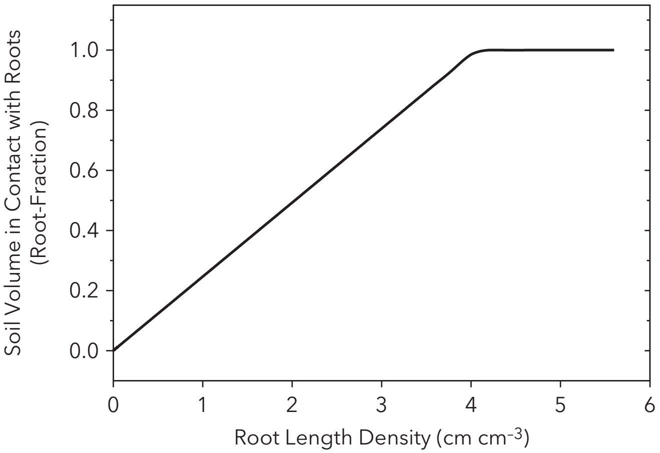


Figure 9 Fraction of soil volume in contact with roots as the function of root length volume (also dependent on time).

plant parts ($Mass_{organ}$) up to the critical ($P_{critical}$), plus P required for new growth (New_P_demand):

$$\text{P\_demand} = \text{Mass}_{\text{organ}} * \left(\text{P}_{\text{critical}} - \text{P}_{\text{actual}}\right) \tag{13}$$

$$\text{New\_P\_demand} = \text{Potential\_growth} * \text{P}_{\text{critical}} \tag{14}$$

The P demand is met through P soil supply and/or mobilization of plant P pools (Fig. 8). If the P soil supply after remobilization of P is less than P demand, then P concentrations in plant parts are reduced inducing P stress. P stress factors are determined based on similar principles as N stress. Models simulating both N and P uptake also compute the maximum and minimum plant N:P ratio on a daily basis; this information is then used to limit P uptake if on any day the actual N:P ratio is below the minimum.

Modeling soil and crop P dynamics is challenging given that there are different soil P pools; there is no standardized procedure for 'identifying" and "quantifying' these pools, and there are soil P chemical forms that are highly specific to the soil type. P uptake is challenged by ensuring that the root model is reliable because P uptake occurs only within a very close proximity of the roots. Simulating the effects of P stress also has its challenges, since P stress has a strong impact on crop duration; P stress generally prolongs the duration. Depending on the severity of P deficiency, leaf appearance rate and crop development rate are reduced, resulting in anthesis delay by up to a month (Singh, 2008). If the impact on delay is not considered, P-stressed plants may compensate, and economic yields may not be different from unstressed plants with a normal (shorter) duration.

4 Modeling potassium dynamics

Potassium (K), just like N and P, is a macronutrient with important functions for crop growth. It activates over 60 enzymes, promotes photosynthesis, regulates stomatal opening, improves N utilization, promotes the transport of assimilates, and increases growth and crop yield. Total K fertilizer consumption in 2014–2015 was 27.8 million tons, and, unlike N and P, almost 23% of K was applied to oilseed crops, and 12.2% was applied to soybean plants (Heffer et al., 2017). Global K application on cereals was at 36% and 14%, 11%, and 7% on maize, rice, and wheat, respectively. K ions are mobile and, therefore, can be leached along the soil profile. Simulation models have been important research tools in studies involving complex and interactive processes of water flow and K transport through the soil profile as well as the effects of management practices on agricultural production and the environment. The high solubility of K has contributed to many studies simulating the movement of water and solutes (Beckett, 1964a,b; Adiscott and Talibudeen, 1969; Barber, 1985, 1995; Frissel, 1978; Dessougi and Claassen, 2001; Šimůnek et al., 2008; Zeng and Brown, 2000). In addition to K solute movement, modeling the root effects on K uptake (Brüggemann et al., 1999; Ahn et al., 2004; Reintanz et al., 2002; Samal et al., 2010; Zhang et al., 2007; Trehan and Claassen, 1998; Dessougi et al., 2002; Steingrobe and Claassen, 2000; Rengel and Damon, 2008) and release characteristics has seen major efforts (Hosseinpur and Motaghian, 2013; Springob and Richter, 1998; Moritsuka et al., 2004).

Most soil K and plant K models are generally focused on specific research or management tasks, for example, solute transport, water quality/waste management, and rhizosphere interactions. Such models, as are cited earlier, simulate K uptake at roots and root hairs level; the nutrient uptake into the root is dependent on the nutrient concentration in the soil solution at the root surface and can be described by a modified Michaelis-Menten equation. The transport of nutrients to roots in the solution phase is modeled by mass flow and diffusion (Barber, 1985). The release of nutrients from the soil solid phase into the solution phase is governed by sorption and desorption processes. The quantity/intensity (Q/I) ratio of potassium has been used to model soil K status. In this approach, immediately available K is related to the intensity factor, the reserve of the non-exchangeable K is referred to as the quantity factor, and the renewal capacity is applied to the buffering capacity (Evangelou et al., 1994; Roy et al., 1991; Hamdan et al., 1999; Wang et al., 2004). Soil properties such as CEC, SOM content, pH, and K mineralogy affect K release, K buffering capacity, and K-fixation characteristics.

Comprehensive soil-plant K models have been developed to capture the effect of K management on crop growth, plant K, and soil K (Greenwood and Karpinets, 1997; Zhang et al., 2007; Koós and Kovács, 2008; Scanlan

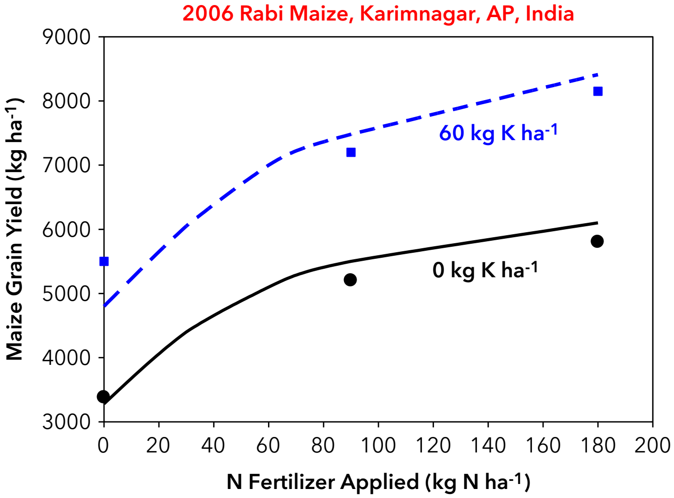


Figure 10 Comparison of simulated and observed maize grain yield response to N and K.

et al., 2015a,b; Singh et al., 2007). Both DSSAT (Singh et al., 2007) and APSIM (Scanlan et al., 2015a) models utilize existing soil-plant-environment modules of crop growth and development, soil and plant water balance, soil and carbon dynamics, and couplings of these processes to simulate the effect of K. The DSSAT-K model has been evaluated for maize, rice, and cotton, and the APSIM-K model has been evaluated for wheat. The plant K uptake in these models is driven by the soil K supply and crop K demand as previously described for plant N and P models. The uptake of K is also dependent on the equilibrium between root and soil solution K concentration. In contrast to slower P mobility and greater rooting dependence in simulating P uptake, K mobility occurs up to twice the distance from roots compared to P. The photosynthetic assimilation rate and water-use efficiency are modified according to shoot K concentration. Crop responses have been evaluated on a few experiments with well-characterized sites (Fig. 10). Additional research to capture the effect of K fertilization on plant abiotic (low- and high-temperature tolerance and drought) and biotic stresses will help highlight some of the key roles of K nutrition.

Generic soil K models, as shown in Fig. 11, account for the flow of K from fertilizers, crop residues, K-fixing soils, and weathering of minerals to exchangeable and solution K pools. The outflows from these ‘available’ pools include plant K uptake, K leaching loss, and K-fixation. Model input for the initialization of soil K pools and transport coefficients is not as challenging as for the soil P model. However, more experiments conducted on a wide range of soils that are also well characterized will help expand pedotransfer functions

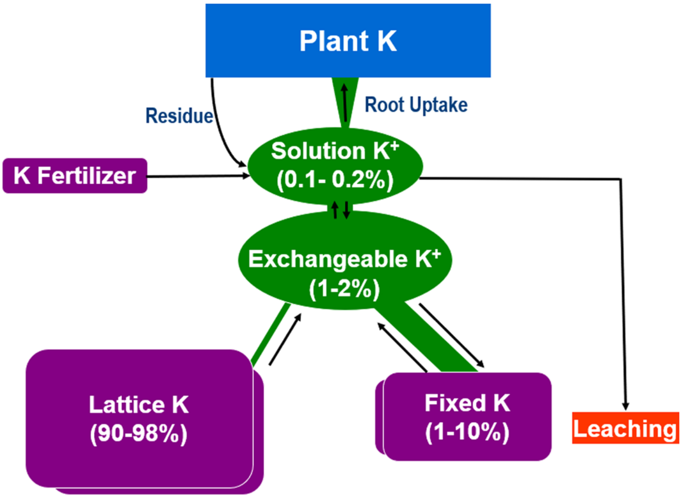


Figure 11 Generic soil K model.

and their utility for quantifying K pools and transfer coefficients without the need for complex data to run K models.

5 Conclusion

The ability to model soil and plant nutrient dynamics is an important component of research involving agricultural systems that are sustainable while addressing the current challenges of scarce resources, climate change and variability, increasing population, and environmental degradation.

The current capability of many agricultural and soil models to predict nitrogen dynamics is well established and generally robust. Inorganic N dynamics is routinely quantified with predictability when compared to measured data. These models are ideally suited for the study of fertilizer use efficiency and resource optimization. Modern fertilizers that allow for the controlled and slow release of N, fertilizer deep placement, and inhibitors for urease and nitrification processes are a relatively new addition to modeling capabilities, but they are increasingly being addressed by the agricultural modeling community.

Agricultural production models that include nutrient dynamics and chemical transport are used to study environmental quality, including N, P, and K leaching into shallow groundwaters. The ability of models to predict the release of GHGs from crop production systems is an important contribution to climate change research and the development of climate change mitigation options.

Organic C and N dynamics are also well characterized in many current models. Unfortunately, challenges related to the initialization of soil organic C pools are often a problem due to a lack of data. However, the main deficiency in current models is in handling other nutrients, including sulfur (S), calcium (Ca), magnesium (Mg), iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), boron (B), molybdenum (Mo), cobalt (Co), and nickel (Ni). The main reason for this deficiency is a lack of data to both develop models for nutrient transformation, solubility, and transport in the soil and to quantify the plant response to nutrient deficiency. Perhaps the most limiting factor is the information on soil properties that drive the nutrient transformation processes and their interactions. For those models that do exist, the lack of data from agronomic studies to parameterize and initialize the models limits the usefulness of the models.

6 Where to look for further information

The use and development of nutrient dynamics models in research has been primarily promoted through training programs, particularly in the developing world. Hence in the developing world, and specifically in Sub-Saharan Africa emphasis should be placed on the inclusion of agricultural systems modeling in the regular curricula of the universities, understanding the limitations of models, and using models in generating ideas and insights, instead of uncritically using model results. The existing nutrient modeling effort can be substantially improved by conducting more research and model evaluation under adverse environmental and soil conditions. The various focus crops and themes within the Agricultural Model Intercomparison and Improvement Project (AgMIP) have challenged modelers to evaluate crop and nutrient dynamics model under a wide range of conditions. AgMIP (https://agmip.org/) also provides useful information and contacts for the existing models.

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