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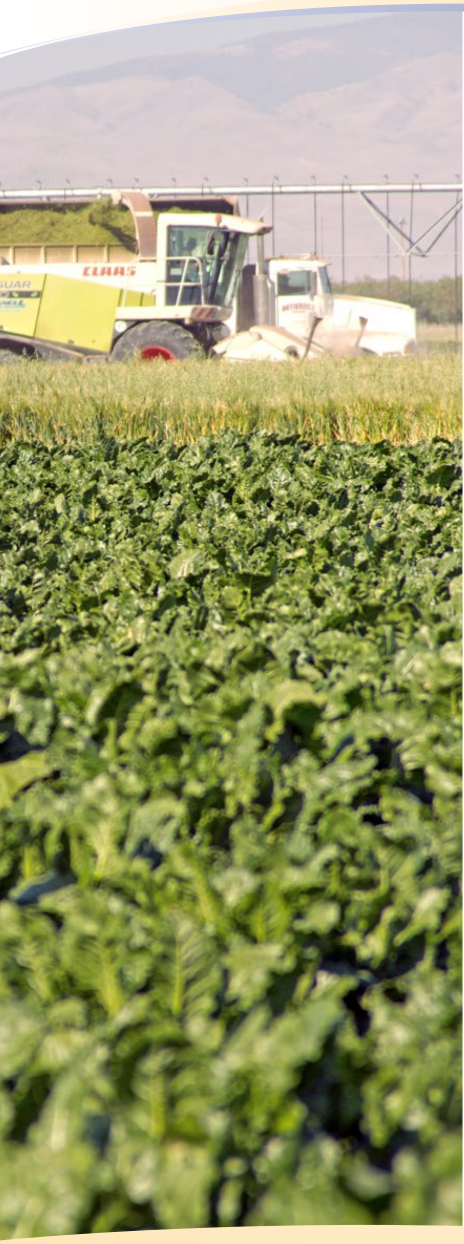

Principles of Nitrogen Cycling and Management

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Use of nitrogen (N) fertilizer on major California crops has led to the degradation of water quality from nitrate (NO_3^-) leaching to groundwater. This outcome is the result of a combination of historic management practices including uniform rates of N fertilizer applied to land of heterogeneous soil types; poor timing, poor placement, or incorrect quantities of seasonal N applications; and irrigation in excess of crop water demand when abundant soil N is available. Where excess irrigation is applied when soil N concentrations exceed uptake capacity, N efficiency is reduced and leads to a greater risk of NO_3^- leaching. Strategies are available to make N management more protective of the groundwater while maintaining or improving productivity. The primary tool for N management is the adoption of a N budget for cropping systems that are specific to each grower and each unit of land. The N budget includes the N requirement based on an estimate of yield potential and crop growth with adjustment from credits from other N sources. Targeted placement of N fertilizer in the root zone combined with timing to match N applications with N uptake, improved irrigation scheduling and uniformity, and the adoption of irrigation designs optimized for different soil types are options to implement an efficient N budget.

In California, certified crop advisors (CCAs) are professionals responsible for the development of N budgets. In the 1990s, control of pesticide use led to the training of pest control advisors (PCA) who provide growers with recommendations based on individual plant protection goals and regulatory compliance. Similar to role of the PCA, the CCA is accountable to develop a N budget with the aim to apply N fertilizer to meet crop production goals in a manner that limits NO_3^- leaching to groundwater. CCAs have the knowledge to balance the needs of the grower with the requirement to protect water quality due to their experience with multiple cropping systems across various soil types. The requirement for continuing education to maintain certification makes CCAs an appropriate audience to deliver updated information and resources. Ongoing interactions with growers allow CCAs to leverage established relationships to adapt to evolving challenges. The ability to leverage trust within social networks is an indispensable asset to support the adoption of N budgets to sustain productivity and improve water quality.

Nitrogen budgeting is a universal approach to N management that is easily adapted to cropping systems. The first component is an estimate of the crop N requirement, including N demand for vegetative and reproductive growth above and belowground. The crop N requirement equals the total N in the harvestable crop removed from the field plus residues left behind, in addition to N allocated to woody portion of permanent crops. For the crop production cycle, N from organic matter amendments and cover crops, NO_3^- in irrigation water, and soil N mineralization are estimated as N credits. Total N credits are deducted from the crop N requirement to derive the N demand to be met by N fertilizer. The remaining N demand is divided by an efficiency factor for N fertilizer where the resulting value is the planned supply of N fertilizer (fig. 1). In order to attain the targeted efficiency and maintain productivity, a combination of improved management techniques is required.

Nitrogen in Agricultural Systems

The principles that govern N in agricultural systems begin with the concepts of supply and availability. The major source of N in agricultural systems since the 1950s is chemical N fertilizer derived from the Haber Bosch process. Hydrogen (H_2) and dinitrogen (N_2) gases are combined under conditions of high heat and pressure to produce ammonia gas (NH_3). Ammonia becomes the primary product for the development of chemical N fertilizer formulations. Burning natural gas during the Haber Bosch produces both heat and carbon dioxide (CO_2) gas that is captured and mixed with ammonia gas to produce the world's top form of N fertilizer known as urea $CO(NH_2)_2$ (Gilbert et al. 2006). Ammonia is also protonated into ammonium (NH_4^+) and combined with anion salts as well as oxidized into nitrate and combined with cation salts. Chemical N fertilizers come in solid, liquid, and gaseous forms. Solid fertilizer delivery to crops includes surface spreading and dissolving granules in irrigation water; liquid fertilizer is a concentrate that is injected into water during irrigation; and gaseous ammonia is either injected or shanked into soil (mainly with annual crops).

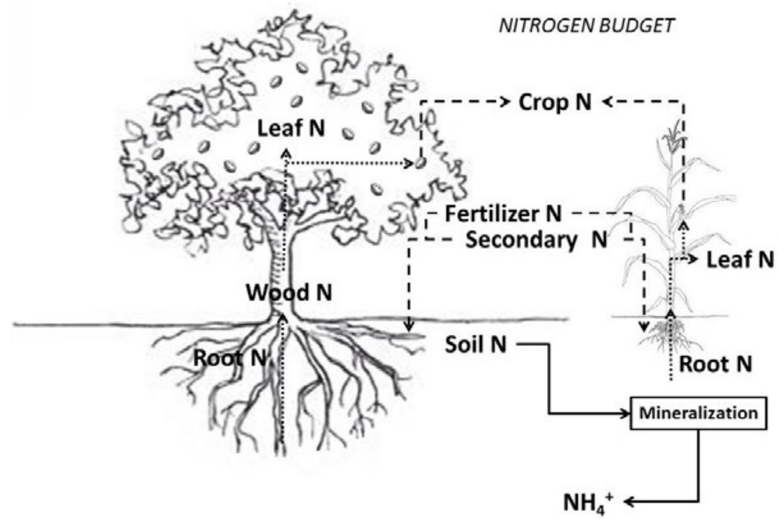

Figure 1. Components of a nitrogen (N) budget for annual and permanent crops include the crop N requirement from crop, leaf, and root N (and wood N for permanent crops). Secondary N sources such as organic matter amendments, cover crops, and nitrate (NO_3^-) in irrigation water in addition to soil N mineralization represent N credits. The crop N requirement minus N credits divided by an efficiency factor equals the supply rate of fertilizer N to match N demand.

Secondary sources of N in agricultural systems include soil organic matter, organic amendments, and N already found in the environment. Soil N is derived from organic matter and includes an active fraction consisting of microorganisms, several intermediate stages, and a stable resistant fraction also referred to as humus. These forms are characterized by their carbon to N (C:N) ratio, where a higher C:N matter takes more time to become plant available and a lower C:N matter takes less time to become available. Organic amendments like cover crops, manure, and compost are also important N sources in agricultural systems. Like soil organic matter, N availability from organic amendments depends on the C:N of the material, with cover crops being the most readily available after incorporation into the soil, followed by animal manure, and compost, where the composting process has stabilized much of the organic N (Chalk et al. 2013). Finally, N availability in agricultural systems is contingent on the transformation of organic N into inorganic N. Other secondary N sources include NO_3^- in irrigation water and N deposition from air pollution such as smog. These environmental inputs are nontrivial amounts of N in agricultural systems, but the amount depends on the region and its air and water quality.

Mineralization is the conversion of soil N into mineral N or inorganic forms. It is a biological process regulated by microorganisms, where ammonium (NH_4^+) is the by-product of decomposition. Several factors affect the rate of mineralization: mainly temperature, but also soil moisture, NH_4^+ concentration, and active soil biological activity. Nitrification is the major pathway of organic N and NH_4^+ into nitrite (NO_2^-) and then into NO_3^-. Nitrification is an oxidation reaction in which the energy found in NH_4^+ is used by autotrophic bacteria and archaea in combination with carbon dioxide to form biomass. The process does not use N; instead, the NH_4^+ is converted into NO_3^-. Nitrification is an aerobic process controlled by NH_4^+ substrate availability, temperature, aeration, and pH. The end product of nitrification is NO_3^-, which is the primary form of N for crops as well as an important pollutant.

Plant-available NH_4^+ and NO_3^- has three major pathways after supply: soil retention and storage, loss from the agricultural system, and crop uptake. Fixation of NH_4^+ to microsites in clay minerals is a physiochemical route for soil retention. The positive charge of the NH_4^+ ion binds tightly and is unavailable for plant uptake or microbial processes. NH_4^+ and NO_3^- that are plant available also compete with microbial organisms for incorporation into their biomass through a process called immobilization. Immobilization of NH_4^+ is fairly common since microbial organisms use both the energy in NH_4^+ and the N to build proteins and biomass (Burger and Jackson 2003). On the other hand, NO_3^- immobilization requires an expenditure of energy by microbial organisms for incorporation into biomass. Often, soils that receive high carbon inputs have a greater potential for NO_3^- immobilization (Drinkwater and Snapp 2007). See figure 2 for a representation of sources and sinks of soil inorganic N.

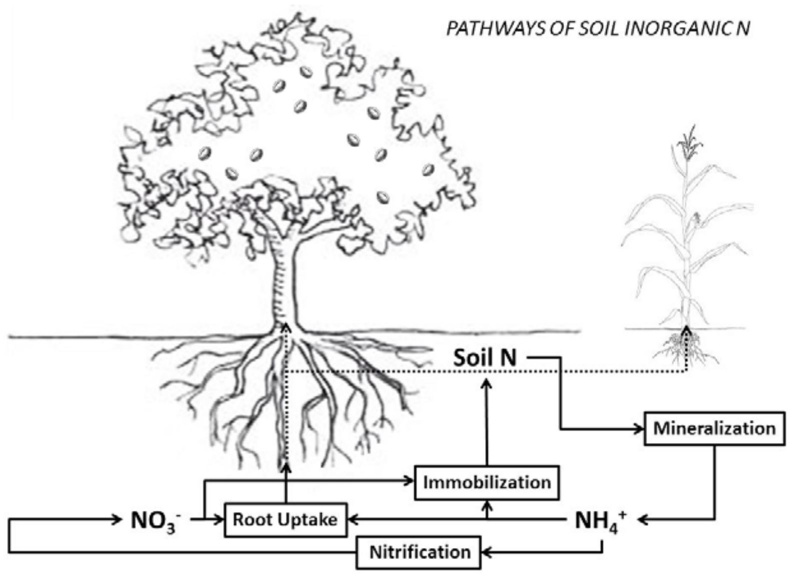

Figure 2. Pathways of soil inorganic N in the form of ammonium (NH_4^+) and nitrate (NO_3^-). Soil N supplies NH_4^+ through mineralization, and nitrification supplies soil NO_3^-. Both NH_4^+ and NO_3^- are taken up into the plant through root uptake or assimilated by microbial organisms during immobilization. Soil inorganic N can be returned back to soil N through immobilization.

Soil retention and storage of N also use biochemical routes. Inhibition of nitrification through the application of chemicals such as nitrapyrin in combination with N fertilizers inhibits nitrification by suppressing populations of NH_3-oxidizing bacteria. During N fertilizer application, lower rates of nitrification increase soil N retention in the form of NH_4^+ and reduce the potential for N losses via NO_3^- leaching and denitrification. Outside of N losses from NO_3^-, NH_3 volatilization is an important loss pathway from the application of anhydrous ammonia or urea. NH_3 volatilization is more prominent when soil is moist and warm and the source of NH_3 is near the soil surface. Furthermore, NH_3 volatilization will take place on alkaline soils because fewer protons are available to convert NH_3 to NH_4^+ under higher pH. NH_3 volatilization can be greatly reduced if urea fertilizer moves below the soil surface through careful management of irrigation water.

Nitrate leaching is the primary pathway of loss of N to groundwater. Excess NO_3^- supplied by N fertilizer or irrigation water or by nitrification of NH_4^+ can move below the rooting zone of crops (Baram et al. 2016). NO_3^-, an anion, is repelled from the surface of soil particles. Furthermore, NO_3^- dissolves in water and moves along with water through the soil profile. As the primary essential nutrient for plants, NO_3^- saturation among crop roots has beneficial outcomes for plant growth. However, excess NO_3^- beyond crop uptake capacity combined with movement of water through the root zone causes NO_3^- to leach, a major pathway of N loss.

Nitrogen is also lost from agricultural systems through gaseous forms. Denitrification is the process under anaerobic conditions where NO_3^- is substituted by oxygen (O_2) as the terminal electron acceptor during cellular respiration of microbial organisms. Soils that are anaerobic or low in O_2 occur when water dominates air in soil pore space or when plant roots use O_2 during cellular respiration. The main species of N gases formed during denitrification in soil depend on increasing N reduction from NO_x gases to nitrous oxide (N_2O) to dinitrogen gas (N_2). NO_x gases are important air pollutants that have implications for particulate matter in air as well as smog formation. N_2O is a greenhouse gas approximately 300 times more potent than CO_2. N_2 gas makes up 78% of our atmosphere and represents a completion of the N cycle. Both NO_x and N_2O are important environmental pollutants to air quality, while N_2 gas, though environmentally benign, still represents another N loss from agricultural systems (Mahmood et al. 2000). NO_x and N_2O gases can also be lost during the process of nitrification (fig. 3).

Uptake of N via crop roots and growth is the primary pathway for efficient N use in agricultural systems. Root N uptake occurs with both NH_4^+ and NO_3^-. Both forms of inorganic N move predominantly in water flow to roots, though NH_4^+ moves far

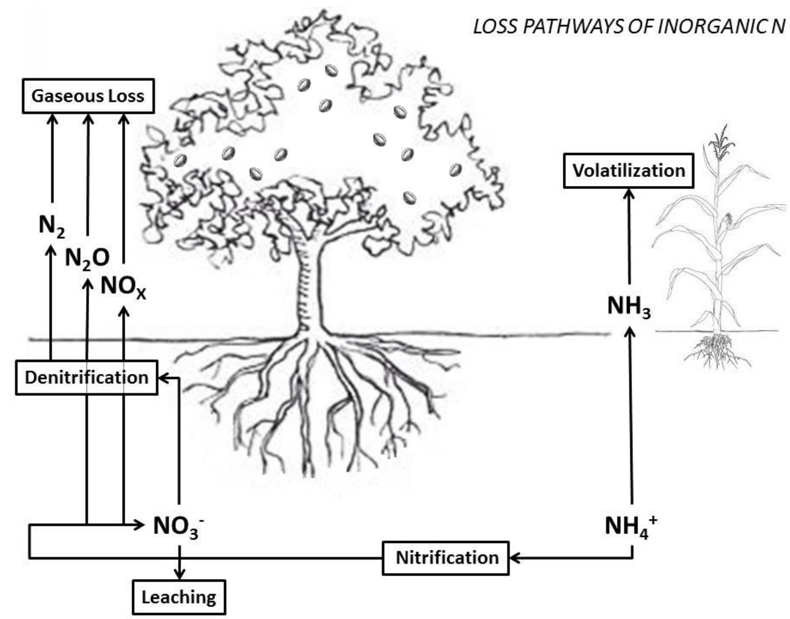

Figure 3. Loss pathways of soil inorganic N in forms of ammonium (NH_4^+) and nitrate (NO_3^-). NH_4^+ can be lost through volatilization as ammonia gas (NH_3). Other gaseous N losses include nitrogen oxide and dinitrogen oxide (NO_x), the potent greenhouse gas nitrous oxide (N_2O), and dinitrogen gas (N_2). Gaseous loss of NO_x and N_2O can occur during nitrification or denitrification. N_2 gas is the final step during the process of denitrification. Leaching is the result of NO_3^- movement below the root zone and has to the potential to be lost to groundwater.

shorter distances and diffusion rates from cation exchange sites affect NH_4^+ far more than NO_3^-. Uptake of NH_4^+ across the root cell membrane is electrochemically favorable: it moves down the electrical potential gradient and down the chemical gradient, since NH_4^+ is not stored in the plant cell. However, NH_4^+ still enters the root through protein transporters that are regulated. As an anion, NO_3^- moves against a strong electrochemical gradient inside plant cells, since cells are more negative. As a result NO_3^- is stored in plant vacuoles. High external NO_3^- movement into roots can be thermodynamically passive, but even then the NO_3^- transporters consume energy. The presence of NH_4^+ and NO_3^- also affects root growth (Bloom et al. 1992). Roots thrive in soil zones rich in N, and while N is required for root growth, much of that N is supplied via from the aboveground portions of the plant.

Nitrogen assimilation is the process in which organic N is formed from inorganic N that is transported from roots to shoots (including leaves) through the xylem along with water. Most NO_3^- reduction to NH_3 occurs in the chloroplast of shoots, while NH_3 in the roots may be incorporated into amino acids at the root itself. Plants may also transport significant amounts of NH_4^+ in the xylem to the shoots. NH_3 that is either absorbed or synthesized from NO_3^- reduction is incorporated into amino acids to form the building blocks of proteins. All these steps of N assimilation require large amounts of energy supplied by carbon substrates from photosynthesis.

Partitioning of plant proteins and amino acids through translocation via phloem is governed by N demand. Actively growing plants with large crop loads that lack limitations for photosynthesis, other essential nutrients, and water result is a high N demand. Plants that are stunted in growth due to stress, deficiencies, or the prevalence of a pest or disease have lower N demand. The most abundant protein used by plants is the enzyme Rubisco, which is responsible for fixation of atmospheric carbon dioxide into energy-rich carbon molecules such as glucose. Plant proteins accumulate in reproductive parts like seeds that are either the harvestable portion of the crop or required for the next crop cycle. However, plant proteins have a finite lifespan and must be continually renewed. As a result, Rubisco is also an important N source for remobilization.

Nitrogen remobilization is another important process in the production of crops. Nitrogen is mobile and can be reallocated to seeds or new leaves or stored in woody tissue. During leaf senescence, liberated N can be transported to growing parts of the plant. Nitrogen uptake is often decreased during periods when N remobilization is active. Periods of senescence are most often associated with dormancy or the end of an annual cycle; however, biotic or abiotic stresses such as pathogens, competition, water, or heat can induce premature senescence. Thus, movement of N from one part of the plant to another part where N is required for ongoing growth and development is an important process to consider for overall N use efficiency, especially if N uptake is limited. See figure 4 for movement of N through plants via uptake,

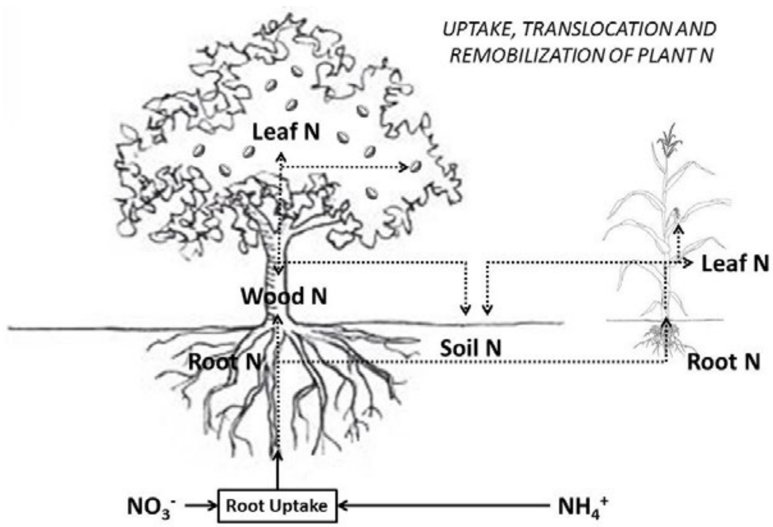

Figure 4. Root uptake of inorganic NH_4^+ and NO_3^- is translocated into roots and leaves. Inorganic N is converted to organic N like amino acids and proteins in leaves during N assimilation and partitioned to actively growing sinks. Remobilization of leaf N during senescence can move additional N into leaves or stored in wood of permanent crops. Crop residues in annual crops as well as leaves in deciduous permanent crop return N to soil.

translocation, and remobilization, as well as senescence of plant leaves or crops residues back into soil N.

Nitrogen Management

The soil and climate of California allow the production of a diverse array of crops. In upland soils (excluding paddy soils for rice), major California crops can be divided into agronomic annuals such as corn, wheat, and cotton; specialty annuals such as tomatoes, cole crops, and leafy greens, and strawberries; and specialty permanent crops such as nuts, deciduous fruits and grapes, and citrus and avocado. These crops have important differences in soil and irrigation management, crop N requirement and timing of uptake, and N removal from the field in harvested products. The following discussion highlights those differences with corresponding references for more crop specific information

Nitrogen management in corn varies due to the diversity of soils used for production and whether the planting is for grain or silage. Many acres of corn are in proximity to livestock operations like dairy farms and are supplied with N from manure spreading or the application of lagoon water. Since manure N depends on decomposition and lagoon water is high in NH_4^+, proper timing of subsequent irrigations can reduce leaching losses. Another important characteristic of corn production is the dependence of N remobilization from leaves to grain for efficient N use. For more detailed information on N management in corn see Mathews, forthcoming.

Nitrogen management in wheat is affected by the crop's low profit potential; N efficiency is a key to profitability. The quality of wheat depends on its protein content, and N management can affect both quality and yield. Currently, a number of monitoring tools are under development to assist the wheat grower with in-season N management decisions. For more detailed information on N management in wheat see Lundy et al., forthcoming.

Nitrogen management in cotton seeks to avoid excess N and maximize N use efficiency. Consequences of excessive N input include an imbalance of vegetative and reproductive growth and more severe insect pressure. Another motivation to avoid excess N is the greater difficulty to induce defoliation that can complicate field preparations prior to harvest. For more detailed information on N management in cotton see Hutmatcher et al., forthcoming.

Nitrogen management in tomato seeks to supply N in concert with crop uptake; this is possible because most fields are drip irrigated. Many tomato growers practice limited rotations, and adjustment of N application to account for residual soil NO_3^- is important to efficiency. For more detailed information on N management in tomato see Hartz 2018.

Nitrogen management in cole crops and leafy greens is affected by the dynamic rotations in which these crops are grown; it is not uncommon for two or three crops per year to be produced in a given field. These crops have quite different N uptake requirements and N removal from harvest, so crop sequence can be important to efficient N management. High NO_3^- content of coastal wells can have a significant impact on N fertilizer requirement. For more detailed information on N management in cole crops and leafy greens see Hartz, Cahn, and Smith 2018.

Nitrogen management in strawberries is affected by the crop's unusual crop growth pattern. Fields are planted in the fall, but limited growth does not occur until spring. Nitrogen efficiency requires sufficient N availability during winter to support the limited growth, while restricting the amount of soil N susceptible to leaching with winter rain. Even at maximum summer growth, rates of crop N uptake is lower than that of most other annual crops. For more detailed information see Hartz, Cahn, and Bolda 2018.

Nitrogen management in tree nuts uses efficient strategies for high N use where timing of application is important. In-season N demand is low until early March as the N required for flowering, early leaf growth, and early nut growth comes from tree N reserves. Later in spring and into August, tree demand is high, as nut growth is rapid. Postharvest uptake is low while active remobilization moves N from leaves into tree storage. As nut trees mature, the proportion of N allocated to vegetation decreases. Thus, yield drives N demand. Early leaf sampling protocols have been developed to help growers determine the potential of N deficiency. For more detailed information see Muhammad et al. 2018b.

Nitrogen management in deciduous fruits and grapes requires greater attention to vegetative growth. The largest proportion of N demand goes into leaf and shoot growth. After harvest, N storage through remobilization decreases N demand. Furthermore, much of the N allocated to vegetative growth is returned to the soil as leaf litter and prunings. Patterns of N management are similar with table grapes. Table grape N budget can vary, since N demand for vegetative growth depends on vine spacing and trellis systems. For more detailed information see Khalsa et al., 2018.

Nitrogen management in citrus and avocado is contingent on different seasons for growth and development. Rapid N uptake occurs from April to November and is contrasted with the period from November to March, when no net uptake occurs. Uptake is low from December to February because demand is low from remobilization of N from shoot to fruit that satisfies fruit N demand. As trees mature, the proportion of N allocated to vegetation decreases. For avocado, N timing seems to have more of an impact on yield than does the overall N rate. For more detailed information see Muhammad et al. 2018a.

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