Terrestrial Nutrient Cycling

- Objectives
  - Inputs, internal transfers, and outputs (losses) of nutrients from ecosystems (= Nutrient cycling)
    - N and P
  - Differences among major elements in biogeochemical cycling

Terrestrial Nutrient Cycling

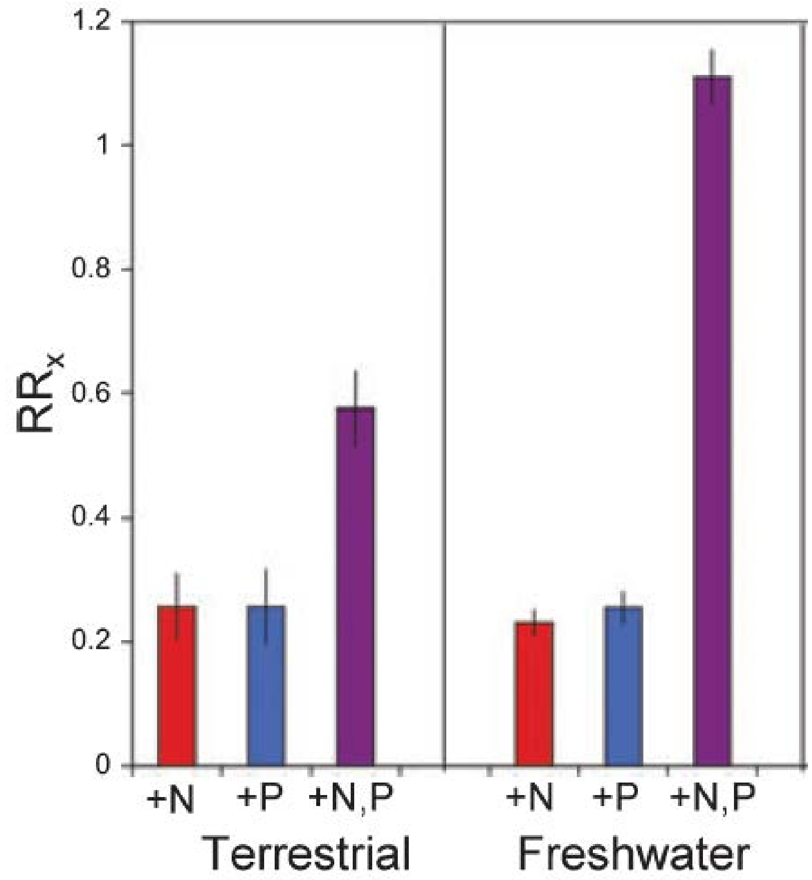
- All organisms need a suite of nutrients to carry out metabolic processes and produce biomass
  - Macronutrients vs. micronutrients
- What is typically the most limiting nutrient in terrestrial ecosystems
  - N, right?
- What is typically the most limiting nutrient in freshwater ecosystems
  - P, right?

Terrestrial Nutrient Cycling

- Elser et al. (2007) compiled data from field studies that manipulated N and/or P supply in terrestrial (173), freshwater (653), and marine (243) ecosystems
  - Net primary production (NPP)
    - Relative increase in NPP with nutrient enrichment
- Meta-analysis to test dominant paradigms about nutrient limitations to productivity of terrestrial and aquatic ecosystems

Terrestrial Nutrient Cycling

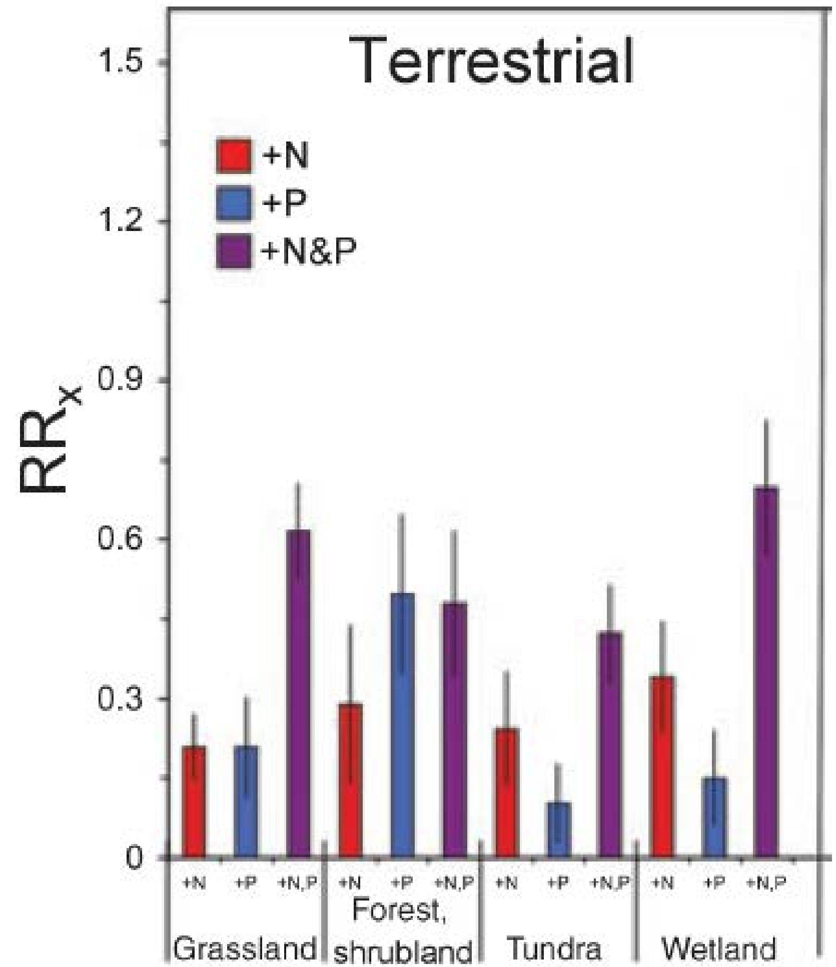
- Across diverse ecosystem types:
  - N & P limitations are equally important in both systems
  - Combined N & P enrichment produces strong synergistic effects → co-limitation
  - Magnitude of the response to N and P enrichment is ~similar between terrestrial and freshwater systems



Elser et al. (2007)

Terrestrial Nutrient Cycling

- Important differences across ecosystem types
- Resource co-limitation evident in most ecosystem types



Elser et al. (2007)

Terrestrial Nutrient Cycling

- Harpole et al. (2011) compiled data from 641 plant communities and found that:
  - >½ studies showed synergistic responses to N & P additions
  - Support for strict co-limitation in 28% of studies
  - Interactions between N & P regulate primary producers in most ecosystems
  - *"Our concept of resource limitation has shifted over the past two decades from an earlier paradigm of single-resource limitation towards concepts of co-limitation by multiple resources…"*

Terrestrial Nutrient Cycling

- Human imprint on nutrient cycling:
  - Substantial alteration of all nutrient cycles
    - >100% increase in N cycling
    - >400% increase in P cycling
  - Leads to more “open” (or “leaky”) cycles of nutrients
  - What are the impacts of increased nutrient cycling (and availability) on ecosystem processes?
    - Belowground resource supply largely controls rates of ecosystem C and H_2O cycling → Increased nutrient supply will have large and important consequences for ecosystem structure and function

Terrestrial Nutrient Cycling

- Human imprint on nutrient cycling:

Table 3. Budgets for nitrogen on the global land surface

	Pre-industrial	Human derived	Total
Inputs			
Biological nitrogen fixation	120	20†	140
Lightning	5	0	5
Industrial N-fixation	0	125‡	125
Fossil fuel combustion	0	25	25
Totals	125	170	295
Fates			
Biospheric increment	0	9	9
Riverflow	27	35	62
Groundwater	0	15	15
Denitrification	92*	17	109
Atmospheric transport to the ocean	6	48	54
Totals	125	124	249

All values are TgN/yr. Unless otherwise indicated, preindustrial values and human-derived inputs are for the mid-1990s from Galloway *et al.* (43) and Duce *et al.* (22). Fates of anthropogenic nitrogen are derived in this paper.
*To balance.
†Net of human activities.
‡Ref. 89 for 2007.

Schlesinger et al. (2000)

Terrestrial Nutrient Cycling

- Nutrient Inputs to Ecosystems:

1. Lateral Transfer
2. Rock weathering
   - P, K, Ca, other cations
   - N only in sedimentary rocks & in limited supplies
3. Biological fixation of atmospheric N
   - Main input of N to undisturbed systems
4. Deposition (rain, dust, gases)
   - Most important for N and S, but occurs for all nutrients
   - Natural or anthropogenic

Terrestrial Nutrient Cycling

- Internal transfers
  - Mineralization
    - Organic to inorganic forms; catalyzed by microbial activity
  - Chemical reactions from one ionic form to another
  - Uptake by plants and microbes
  - Transfers of dead organic matter (e.g., litterfall)
  - Exchange of nutrients on surfaces within the soil matrix (e.g., CEC)
  - Movement down the soil profile with H_2O (but not leached out of the system)

Terrestrial Nutrient Cycling

- Plant nutrient demand is largely met by internal transfers
  - Most natural systems are “closed” systems with conservative nutrient cycles

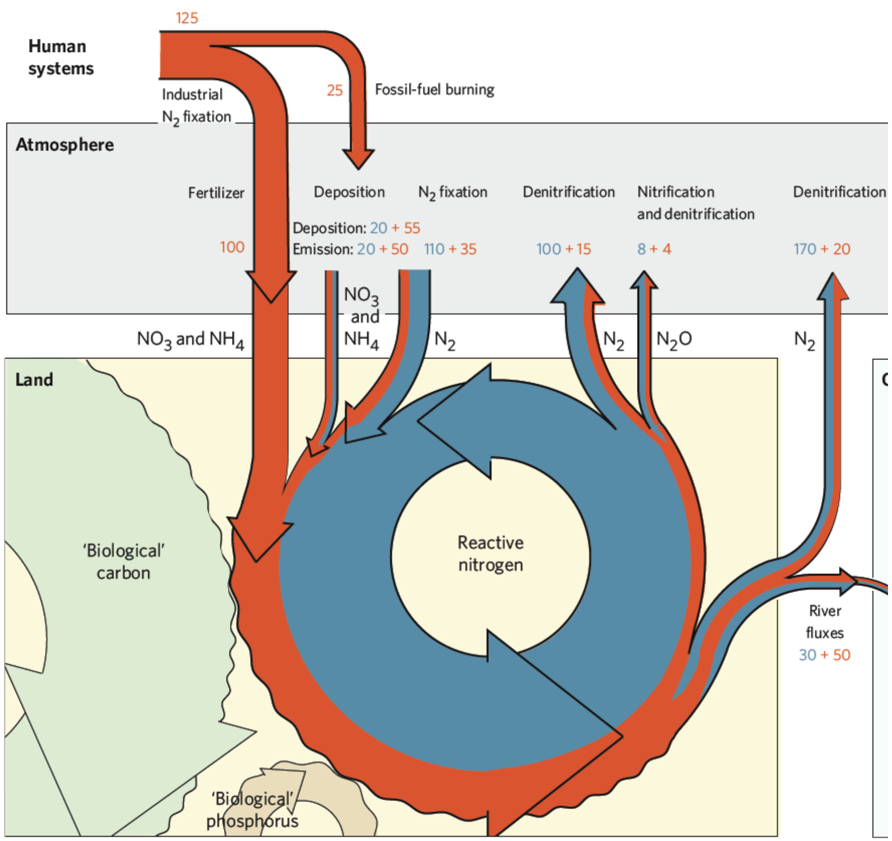
Table 7.1. Major Sources of Nutrients that Are Absorbed by Plants[a].

	Source of plant nutrient (% of total)		
Nutrient	**Deposition/fixation**	**Weathering**	**Recycling**
Temperate forest (Hubbard Brook)			
Nitrogen	7	0	93
Phosphorus	1	< 10	> 89
Potassium	2	10	88
Calcium	4	31	65
Tundra (Barrow)			
Nitrogen	4	0	96
Phosphorus	4	< 1	96

[a] Data from (Whittaker et al. 1979, Chapin et al. 1980b)

Terrestrial Nutrient Cycling

- Plant nutrient demand is largely met by internal transfers



Gruber & Galloway (2008)

Terrestrial Nutrient Cycling

- Losses (outputs)
  - Leaching
  - Gaseous loss (trace-gas emission)
  - Wind and water erosion
  - Disturbances (e.g., fires, harvest)

Simplified N Cycle

Terrestrial Nutrient Cycling

- Nitrogen Fixation
  - Main input of N to terrestrial ecosystems under natural/pristine/unpolluted conditions
  - Conversion of atmospheric N_2 to NH_4^+ by nitrogenase enzyme
  - Requires abundant energy, P, and other cofactors
  - Inhibited by oxygen (anaerobic process)
    - Leghemoglobin in plant nodules scavenges O_2 & produces anaerobic conditions
  - Minimal at low temperatures

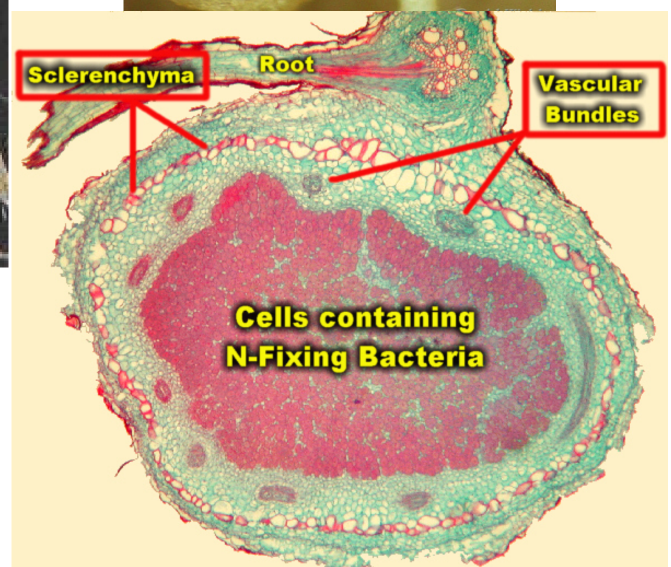
Terrestrial Nutrient Cycling

- Carried out exclusively by microbes
  1. Symbiotic N fixation (*Rhizobium, Frankia*)
     - ~5 - 20 g N m^{-2} yr^{-1}
  2. Heterotrophic N fixation (rhizosphere, decaying wood, other carbon-rich environments)
     - ~0.1 - 0.5 g N m^{-2} yr^{-1}
  3. Photoautotrophs (cyanobacteria; lichens; mosses)
     - ~2.5 g N m^{-2} yr^{-1}
  – ***All this N becomes available to other organisms via production & decomposition of N-rich litter
     - Enters the internal transfer/recycling loop

Rhizobium and *Frankia* nodules

Legume/*Rhizobium* nodules

Leghemoglobin (red)



Schlerenchyma reduces O_2 diffusion into the nodule

Alnus/*Frankia* nodules

Terrestrial Nutrient Cycling

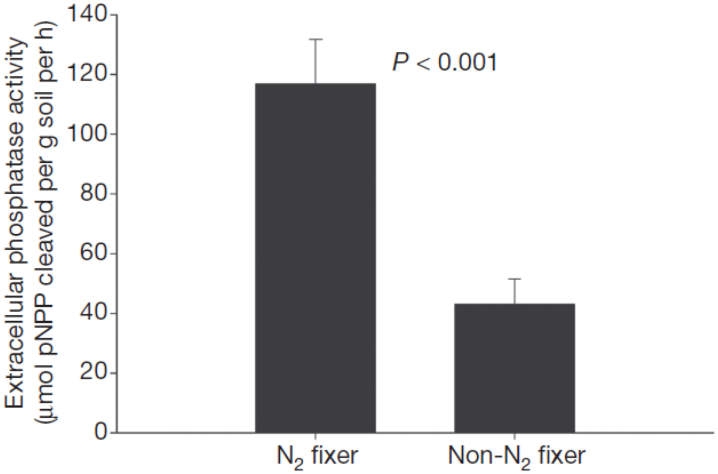
- Paradox of N limitation and fixation:
  - N frequently limits terrestrial NPP
    - N_2 is the most abundant component of the atmosphere, but it is not available to most organisms
      - Why?
  - Why doesn’t N fixation occur everywhere and in all species???
    - Occurs most frequently in P-limited tropical ecosystems (Houlton et al. 2008)
  - Why don’t N fixers always have a competitive advantage (at least until N becomes non-limiting)???

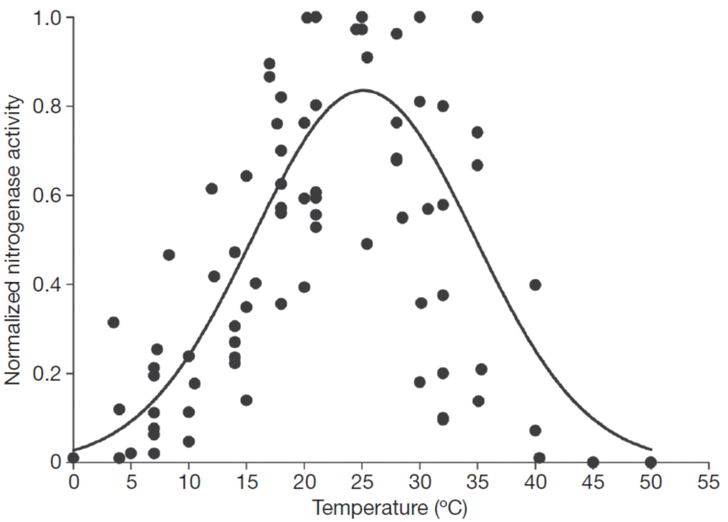
Terrestrial Nutrient Cycling

- Limitations to N fixation exist
  - Energy availability in closed-canopy ecosystems is low
    - N fixation cost is 2-4x higher (3-6 g C per 1 g N) than cost of absorbing NH_4^+ or NO_3^- from the soil solution
    - Restricted to high-light environments where C gain is high, competition for light is low, and inorganic N is not abundant
  - Nutrient limitation (e.g., P; or Mo, Fe, S)
    - Nitrogenase requires P and Fe, Mo & S cofactors to reduce N_2
    - May be the ultimate control over N fixation in many systems
  - Grazing / Consumption
    - N fixers are often preferred forage for herbivores

Terrestrial Nutrient Cycling

- Limitations to N fixation exist (Houlton et al. 2008)
  - Advantage to symbiotic N fixers in P-limited tropical savannas and lowland tropical
    - Ability of N fixers to invest nitrogen into P acquisition
  - Temperature constrains N fixation rates and N-fixing species from mature forests in the high latitudes

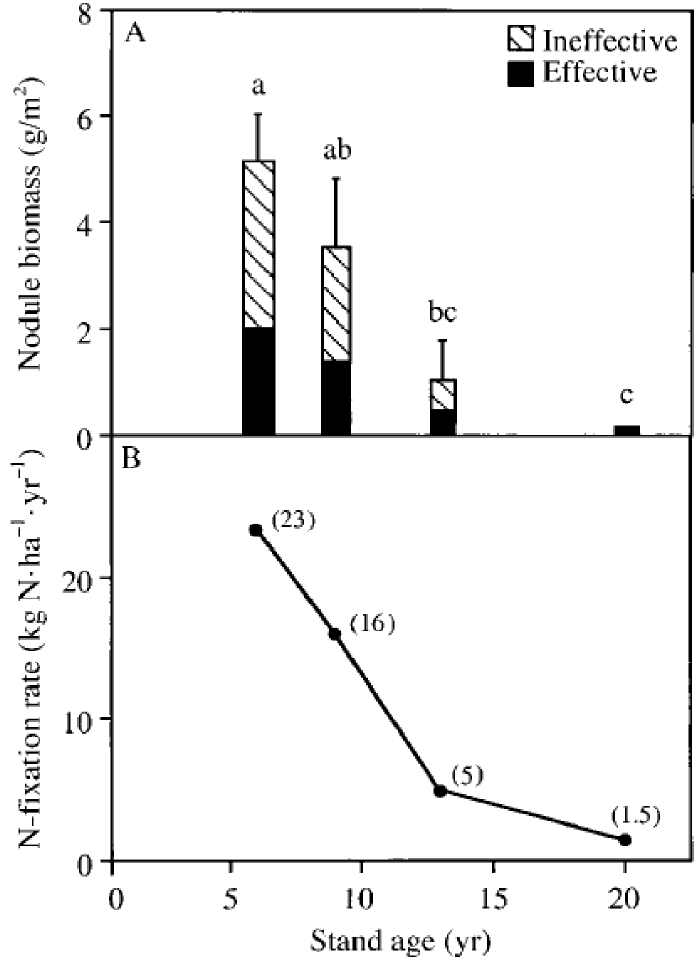




Terrestrial Nutrient Cycling

- N fixation typically declines with stand age
  - Other forms of N become more available
  - N fixation cost becomes too high
  - P (or some micro-nutrient) becomes limiting
  - GPP decreases and/or C partitioning shifts from below- to aboveground?

Acacia koa

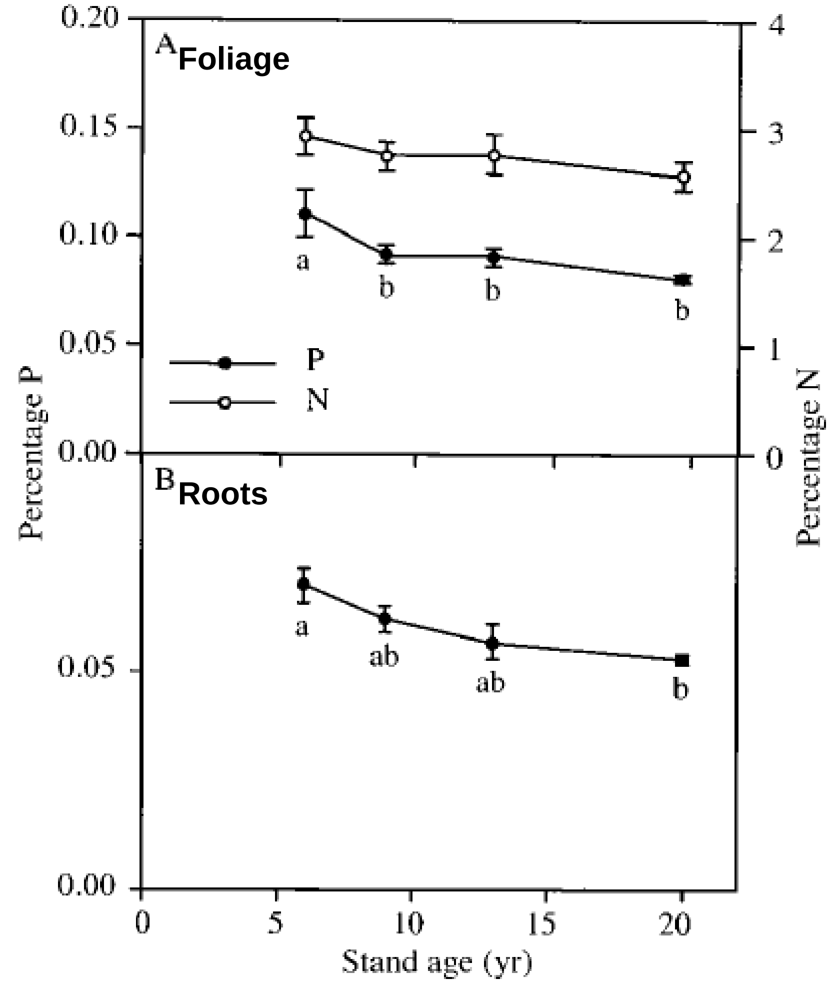


Pearson & Vitousek (2001)

Terrestrial Nutrient Cycling

- Foliar N ~constant
- Foliar and root P decreased with age
  - N fixation is P limited in this ecosystem
    - ???

Acacia koa



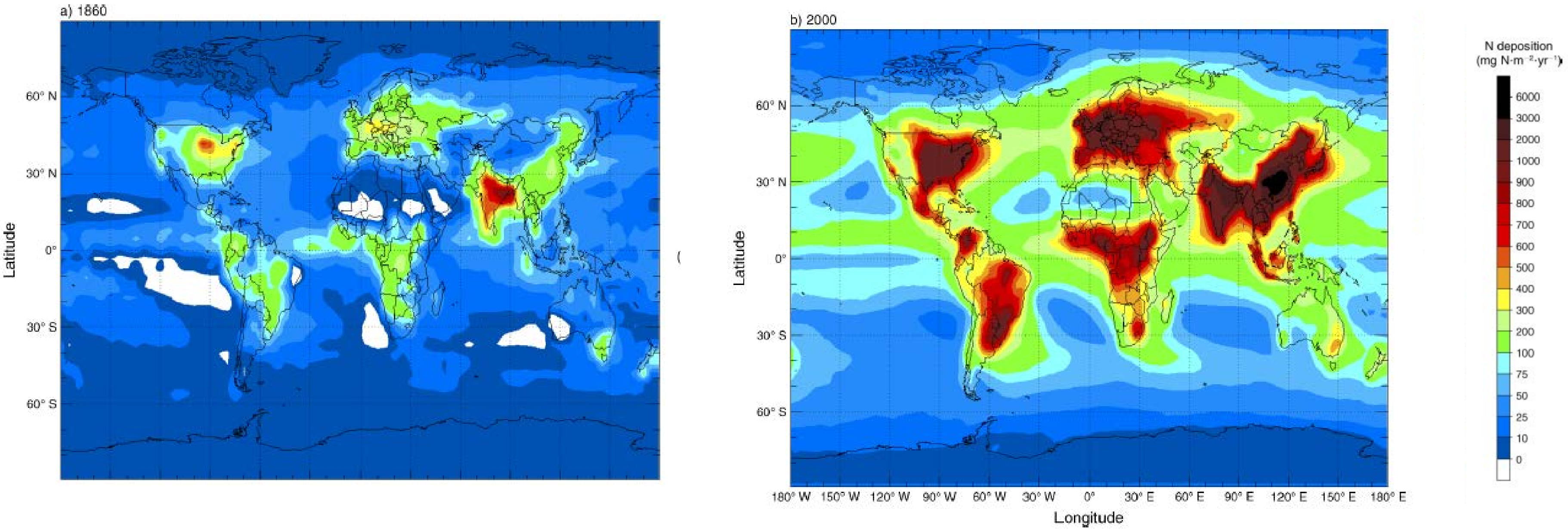
Pearson & Vitousek (2001)

Terrestrial Nutrient Cycling

- N Deposition
  - ~0.2 - 0.5 g N m^{-2} yr^{-1} in undisturbed systems
  - Dissolved, particulate, and gaseous forms
    - Wet deposition, cloud-water deposition, dry deposition
  - Human activities are now the major source of N deposition (1 - 10 g N m^{-2} yr^{-1}; 10-100x natural rates)
    - Burning of fossil fuels (NO_x flux is 80% anthropogenic)
    - Fertilizer use & domestic husbandry
      - NH_3 to atmosphere $\rightarrow$ NH_4^+ deposition on land
    - Substantial capacity of ecosystems to store this N
      - Eventually, losses to atmosphere and groundwater ↑↑↑

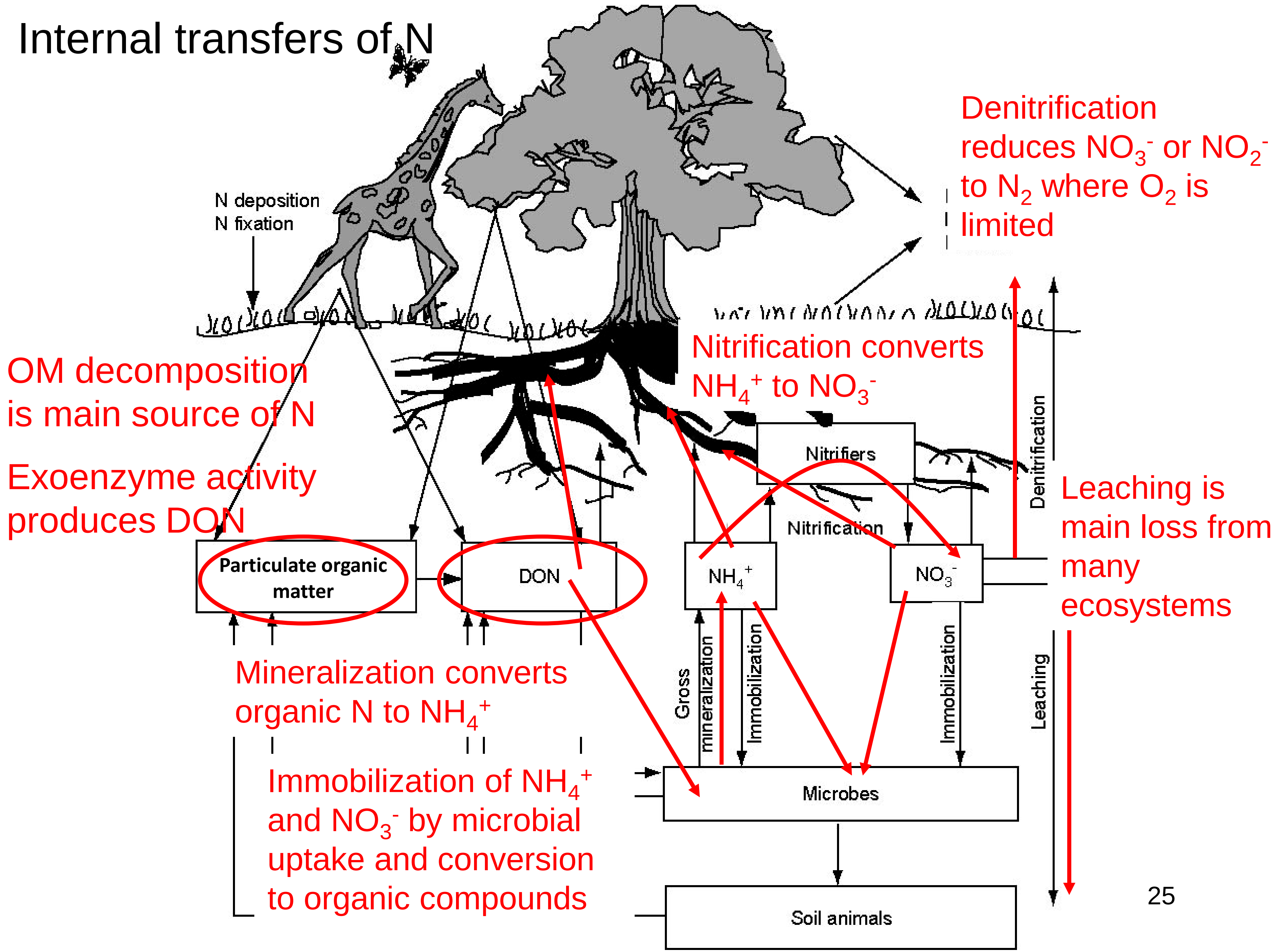
Terrestrial Nutrient Cycling

- N Deposition



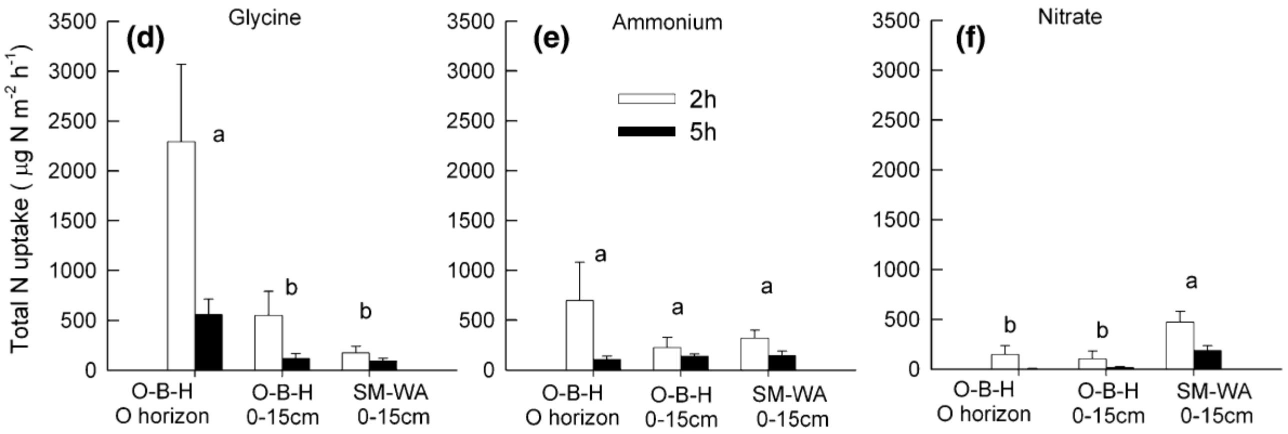
Bobbink et al. (2010)

Internal transfers of N



Terrestrial Nutrient Cycling

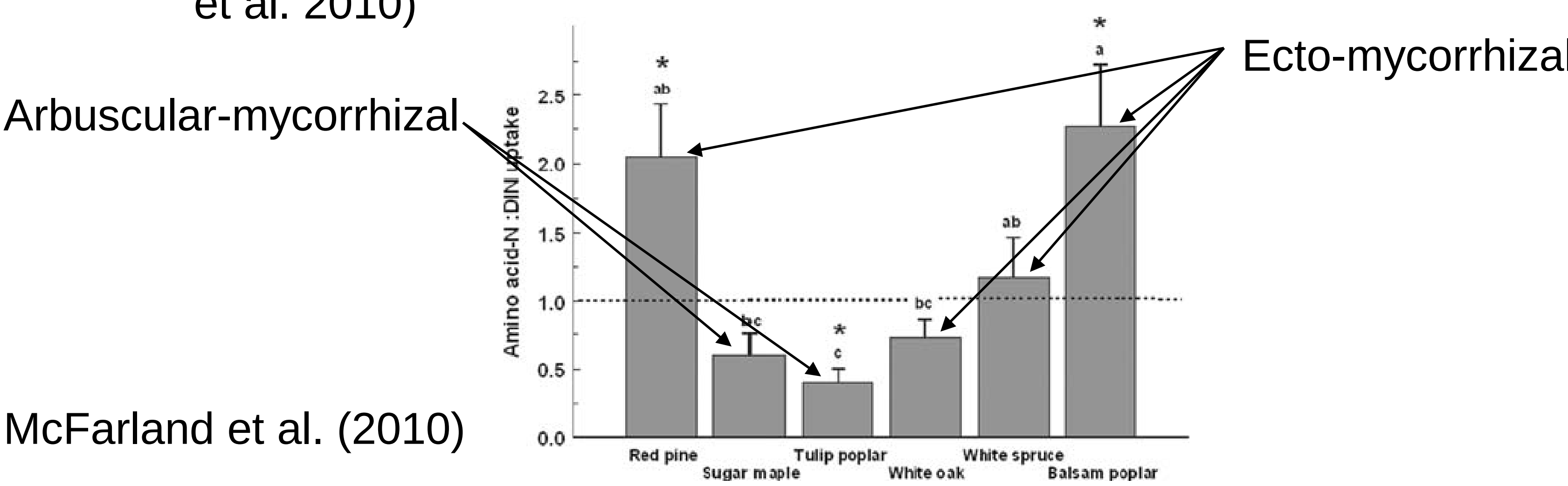
- DON Uptake by plants (amino acids; glycine)
  - Can be an important source of N to plants in at least some systems
    - O-B-H = 77% of Total N uptake
      - Recalcitrant litter, slow N cycling, and thick amino-rich organic horizon
    - SM-WA = 20% of Total N uptake
      - Labile litter and high rates of amino acid production and turnover (i.e., rapid mineralization and nitrification)



Gallet-Budyanek et al. (2010)

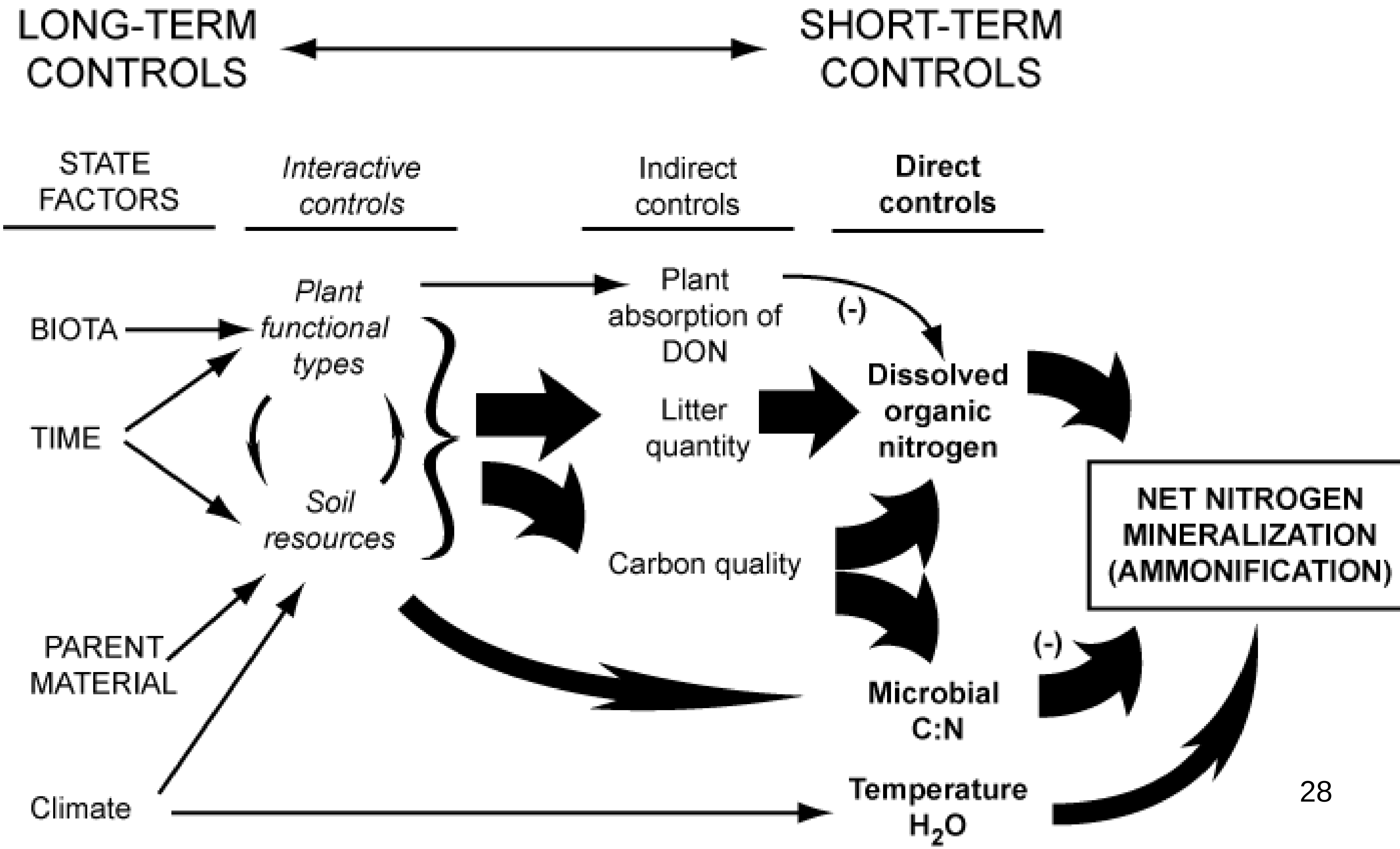
Terrestrial Nutrient Cycling

- DON Uptake by plants (amino acids; glycine)
  - "*We conclude that while root uptake of amino acids in intact form has been shown, evidence demonstrating this as a major plant N acquisition pathway is still lacking*." (Jones et al. 2005)
  - "*We conclude that free amino acids are an important component of the N economy in all stands studied; however, in these natural environments plant uptake of organic N relative to inorganic N is explained as much by mycorrhizal association as by the availability of N forms per se*." (McFarland et al. 2010)



McFarland et al. (2010)

Mineralization results from microbial break-down of SOM, releasing “excess” NH_4^+ as microbes use C



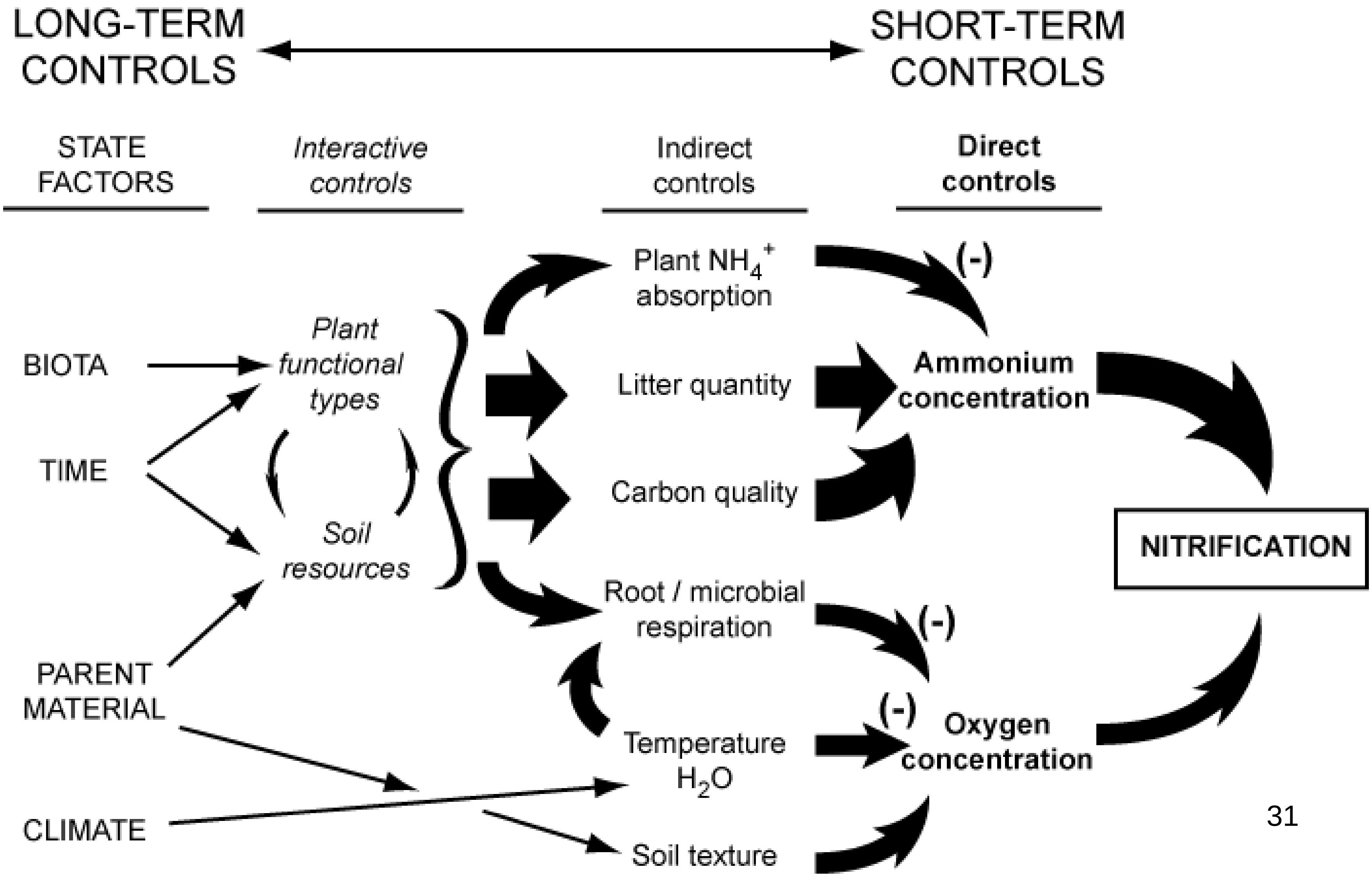
Terrestrial Nutrient Cycling

- Immobilization of NH_4^+ depends on C status of microbes
- Many microbes are C-limited, so they use the C skeleton and excrete excess N as NH_4^+
  - Gross mineralization = the total amount of NH_4^+ released by mineralization (i.e., ammonification)
- Some microbes are N-limited, which results in immobilization (at least temporarily)
  - Critical C:N of litter is ~25
- Net mineralization is “excess” NH_4^+ (and NO_3^-)
  - Net = gross mineralization - immobilization (- loss)

Terrestrial Nutrient Cycling

- N mineralization rate
  - Depends on:
    - Availability of substrate (DON)
    - Availability of NH_4^+ in soil solution
    - C:N ratios in microbes and substrates
    - Microbial activity and growth efficiency
  - NH_4^+ can be adsorbed onto clays, volatilized as NH_3 and/or used in nitrification reactions
    - N "loss" pathways substantially reduce net N mineralization below gross N mineralization
      - Plants/mycorrhizae excluded from mineralization assays

Nitrification: nitrifying bacteria convert NH_4^+ to NO_2^- and then NO_3^-

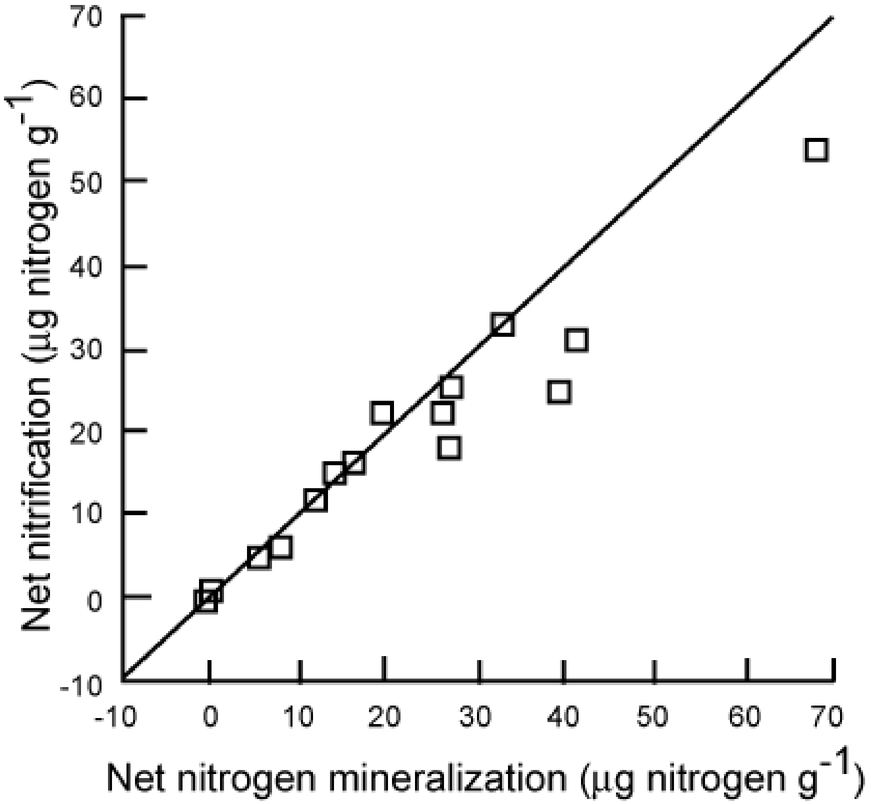


Terrestrial Nutrient Cycling

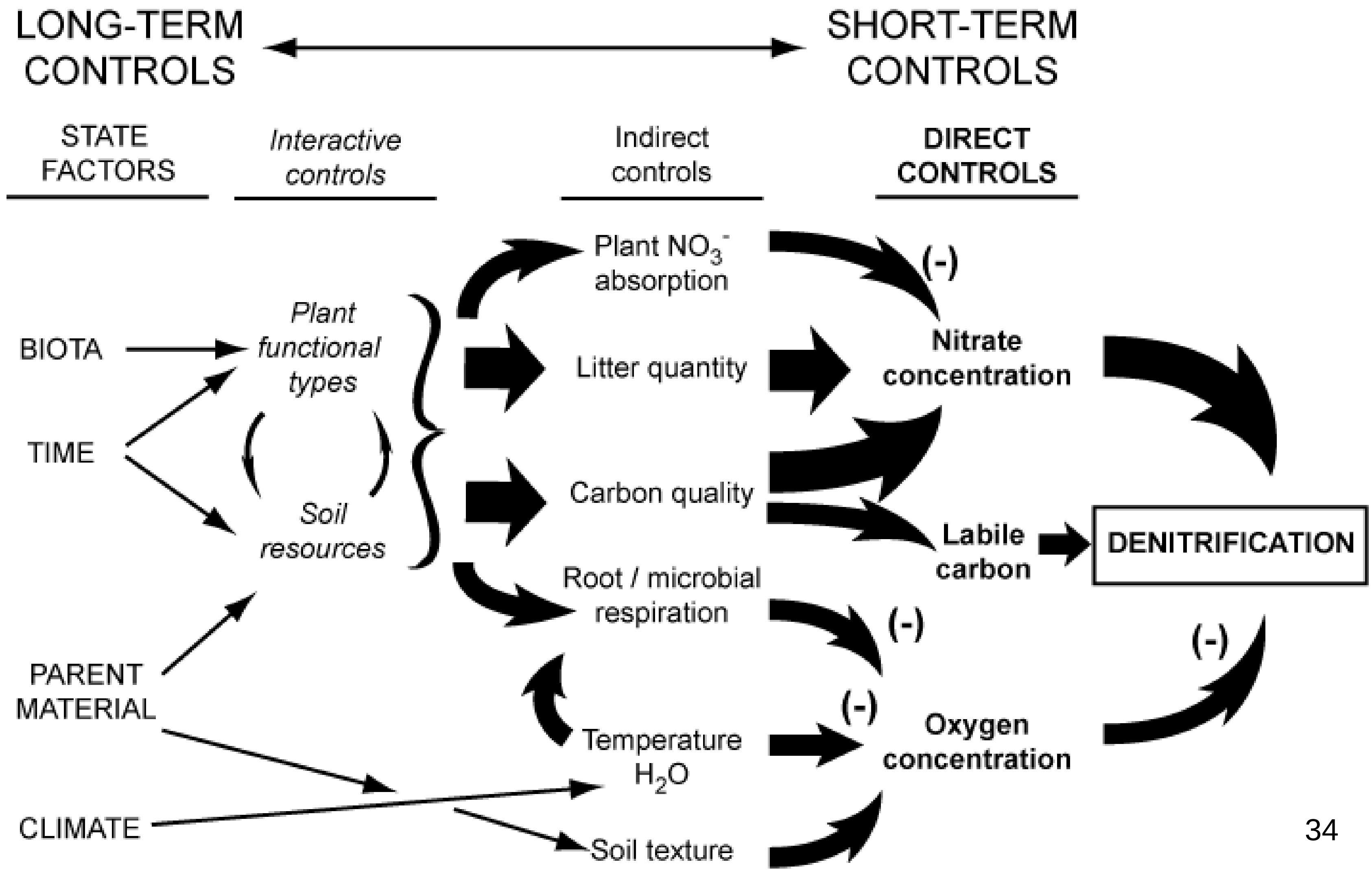
- Nitrification is a 2-step process
  - $NH_4^+ \rightarrow NO_2^-$ (*Nitrosolobus*); then $NO_2^- \rightarrow NO_3^-$ (*Nitrobacter*)
    - Chemoautotrophs that gain energy from NH_4^+ or NO_2^- oxidation
- NH_4^+ availability is most important determinant of nitrification rate
  - Also need O_2 (aerobic process)
- Heterotrophic nitrification is generally less important and less well understood
- % of NH_4^+ that undergoes nitrification?
  - 0-4% in temperate forests; 100% in tropical forests

Terrestrial Nutrient Cycling

- % of soil NH_4^+ that undergoes nitrification?
  - <25% in temperate forests vs. 100% in tropical forests



Denitrification occurs where low O_2, high NO_3^-, and sufficient organic C occur



Terrestrial Nutrient Cycling

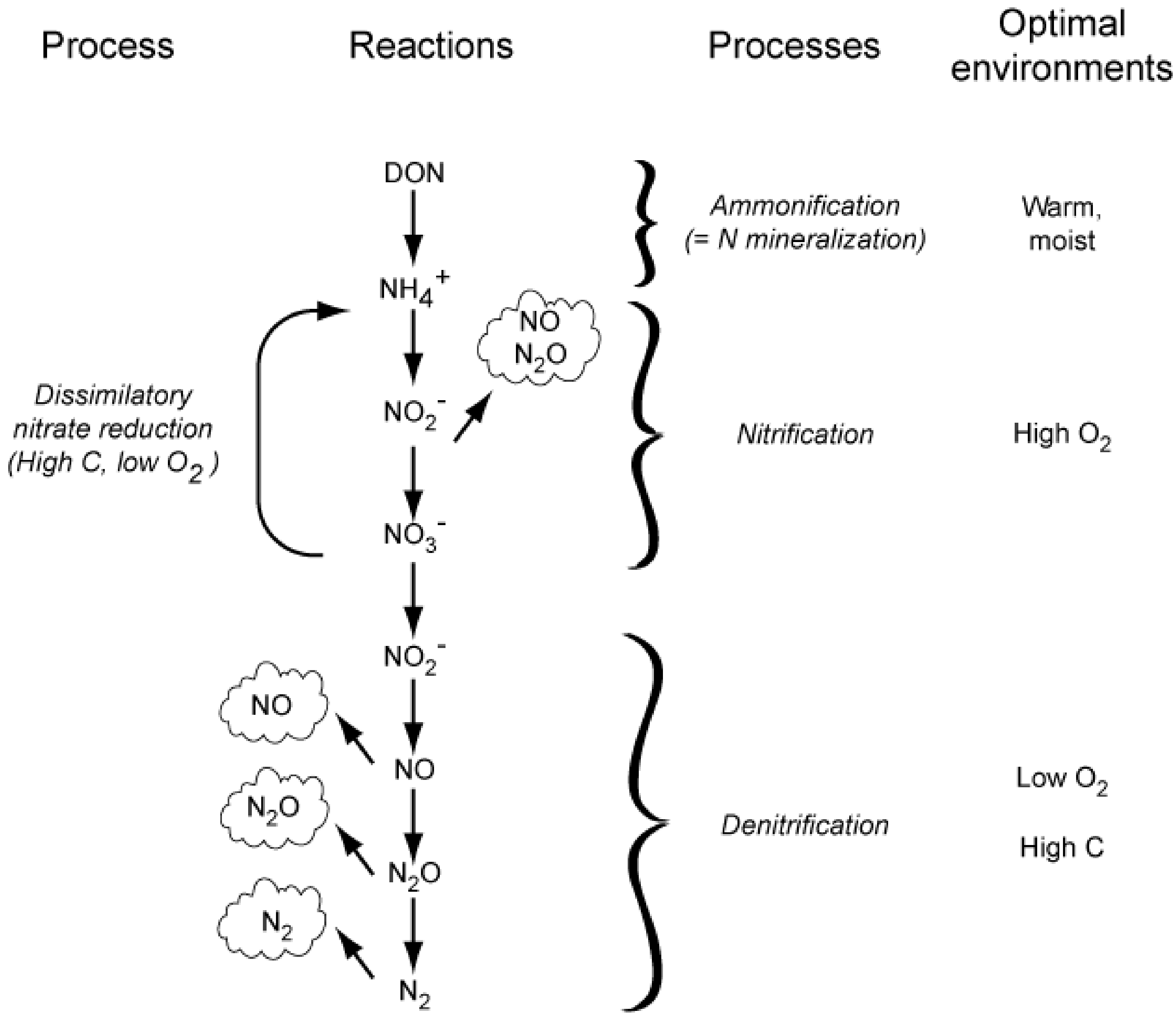
- Denitrification:
  - Produces NO and N_2O, and N_2 in anaerobic conditions
    - NO and N_2O, also produced during nitrification, are important greenhouse gases
  - NO_3^- supply is main limitation
    - NO_3^- is produced in aerobic conditions?
  - Mainly heterotrophic
    - Organic C supply is necessary
      - Use NO_3^- as an electron acceptor to oxidize organic C for energy
  - Soils where O_2 supply is spatially or temporally variable have highest denitrification rates

Terrestrial Nutrient Cycling

- N loss (output) pathways:

1. Gaseous losses
   - NH_4^+ volatilization to NH_3 (pH > 7)
   - Nitrification releases NO, N_2O
   - Denitrification releases NO, N_2O, N_2
2. Solution losses (NO_3^-) / leaching
   - Important pollutant w/ disturbance; where N deposition → N saturation; ag fields; feedlots
3. Erosion
4. Disturbance (fire, harvesting, etc.)

Processes involved in N cycling and gaseous emissions

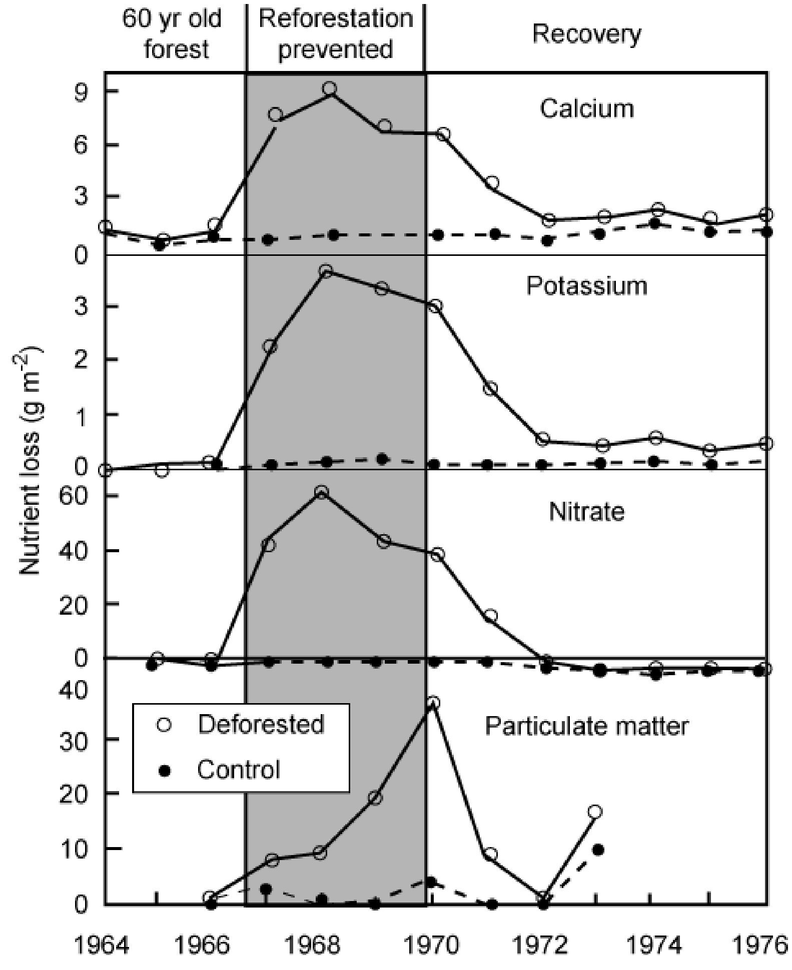


Terrestrial Nutrient Cycling

- N gaseous “species”
  - NH_3 reduces atmospheric acidity as it is converted to NH_4^+, which can be deposited elsewhere
  - NO & NO_2 (NO_x) are highly reactive
    - Lead to formation of tropospheric O_3 (smog)
    - Large contributors to acid rain and N deposition
  - N_2O is relatively long-lived (150 yrs) and not chemically reactive in troposphere
    - Potent greenhouse gas (200x more effective than CO_2)
    - Destroys stratospheric O_3
  - N_2 dominates atmosphere (78%) and has a MRT of 13,000,000 years

Terrestrial Nutrient Cycling

- N loss (output) pathways:
  - –N solution losses can be high with:
    - High N deposition
    - Disturbance
  - –Primarily NO_3^- is lost via leaching
    - Can lead to important loses of cations to maintain balanced charge in soil soution



Bormann & Likens (1979)

Terrestrial Nutrient Cycling

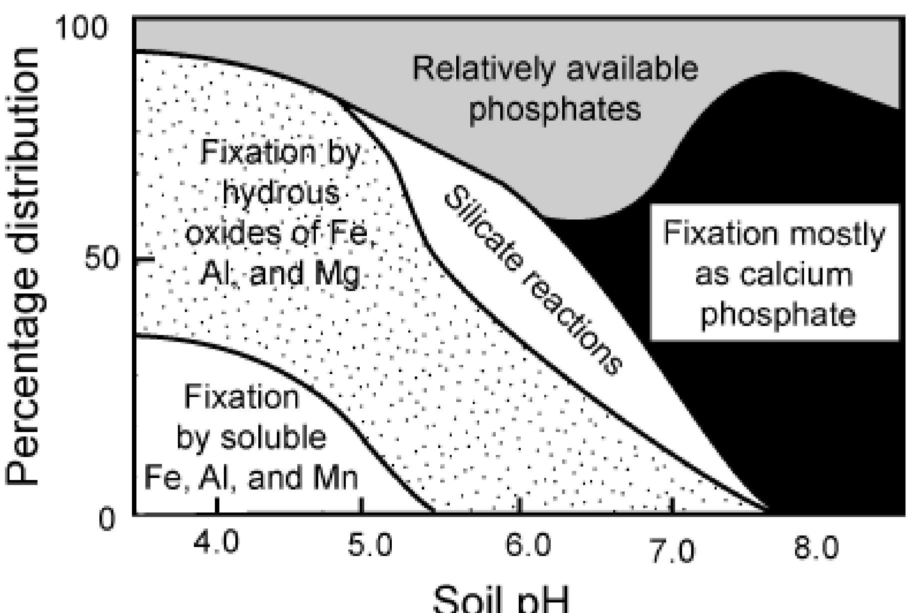
- Phosphorous cycling:
  - Weathering of primary minerals (apatite) is main input of new P into ecosystems
    - $Ca_5(PO_4)_3 + H_2CO_3 \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4HCO_3^{-} + H_2O$
    - Phosphate (PO_4^{3-}) is primary form of available P in soils
  - Phosphate does not undergo redox reactions
  - No important gas phases; only dust in atmosphere
  - Internal transfers predominate (esp. in old sites)
    - Organic P is bound to C via ester linkages (C-O-P)
      - P availability not as closely tied to decomposition as N
    - Roots and mycorrhizae produce phosphatase enzymes that cleave these linkages without breaking down C skeleton

Terrestrial Nutrient Cycling

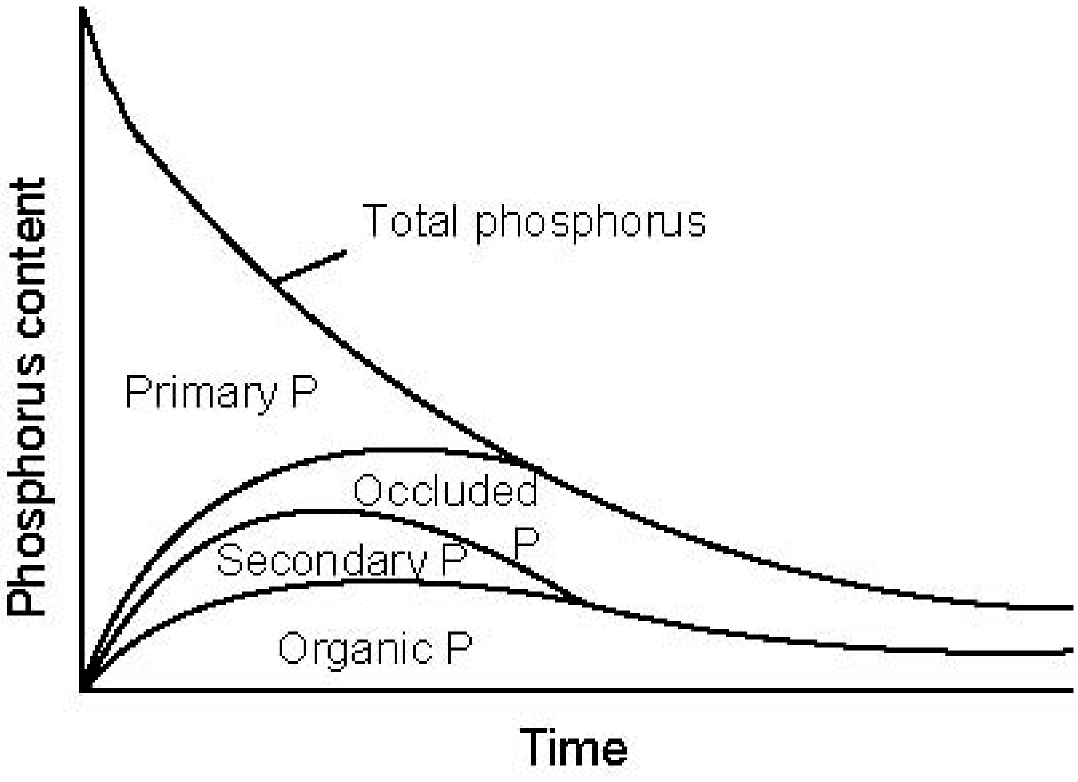
- Phosphorous cycling:
  - Inorganic P from weathering & decomposition can be:
    1) Taken up by plants and microbes
       - Tight cycling of P between organic matter and plant roots
       - Microbes account for 20-30% of organic P in soils
         - » C:P controls balance between mineralization & immobilization
    2) Adsorbed onto soil minerals (unavailable)
    3) Precipitated out of solution (unavailable)
       - Due to 2 & 3, ~90% of P loss occurs via surface runoff and erosion
  - P often limits ecosystem development over long time periods as primary minerals weather
    - Deposition becomes important source of P as ecosystems age (i.e., as substrate weathers)

Terrestrial Nutrient Cycling

- Much of the P cycle in soils is geochemical
  - At low pH, 'fixation' by Fe, Al, Mn and Mg oxides dominates
  - At high pH where $CaCO_3$ is present, P is 'fixed' as $Ca_3(PO_4)_2$
  - Occlusion ('fixation') of P makes it unavailable
    - Over ecosystem development, P typically becomes the primary limiting nutrient (over long time scales)

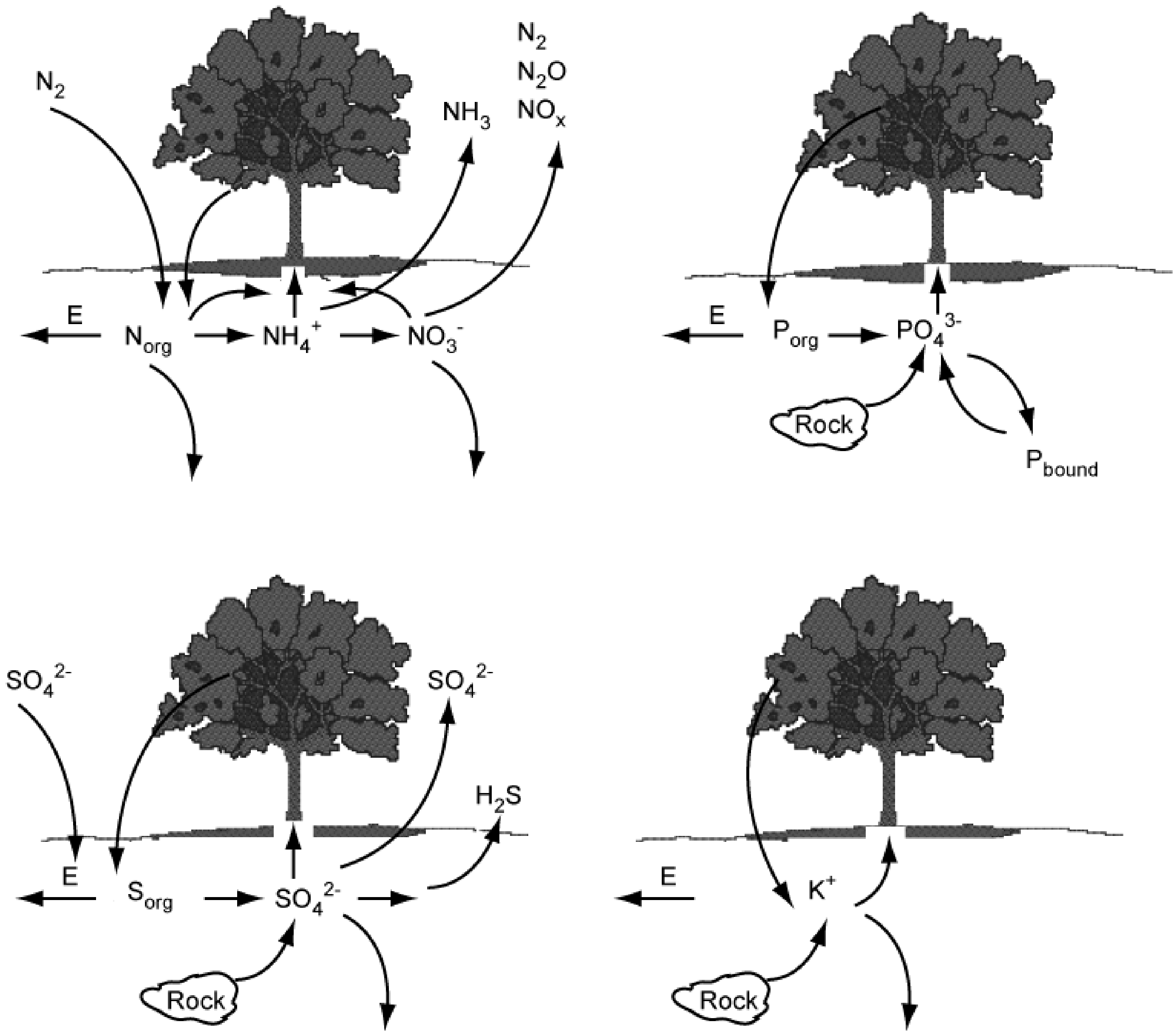


Terrestrial Nutrient Cycling



Walker and Syers (1976)

Contrasting Biogeochemical Cycles



Terrestrial Nutrient Cycling

- Interactions among Element Cycles
  - Supply rate of the most limiting nutrient largely determines rate of cycling of all essential nutrients
    - Function of absorption by vegetation
      - Dynamic balance between rate of supply in soil and nutrient demands of vegetation
    - Vegetation has a limited range of element ratios (stoichiometry)
    - Most strongly limiting element has greatest impact on NPP
      - Absorption of other elements is adjusted to maintain relatively constant stoichiometry
      - But plants can absorb more nutrients than they need (to a certain point) and “store” them for later
    - Many/most ecosystems characterized by nutrient co-limitation