Tree Essential Elements Manual (Part 3)

(water, nitrogen issues & element problems)

Dr. Kim D. Coder, Professor of Tree Biology & Health Care / University Hill Fellow
University of Georgia Warnell School of Forestry & Natural Resources

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
1785
Warnell School of Forestry
& Natural Resources

Scope & Disclaimer: This training manual is part 3 of a three part educational product designed for helping tree health care professionals appreciate and understand essential element requirements in trees. This manual is a synthesis and integration of current research and educational concepts regarding how trees utilize different essential elements and how diagnosis of essential element problems can be difficult. This educational product is for awareness building and professional development. This product does not present tree essential element fertilization processes or product formulations. This is not a tree health care fertilization standard.

At the time it was finished, this training manual contained educational models concerning tree essential elements thought by the author to provide the best means for considering fundamental tree health care issues surrounding essential element use, deficiencies and toxicities. The University of Georgia, the Warnell School of Forestry & Natural Resources, and the author are not responsible for any errors, omissions, misinterpretations, or misapplications from this educational product. The author assumed professional users would have some basic tree and soil background. This manual was not designed, nor is suited, for homeowner use. Always seek advice and assistance of professional tree health care providers.

This training manual is copyrighted by the author. This educational product is only for noncommercial, nonprofit use and may not be copied or reproduced by any means, in any format, or in any media including electronic forms, without explicit written permission of the author. This manual is a revision and correction of previous publications by the same author published in May of 2011, July of 2012, and March of 2017.

Scientific Citation:
> Coder, Kim D. 2021. **Tree Essential Elements Manual (Part 3).** University of Georgia Warnell School of Forestry & Natural Resources Outreach Publication WSFNR21-19C. Pp.68.

**UNIVERSITY OF
GEORGIA**
Warnell School of Forestry
& Natural Resources

Tree Essential Element Manual

Water: The 20ᵗʰ Essential "Element"

     A critical inorganic component of tree life is water. Roughly 80% of all variation in tree growth is water related, either through water concentration in the soil, aeration interactions, and/or drainage in the soil. Water is an essential "element" of trees. Although it is composed of two essential elements, it functions as a critical feature of everything living. Water dissolves, surrounds, transports, and buffers essential elements. An essential element bath and coating of life is provided by water.

     Water is the catalyst of life. When water availability is constrained at minute levels, life slows, declines, and fails. The properties of water make it both unusual chemically and critical biologically. Water is relatively tiny as a compound, but acts large because of its electro-chemistry. Tree water is a solution and stage of living processes. Water acts as an essential "element" of tree life.

Essentially Wet!
     Water is essential to tree life as well as the most limiting resource. The value of water lies with its chemical properties, physical reactions, and biological uses. Figure 1. Water is the single most important molecule in trees as well as the ecological systems which sustain trees. Within each living tree cell is a water-based solution which contains, supports and dissolves a variety of elements, materials and molecules responsible for life. For example, water is the starting point for photosynthesis capturing energy from the sun, a hydraulic fluid, a transport stream, and solvent. Water comprises ~80% of living tree mass, on average.

Molecular Form
     A water molecule -- the most basic unit -- is composed of three atoms covalently bonded to-gether. These bonds involve sharing electrons between atoms. Two of the three atoms are small hydro-gens, each with a single negatively charged electron surrounding a positive charged proton and 1 or 2 neutrons. The third atom in water is a massive oxygen which has an atomic structure which easily captures and holds up to two negatively charged electrons. These electron sharing covalent bonds between atoms in a water molecule are strong.

     There are many kinds of water. Water can exist in nine (9) different forms (isotope combina-tions). There are two (2) types of naturally occurring hydrogen available for use, which vary in their nuclear components. There are three (3) naturally occurring oxygen types available. The lightest form of water is by far the most common -- molecular weight 18 amu. Heavier isotopes of naturally occurring water (molecular weights = 19-22) may not be as biologically active as standard water and are extremely rare. Figure 2.
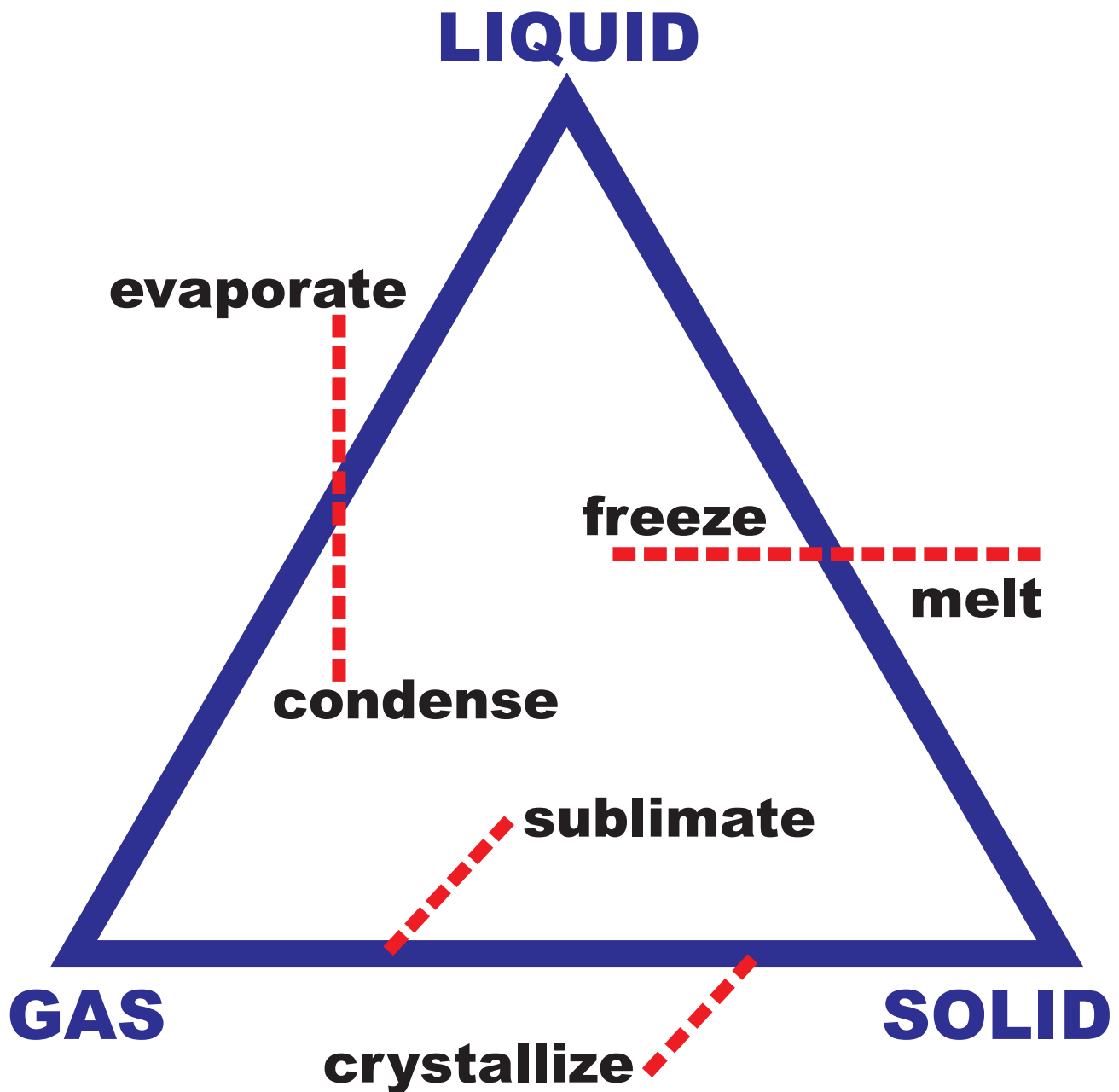
Figure 1: Diagram showing states of water and
names of transitions between states.

WATER FORMS

total hydrogen mass	oxygen mass	percent water form on Earth
2 (^{1}H,^{1}H)	16	99.74 %
2	17	0.04 %
2	18	0.20 %
3 (^{2}H,^{1}H)	16	0.01 %
3	17	0.000004 %
3	18	0.00002 %
4 (^{2}H,^{2}H)	16	0.000001 %
4	17	(4×10^{-10}) %
4	18	(2×10^{-9}) %
		100%

^{3}H is a synthesized radioactive hydrogen with a ~12.3 year half-life.
The rest of synthesized hydrogens & oxygens have short half-lifes (< few seconds).

Figure 2: Percent of nine (9) naturally occurring water molecule forms in the atmosphere.

(Note percents are NOT in decimal form).

Charge Exposure

In binding with oxygen, hydrogens tend to loose their negatively charged electrons for most of the time. The almost continuous loss of negatively charged electrons from both hydrogens partially exposes their positively charged proton centers. The capture of two extra negatively charged electrons for most of the time by oxygen, adds a partial negative charge to oxygen. The ability of oxygen to steal electrons (unequal sharing) from its hydrogen partners generate a partial charge separation within water molecules. The partial positive and negative charges balance out within one water molecule leaving no net charge.

Individual molecules of water have a slight tendency to completely ionize or disassociate. Chemically two water molecules can break apart into one H_3O^+ ion and one OH^- ion, or an average disassociation of one H+ (proton) and one OH- (hydroxy group). A chemical balance exists between water molecules in ionized and non-ionized states, with most in a non-ionized form. At a neutral pH (pH = 7), one in 10 million water molecules are ionized. As pH becomes lower (more acidic), more H^+ ions exist per liter of water. A pH of 4 means the concentration of H^+ is one in 10,000. Water molecules generally stay in one molecular piece, unequally sharing hydrogen electrons. Figure 3.

Sticky Shapes

Part of understanding partial charge attraction is examining the shape of a water molecule. There are many ways to envision three atoms in water attaching to each other. Water molecules are not straight or in a 90° L-shaped. Oxygen has four possible attachment points for hydrogens -- the corners of a tetrahedron, but can only bond with two hydrogens. Figure 4. The two hydrogens can only be attached to a single oxygen in one way. Hydrogens are always at a $\sim105^o$ (104.5^o) angle away from each other around a much larger and massive oxygen atom. At this angle, each hydrogen presents a partial positive charge to other water molecules and materials. Oxygen presents two variable partial negative charges to other molecules. Figure 5.

The interactions between water molecules involve partial negative charges attracting partial positive charges among all other water molecules. This partial charge attraction is called "hydrogen bonding." Hydrogen bonding is not as strong as a covalent bond between atoms, but is strong enough to require some energy to break (i.e. 4.8 kilocalorie/mole). Hydrogen bonding can also occur over longer distances (1.8X longer) than short covalent bonds between atoms in a water molecule.

H-Bonds

As a liquid, every water molecule is surrounded with other water molecules except those at an edge or surface. Within liquid water, each molecule is held within an ephemeral framework of 0-4 hydrogen bonds from all directions. The mutual attraction between water molecules is called "cohesion." Even though one hydrogen bond slips to another molecule, the average number of these bonds per water molecule remains roughly the same for each energy level. As temperatures climb, more hydrogen bonds break. At the liquid water surface, more molecules escape from liquid into a gas form with increasing temperature. Figure 6.

Hydrogen bonding occurs when hydrogen is positioned between two strongly electronegative atoms. Oxygen (O), fluorine (F), nitrogen (N), and chlorine (Cl) can participate in compounds with hydrogen bonding. Both oxygen (O) and nitrogen (N) form hydrogen bonds which can positively influence the shape or conformation of biological molecules. Both chlorine (Cl) and fluorine (F) pull apart and disrupt biologics.

pH	ionized water proportion
2	1: 100
3	1: 1,000
4	1: 10,000
5	1: 100,000
6	1: 1 million
7	1: 10 million
8	1: 100 million
9	1: 1 billion

Figure 3: Ionic proportions of water at various pH levels.

1

side D
back side

side A
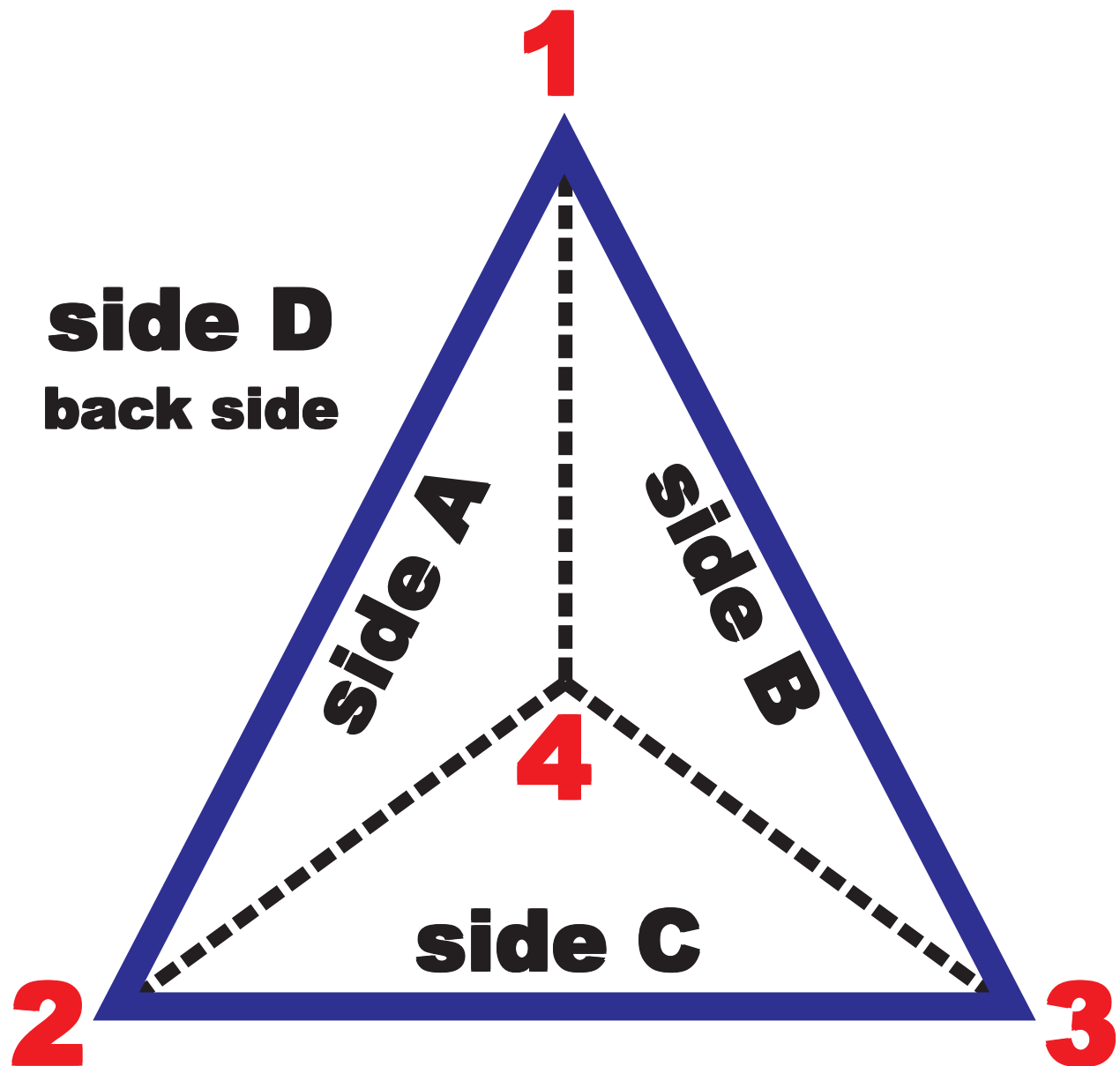
side B

4

side C

2

3

Figure 4: Oxygen bond attachment geometry is in the form
of a tetrahedron with four corners (1-4) and four
sides (A-D), only two corners can be
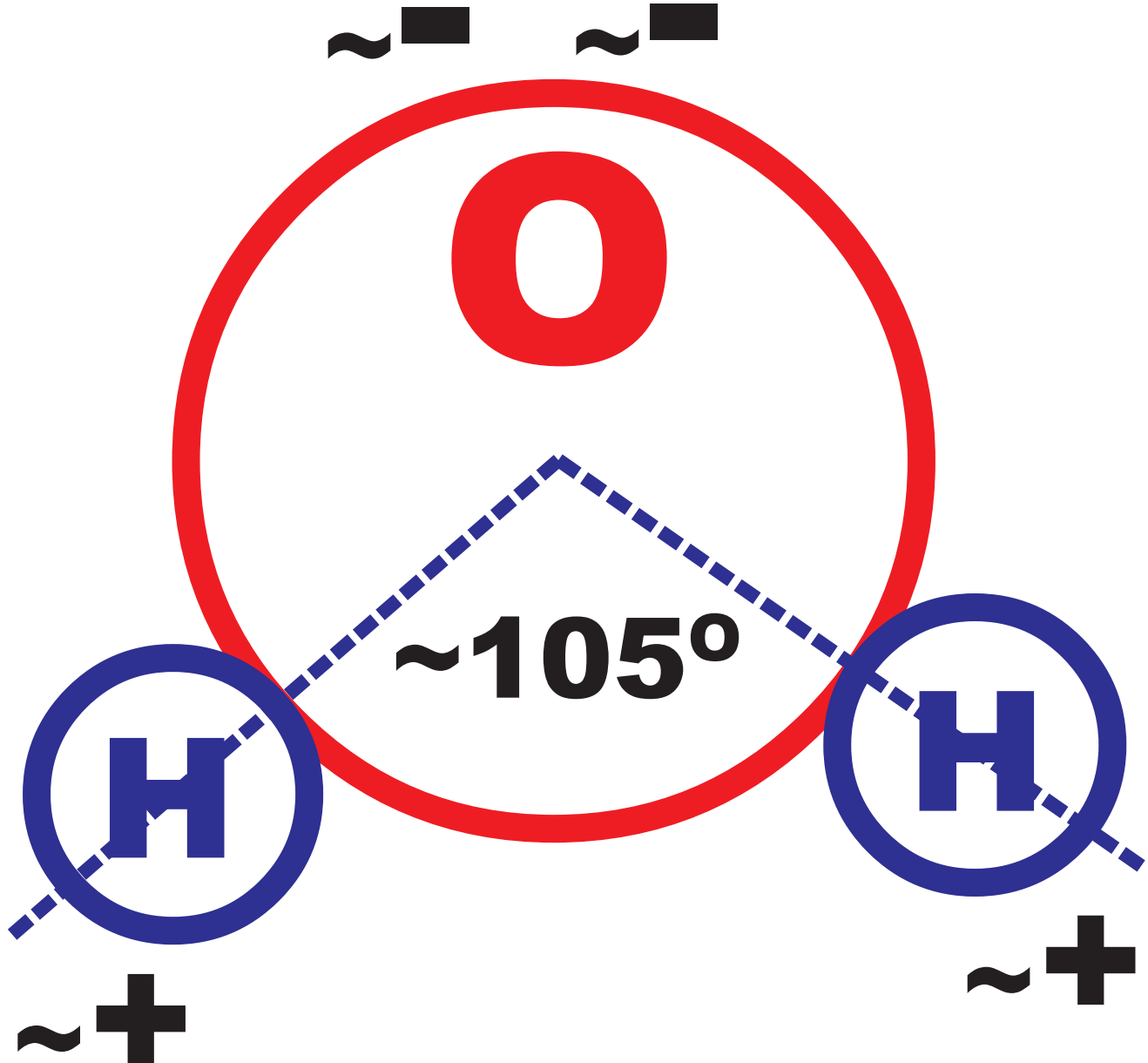filled with hydrogens.

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
1785
**Warnell School of Forestry
& Natural Resources**

Figure 5: Diagram of water molecule with oxygen (O) and two hydrogen (H) atoms. Hydrogen atoms are always separated by ~105° as they glide over the oxygen perimeter, never on opposite sides. Oxygen draws electrons away from hydrogens generating a polar molecule with partial negative charges (~-) on the oxygen side and partial positive charges (~+) on the hydrogen side.
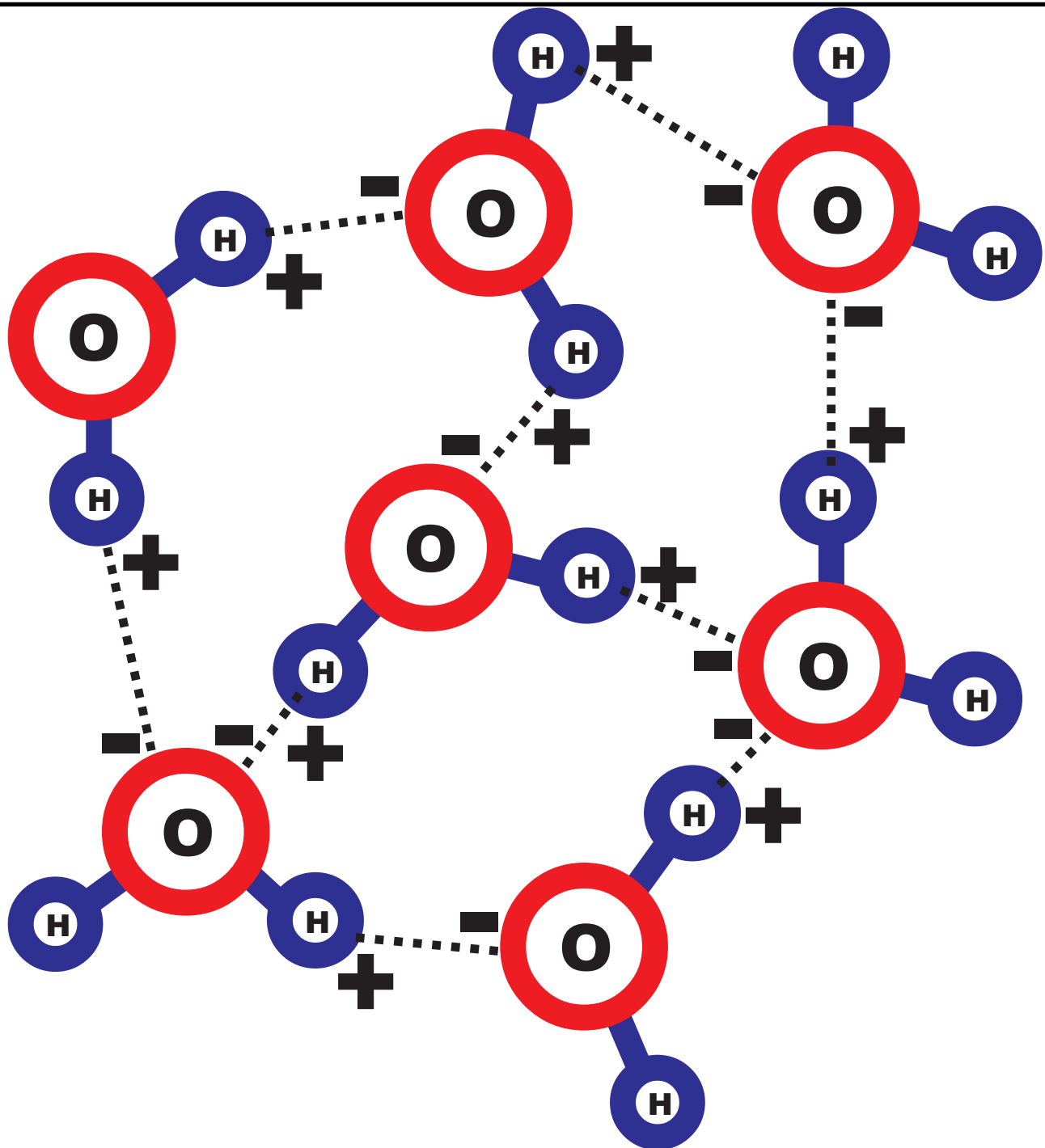
Figure 6: Diagram of seven water molecules interacting with each other due to partial electrostatic charges (associated with 0 to 4 hydrogen bonds). Dotted lines represent hydrogen bonds. Remember, this is a simple two dimensional diagram, while water molecules are in a four dimensional framework of constantly shifting hydrogen bonds.

Complex Structures

Water is not a random host of individual molecules interacting, but a matrix with varying characters. Because of hydrogen bonding, water develops complex geometric relationships with surrounding water molecules which exist in few other materials. The potential for a maximum of four hydrogen bonds coming from a single water molecule allows water to mimic a four-sided, three dimensional structure called a tetrahedron, rather than a flat, two-dimensional triangle. As these tetrahedrons stack-up, they form small areas of structure which approximate a crystalline form.

As more crystalline areas develop and line-up with each other, water can be described as having a semi-crystalline form in a liquid state. This semi-structure confers stability which makes water unique. Water is dominated by this stable semi-crystalline structure up to about 105°F (40.5°C). At this temperature the energy within water is great enough to prevent most large structural areas of hydrogen bonding from occurring. This stability temperature is biologically significant because water which surrounds, supports, and interfaces with many tree enzymes and molecular conformations begin to subtly (and negatively) change properties above this temperature.

Ice Floats

As liquid water cools, more and more hydrogen bonds are formed and maintained. This increased attraction with decreasing temperature continues until 40°F (4°C) when water is at its densest. As liquid water continues to cool, hydrogen bonding of cold water begins to reorganize into larger areas of crystalline-like structures. As energy content in liquid water declines to 32°F (0°C), hydrogen bonds set-up a liquid crystal structure made of many tetrahedron shapes.

As water freezes, the tetrahedrons bonds are set into true crystal forms. This water crystal formation is a solid which is less dense than the liquid from which it formed. The four hydrogen bonds and the packing density of tetrahedron crystals formed at freezing separates individual water molecules by more space than is present between water molecules in a liquid form. Ice floats because it is less dense than liquid water. The lower density tetrahedron structure of solid water allows ice to float, and provides basic building blocks and shapes found in snowflakes and frost.

Little Big Size

The most abundant form of water has the smallest molecular weight of 18 mass units with 16 mass units coming from a single oxygen. Other molecules similar to the mass and size of water molecules quickly evaporate and exist as a gas at tree growth temperatures. Because of hydrogen bonding, water molecules are "sticky," attracting each other and demonstrating properties expected of a much different, much heavier and larger compound. Water interacts with any material having at least small irregularities in electronic composition. Water will adhere to many surfaces which have many forms of partial charges and ionic terminals.

Electric Shells

Many tree essential elements dissolve readily in water and form ions, either positively charged "cations" or negatively charged "anions." Figure 7. Ions come from the disassociation or separation of a molecule. Table salt easily ionizes into positive cation sodium (Na+) and negative anion chlorine (Cl-) when stirred into water. The full charges on the ions cause the partially charged water molecules to line-up and surround each in a hydration sphere or layer. The ions then tend to behave as much larger molecules because they are blanketed with many water molecules attracted by their charge. Figure 8.

element name	element symbol	most common form(s) available for tree
carbon*	C	HCO_3^- CO_2
oxygen*	O	O_2 H_2O
hydrogen*	H	H_2O
nitrogen*	N	NO_3^- NH_4^+ $CO(NH_2)_2$
potassium	K	K^+
calcium	Ca	Ca^{+2}
magnesium	Mg	Mg^{+2}
phosphorus	P	$H_2PO_4^-$ HPO_4^{-2}
sulfur*	S	SO_4^{-2} SO_2
chlorine*	Cl	Cl^- Cl_2 ClO_3^-
iron	Fe	Fe^{+2} Fe^{+3}
manganese	Mn	Mn^{+2} Mn^{+4}
zinc	Zn	Zn^{+2}
boron*	B	H_3BO_3
copper	Cu	Cu^+ Cu^{+2}
silicon*	Si	H_4SiO_4
molybdenum	Mo	MoO_4^{-2}
nickel	Ni	Ni^{+2} Ni^{+3}
cobalt	Co	Co^{+2} Co^{+3}

* = trees can take up element as neutral molecule

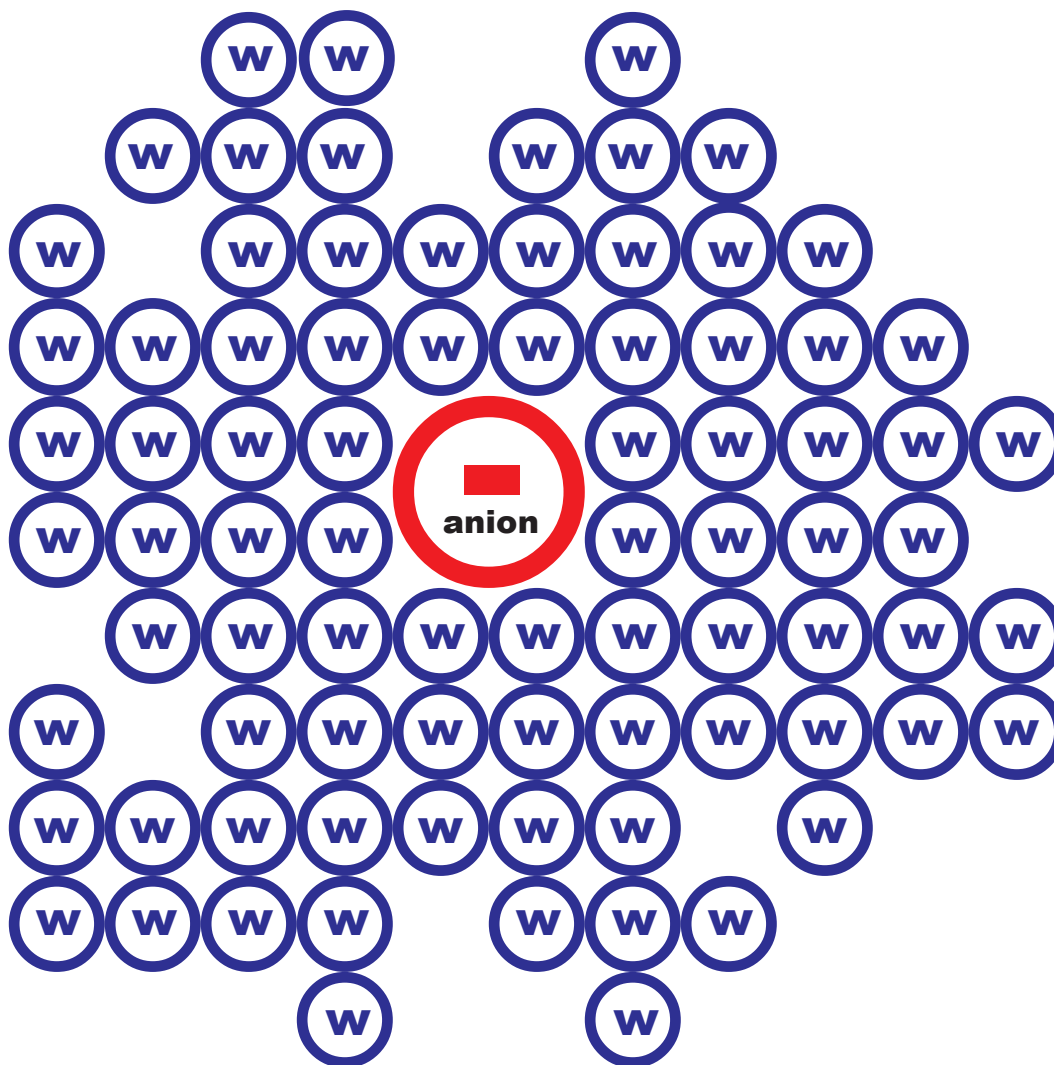Figure 7: Tree essential elements usual ionic uptake forms.

Figure 8: Two-dimensional diagram of water molecules
surrounding an ion with a negative charge generating
a hydration sphere effectively increasing ionic size.
The partial positive charges on water molecules
line up toward the negative ion.

In soil, most essential elements are not dissolved in solution but held within organic materials or mineral compounds. There are always a small portion of these elements dissolved in water and attracted to various charges on soil particles. Small water molecule charges, in-mass, tug at any surface materials surrounding them (dissolving them). An individual water molecule is very small compared to most other materials and can be drawn into the smallest of pores or spaces. This physical property helps water dissolve many things. Water infiltrates and coats life and its resources.

Biology

Water provides a solution and climate for specific biochemical reactions to occur. The structure or configuration of enzymes depend upon water's structural support. In addition, many reactions and their associated biological catalysts are temperature sensitive. Water provides a constant temperature bath and a stable environment for life-functions. Water is also a component or product of some biological reactions.

For example, the photosynthetic system in a tree depends upon oxidation of water to provide electron resources needed for capturing light energy. The oxygen in O_2 gas released in photosynthesis is derived from water. The hydrogens and electrons from water are used for chemical reduction of CO_2 captured from the air. Water provides electrons, hydrogens, and oxygen to capture light energy, make tree food, and produce oxygen!

Water is the 20th tree essential "element."

Special Case of Nitrogen

Described in its most basic form, a tree is a collection of carbon chains with a few other elements attached. What elements a tree requires for life may not be readily available within the environment in which it stands. Within terrestrial environments, usable nitrogen is usually in short supply — if not the most growth-limiting of all essential elements. Nitrogen is one of the key connectors between, and modifiers of, carbon chains.

Nitrogen affects molecular interactions, compound shapes and functions, and chemical symmetry of life-maintaining materials. In ecosystems, usable nitrogen is the most precious of elements — carefully used, relentlessly recycled, and biologically hoarded. If carbon represents the structure of life, nitrogen is the ignition key. Energy bound within organic carbons can only be held and retrieved by utilizing nitrogen.

Essentially

Nitrogen is an essential component of tree life. Figure 9. Nitrogen is considered a myri-element averaging around 17,000 ppm in living tree tissues, and with only carbon, oxygen, and hydrogen found in greater quantities.

For trees, nitrogen represents a good news / bad news problem. The good news is the atmosphere surrounding trees is at least 78% nitrogen gas (dinitrogen or N_2). Every acre of land has a blanket of more than 36,000 tons of nitrogen overhead. The bad news is almost all these nitrogen atoms are tightly bound together and act as an inert gas with low chemical energy. Atmospheric dinitrogen gas is held in a two atom, triple-bonded molecule. Figure 10. Few living systems have the biological machinery necessary to break apart nitrogen gas. For trees, nitrogen is everywhere with not a molecule to use.

Making N Usable

Living tree systems must utilize fixed or reduced nitrogen (energized N) for incorporation into amino acids, nucleic acids, and proteins. Reduced nitrogen has been energized and made chemically reactive by addition of electrons. Reduced nitrogen is electron-dense, and viable as a biological building component or a reaction coupler inside a tree. Reduction, fixation, or a change in oxidation states, is essential for nitrogen use by a tree.

For example, nitrate (NO_3^-) is a common nitrogen containing anion in soil and is often artificially enriched on sites. The nitrogen portion of nitrate must go through four major changes in form, each with an associated energy addition (increasing electron density), before the nitrogen can be used within a tree. In this case, oxidation state values must be forced from a +5 in NO_3^- (low energy, fairly benign nitrate anion) to -3 in NH_4^+ (a small, high energy, potentially toxic ammonium cation), an eight electron input difference.

Come On In !

Moving nitrogen inside a tree presents a number of unique constraints and solutions. Transporting some materials across root cell membranes can be accomplished by simple diffusion where materials move from high concentrations to places of low concentrations. Transport can also be associated with

element	symbol	average in tree (parts-per-million)	relative proportion in trees
group 1: (mega-)			
carbon	C	450,000 ppm	1,000,000
oxygen	O	450,000 ppm	1,000,000
hydrogen	H	60,000 ppm	133,000
group 2: (myri-)			
nitrogen	**N**	**17,000 ppm**	**38,000**
potassium	K	12,500 ppm	28,000
calcium	Ca	10,000 ppm	22,000
group 3: (kilo-)			
magnesium	Mg	2,500 ppm	5,500
phosphorus	P	2,250 ppm	5,000
sulfur	S	1,500 ppm	3,300
group 4: (hecto-)			
chlorine	Cl	250 ppm	550
group 5: (deka-)			
iron	Fe	75 ppm	170
manganese	Mn	45 ppm	100
zinc	Zn	38 ppm	85
boron	B	30 ppm	65
copper	Cu	20 ppm	45
group 6: (deci-)			
silicon	Si	0.7 ppm	1.5
molybdenum	Mo	0.5 ppm	1.1
nickel	Ni	0.4 ppm	0.9
cobalt	Co	0.2 ppm	0.4

Figure 9: List of tree essential elements divided into concentration groups (average concentration within trees), and relative proportion in trees with carbon and oxygen levels set at one million.
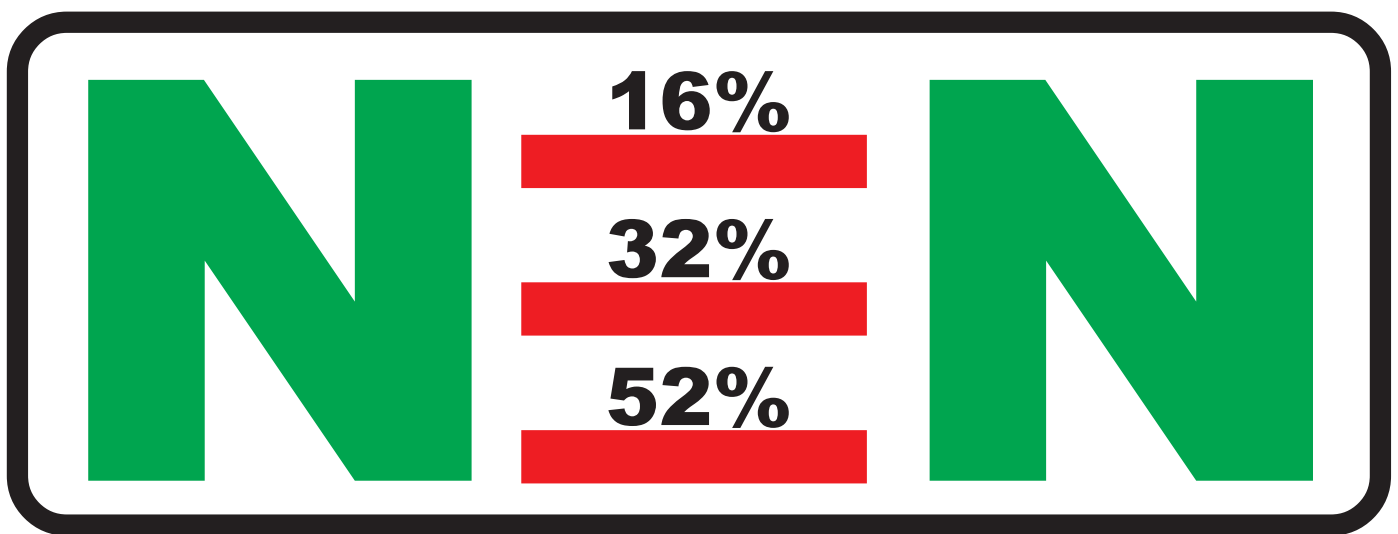
Figure 10: Atmospheric dinitrogen gas (i.e. low energy, almost inert, tightly bound) listed with the relative energy required to break each bond.

moving electrostatically charged ions from places with like-charges to places of opposite-charges. Active transport systems are used by root cells for nitrogen uptake.

Active transport mechanisms require energy for maintenance and for moving individual items. These transport mechanisms function both at cell membranes and at internal tonoplasts (vacuole membrane). Carriers on membranes are used to move materials, while cells attempt to maintain a near neutral internal electric charge balance. Active transport is required for uptake of anions (NO_3^-, Cl^-, $H_2PO_4^-$, SO_4^{2-}); excretion of selected cations (Na^+, Ca^{++}, Mg^{++});   and, not required for potassium ions (K^+) which serve as universal charge balancing.

Nitrate Forms

Ecologically, most nitrogen compounds are quickly converted to nitrates under aerobic conditions. Ammonium is a small molecule, is easily available on exchange sites in soil, and is already in a reduced state. Unfortunately, ammonium can quickly initiate toxicity problems. Urea can be taken up as applied to a limited extent, but is quickly (3-5 days) converted to ammonium in soil. Various types of nitriform products bind nitrogen within various length carbon chains which must be broken apart biologically to allow nitrogen to be used. Figure 11.

Nitrate (NO_3^-), and to a lesser degree ammonium, uptake into a tree from soil is an energy dependent process. Nitrate is taken into a tree against concentration, hydrostatic pressure, and electrostatic charge gradients. This uptake process is not simple diffusion, but an active process requiring energy to transport nitrate across cell membranes, as well as energy to produce and maintain a carrier system.

Carried

The presence of nitrate in soil stimulates carrier activity (and its own uptake) by a tree. Nitrate uptake also stimulates production of nitrate reduction machinery inside root cells. Nitrate presence in the root area is a signal to a tree to expend energy for transport and processing of nitrate. Tree roots without adequate energy and carbon chain supplies will be stressed by nitrate presence in the soil. Actual nitrate uptake is usually much less (4-5X) than the full nitrate uptake capacity of tree roots.

Nitrate can not move into tree root cells passively with water as do many of the other essential elements. Nitrate, because of its mass, size, and charge must be actively transported into tree root cells using one of three specialized carrier systems:

1) a low capacity carrier always available and present in the absence of nitrate;

2) a inducable carrier generated under low nitrate concentrations. (Note this carrier
is not generated and maintained unless there is nitrate present in the rhizosphere.); and,

3) a carrier which functions under high nitrate concentrations.

Easing Transport

Nitrate is transported using carriers which breach cell membranes. Figure 12 shows two primary types of carriers used by tree cells to move nitrate from one side of a membrane to the other (either apoplast / symplast interface or symplast / symplast interface). Symporters move two items in the same
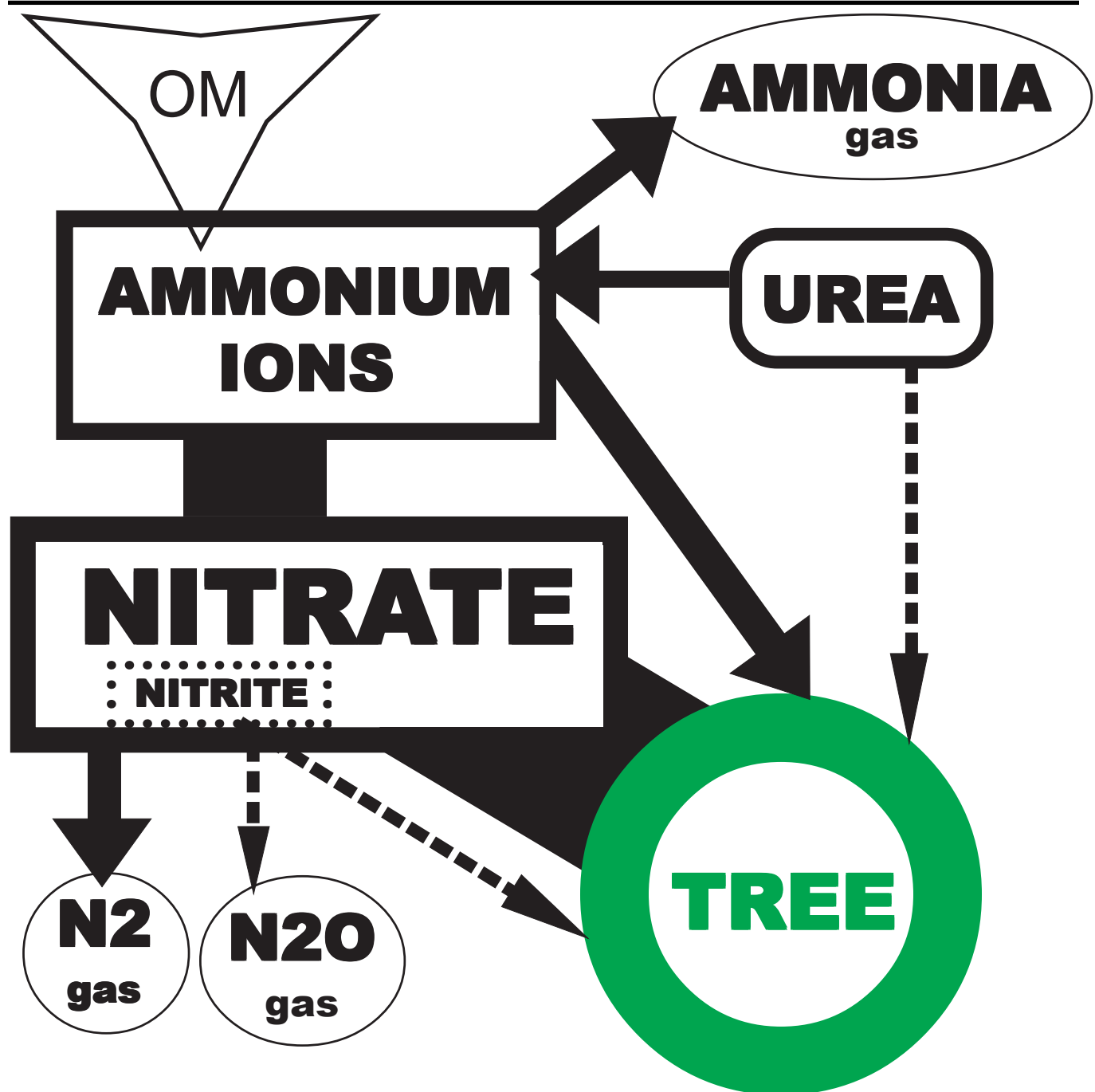
Figure 11: Possible pathways of reduced nitrogen in soil
transformed from urea fertilizer and moved into a tree
or lost to the atmosphere.

Figure 12: Secondary nitrate (NO3-) symport carrier transports nitrate and proton (H+) simultaneously into cells maintaining electrostatic charge balance. Primary nitrate (NO3- = 62 mass units) antiport carrier transports nitrate inward and carboxylate (HCO3- = 61 mass units from organic acids) outward maintaining a mass and charge balance.

direction usually maintaining a balanced charge across the membrane. Antiporters move two items in opposite directions usually maintaining a mass and / or charge balance.

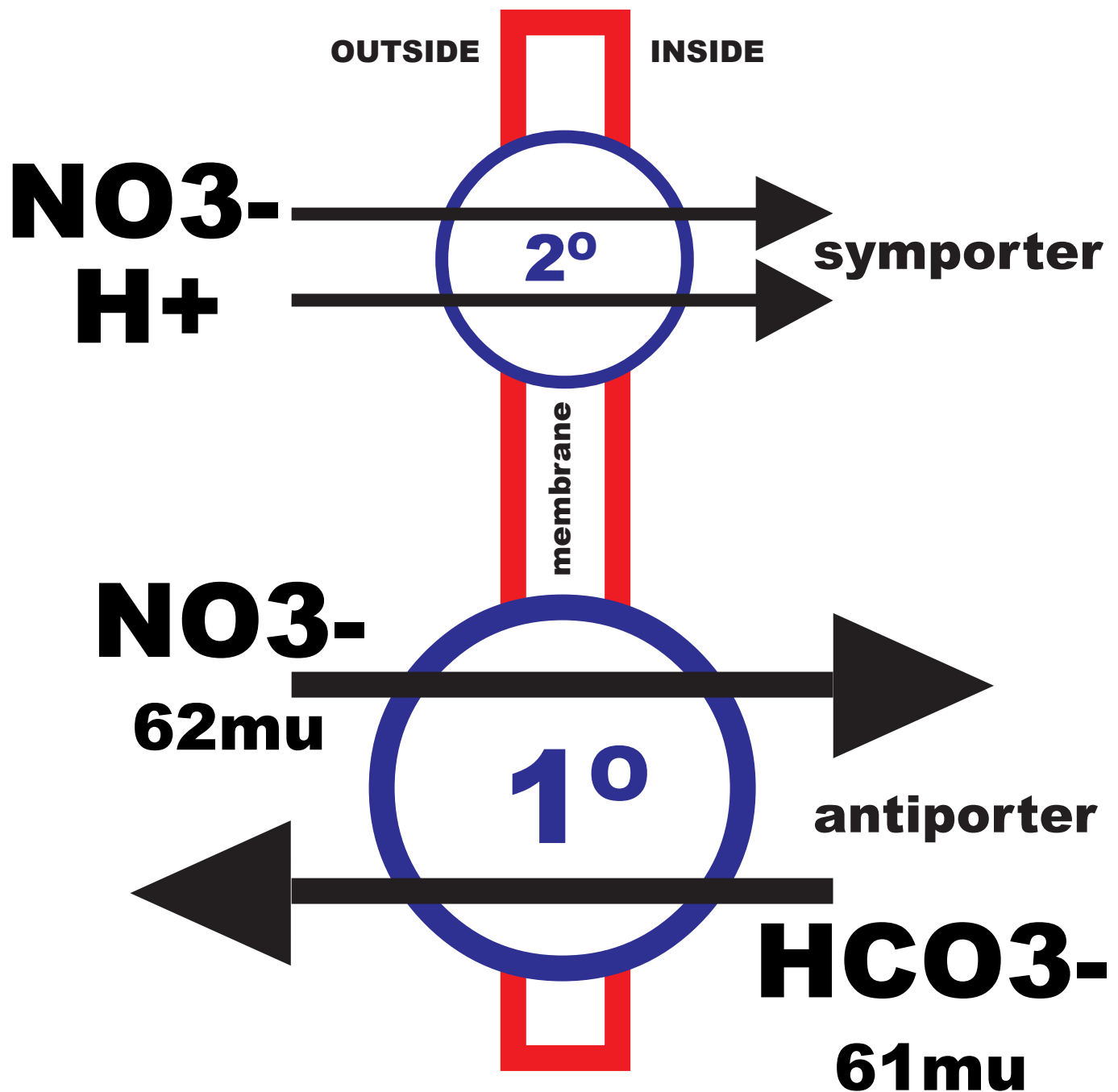Nitrate can be moved into a tree by a symporter carrier, where a molecule of nitrate is transported into a cell simultaneously with a proton ($H+$) to maintain the balance of electrostatic charges. This leaves an $OH-$ outside in the soil. Nitrate (NO_3- mw = 62 mass units) is primarily transported by antiports which move nitrates into a cell and an ion of like charge (and similar size) outward. This cotransported ion of similar charge and size is a carboxylate anion (HCO_3- mw = 61 mass units) from organic acid origins. The presence of HCO_3- inside root cells stimulates nitrate uptake and is essential for operation of the primary nitrate carrier.

Ammonium is positively charged and small enough to enter tree root cells with water. Because of nitrogen demands, ammonium ions can also be actively transported into tree root cells using two types of carriers, one transports ammonium under low concentrations and one function at high ammonium concentrations.

Nitrate Reduction

Once inside root cells, nitrate is reduced by nitrate reductase (NRe) enzyme, which is the first step in reducing nitrates into a usable form. Figure 13. This process is accelerated and maintained by light, CHO, cytokinin, high CO_2 concentrations, and anaerobic conditions. This process is inhibited by darkness, glutamine build-up, oxygen, magnesium ions, and low CO_2 concentrations.

NRe is a monstrous, enzymatic catalyst which requires molybdenum (Mo) and iron (Fe) to function. This enzyme is the only major use for Mo in a tree and its requirement can be circumvented (if required) by adding only ammonium-based nitrogen. NRe is energy-expensive to construct and maintain with a half-life of only a few hours. NRe activity is initiated within 40 minutes of nitrate presence in soil and reaches a maximum after three hours. It is estimated up to 25% of tree energy from photosynthesis is used in nitrate assimilation. NRe only purpose is to make the initial reduction step on nitrate.

To accomplish the first step in nitrogen reduction, NRe facilitates transfer of two electrons (energy from carbon respiration) to nitrate (NO_3-), which yields nitrite (NO_2-). This process occurs in root cell cytosol. When excess nitrate is available, nitrate is moved beyond the initial cell of uptake and reduced in xylem parenchyma. In some tree species, a small portion of nitrate (usually the remains of excessive loads) are shipped to leaves for reduction. NRe is not a limiting factor for tree nitrogen utilization (availability of nitrate to roots is limited).

Nitrite Reduction

Nitrite (NO_2-) is moved quickly to plastids (cell organelles) to minimize toxicity. The next three steps in nitrogen reduction is facilitated by nitrite reductase (NitRe), an enzymatic catalyst which requires iron (Fe) and sulfur (S). NitRe facilitates the reduction of nitrite by transferring six electrons (3 ETMs) which yields ammonium (NH_4+).

Ammonium can become easily toxic in a cell and is not readily stored. Ammonium is not normally transported in xylem unless large amounts are present and can not be processed in roots. Ammonium is quickly moved into an organic framework (carbon skeleton) with the result called an amino acid. Figure 14. Amino acids can be used as building blocks for other compounds, for storage, or for transport out of a cell and throughout a tree. Cellular assimilation of ammonium ions requires a strong and continuous carbon chain source transported from the photosynthetic process and from local storage materials. Figure 15.

NITRATE
NO3- + [2e-, 2H+]

NRe (Fe & Mo) enzyme

NITRITE
NO2- + [6e-, 8H+]

NitRe (Fe & S) enzyme
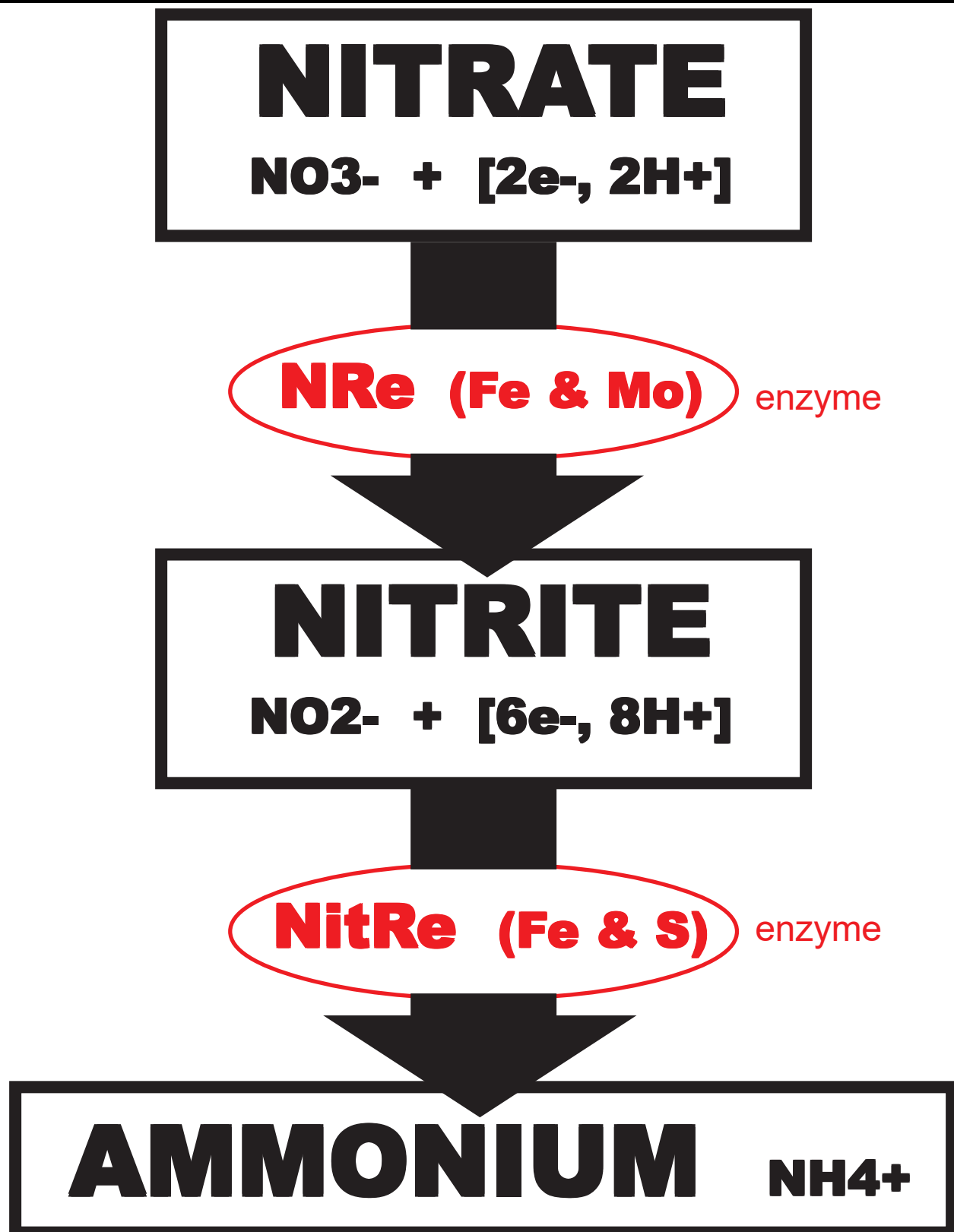
AMMONIUM NH4+

Figure 13: Pathway inside tree cells moving nitrate taken
from soil to ammonium ions sequestered in cellular pool.

STRUCTURAL AAs

idealized formula	name
2C1N	glycine
3C1N	serine
3C1N	alanine
3C1N	cysteine (S)
4C1N	aspartate
4C1N	threonine
4C2N	asparagine (A)
5C1N	glutamate
5C1N	valine
5C1N	methionine (S)
5C1N	proline
5C2N	glutamine (A)
6C1N	leucine
6C1N	isoleucine
6C2N	lysine
6C3N	histidine
6C4N	arginine
9C1N	tyrosine
9C1N	phenylalanine
11C2N	tryptophan

Figure 14: Basic amino acids used in trees for enzyme and protein structures (considered structural amino acids). "C" = carbon; "N" = nitrogen; (S) = sulphur containing; (A) = amide.

normal ammonium processing

$$1N_{(NH4+)} +5C1N = 5C2N$$

(glutamine)

high ammonium processing

$$1N_{(NH4+)} +5C = 5C1N$$

(glutamate)

occasional ammonium processing

$$1N_{(NH4+)} +4C1N = 4C2N$$

(asparagine)

Figure 15: Three primary ammonium ion insertion points onto carbon chains generating amino acids.

Locking-Up Ammonia

Because of ammonium toxicity, there are two primary pathways (and one secondary pathway) for utilizing this reduced nitrogen compound. Figure 16. The first primary system for incorporation of ammonium into an amino acid is called the glutamate cycle (requiring magnesium (Mg) and zinc (Zn)). Ammonium is added to glutamate (a 5C1N amino acid) and energized (with 1 ATP) to produce glutamine (a 5C2N amide), which is a transport and storage form of nitrogen. Figure 17.

Glutamine (5C2N) and oxoglutarate (5C) are then combined to produce two glutamates (two 5C1N). Figure 18. One of the two glutamates generated is used to start the ammonium assimilation process again while the other is shipped away for tasks like protein synthesis. The net result is one ammonium successfully incorporated into an amino acid which can be stored or used to transport nitrogen throughout a tree.

Glutamate (5C1N) is the feedstock leading to the other 19 amino acids (actually 18 amino acids and an amide) a tree's life is built around. There are over 200 amino acids in trees, although only 20 are structural forms used for enzymes and proteins. Glutamate is the starting material for amino acids, proteins, nucleic acids, nucleotides, coenzymes, and porphyrin rings (chlorophyll and phytochrome). Both glutamate (5C1N) and glutamine (5C2N) can be safely stored for later use or transported to the rest of a tree.

Alternative Assimilation

The second primary system for incorporation of ammonium into an amino acid is a direct carbon chain addition when ammonium ion concentrations are at high levels approaching toxicity (ammonium overdose). Ammonium is added to oxoglutarate (a five carbon organic acid from photosynthesis -- 5C) to generate a glutamate (5C1N). This pathway quickly moves toxic ammonium into storable and transportable glutamate (5C1N) but is energy-expensive and only functions at relatively high levels of ammonium. Figure 19.   Figure 20 shows a further step in shifting amino nitrogen to another storage and transport form called asparagine (4C2N).

Third Assimilation

A third ammonium incorporation pathway (of secondary importance) is the aspartate / asparagine process. This pathways is usually used for transferring amino-nitrogens not assimilating ammonium ion. Ammonium is added to the amino acid aspartate (4C1N) and generates asparagine (4C2N), a amide transport and storage form of nitrogen.   Asparagine is used for nighttime nitrogen storage. In daylight, and with strong protein synthesis in the tree, aspartate is continually moved to asparagine. Figure 21.

Accounting

From an energy standpoint, uptake and reduction of nitrogen with incorporation into an organic framework is one of the most expensive tasks a tree performs. It would hardly be worthwhile if usable nitrogen in the environment was not at a premium. Trees spends a great deal of energy and carbon chain stock in order to capture and control nitrogen. In this case, to move from soil nitrate to glutamine inside a tree cell requires at least 12 ATPs of energy per nitrogen. To reduce atmospheric dinitrogen gas into glutamine requires at least 16 ATPs of energy per nitrogen plus creation and maintenance of an oxygen free nodule.

Under perfect conditions in a perfect world, a tree should spend about 1 glucose (6C) in respiration for every 2 nitrates processed. This cost does not include carbon skeletons used for nitrogen attachment, as well as the cost of uptake from soil. In reality, there is a 5:1 ratio of carbon spent for every

N2
dinitrogen
gas

NO3-
nitrate
anion

nitrogen
fixation

soil
uptake

NH4+
ammonium
cation
pool
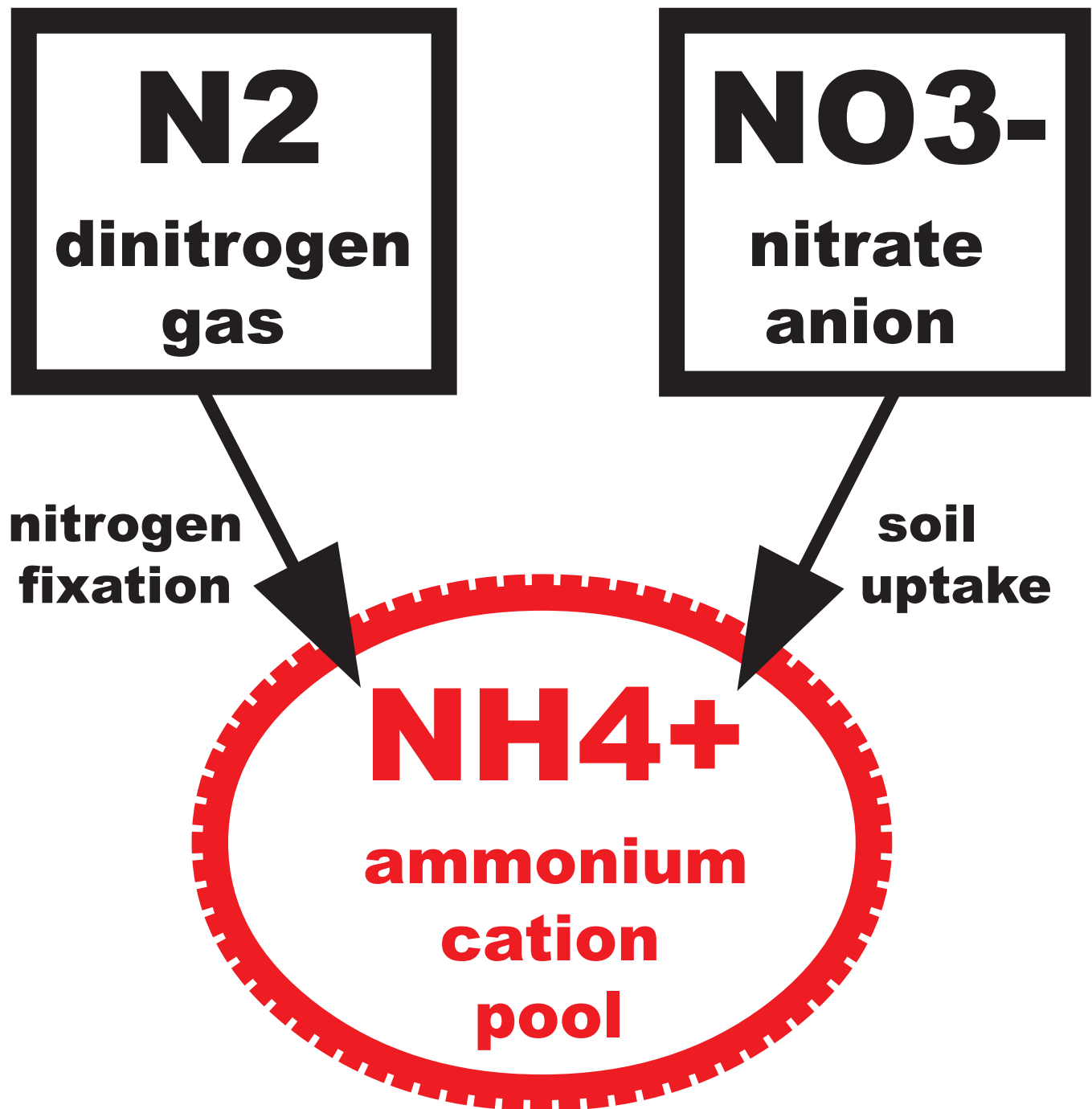
Figure 16: Primary external nitrogen sources supporting
the ammonium cation pool inside tree root cells.

GLUTAMINE
C
C-N
C
C
C-N
5C2N

ASPARAGINE
C
C-N
C
C-N
4C2N

GLUTAMATE
C
C-N
C
C
C
5C1N

ASPARTATE
C
C-N
C
C
4C1N

N = nitrogen; C = carbon

Figure 17: Idealized structure of nitrogen transport & storage amino acids showing location & number of nitrogens.

glutamate cycle

NH4+

5C1N
glutamate

+ATP

5C2N
glutamine

+ETM

5C1N

5C1N

5C
oxoglutarate

high NH+
concentration
bypass
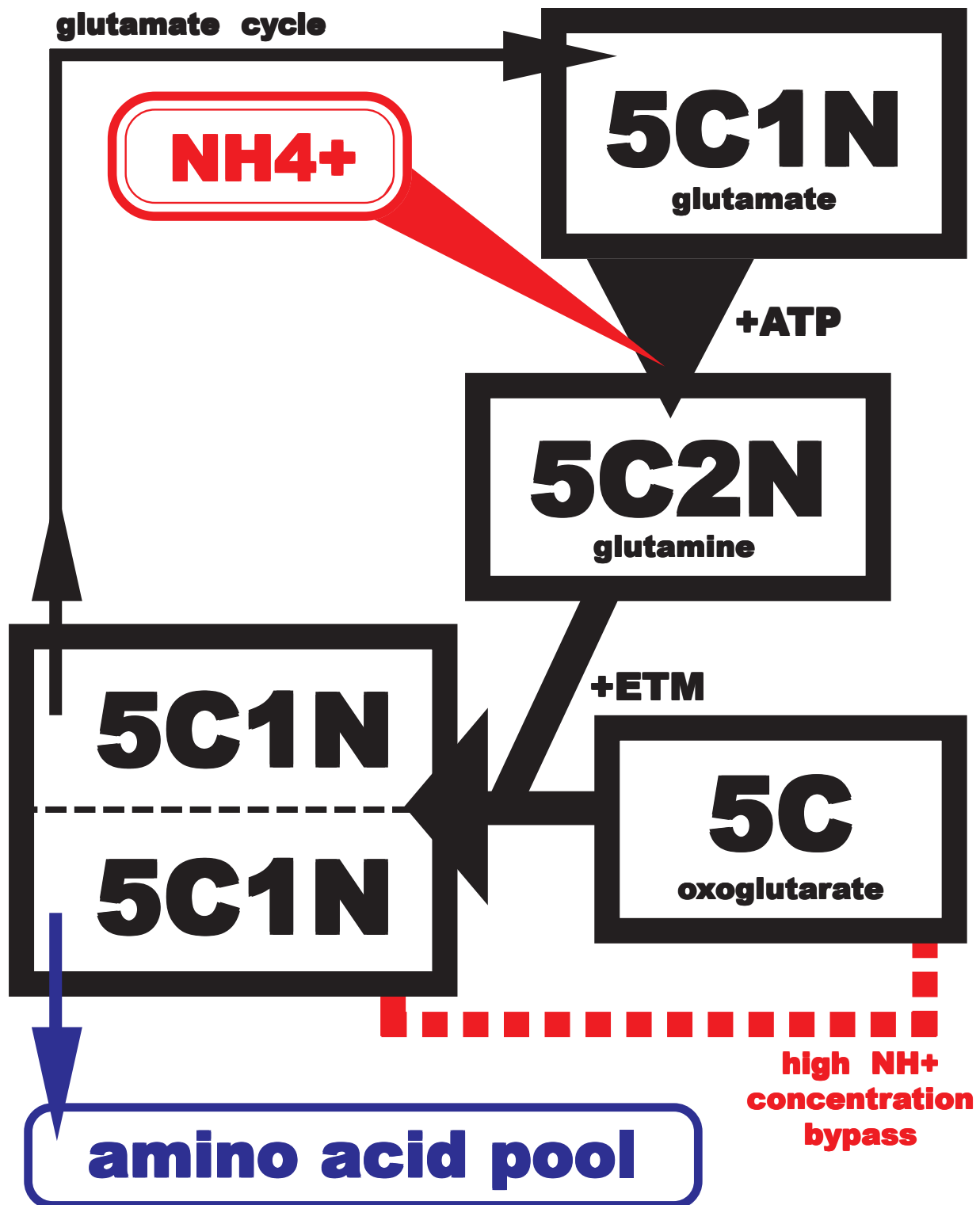
amino acid pool

Figure 18: Pathway inside tree cells for accumulated ammonium ions (NH4+) being consolidated into a carbon framework generating two amino acids. (i.e. glutamate cycle)

High NH4+ Concentration Bypass
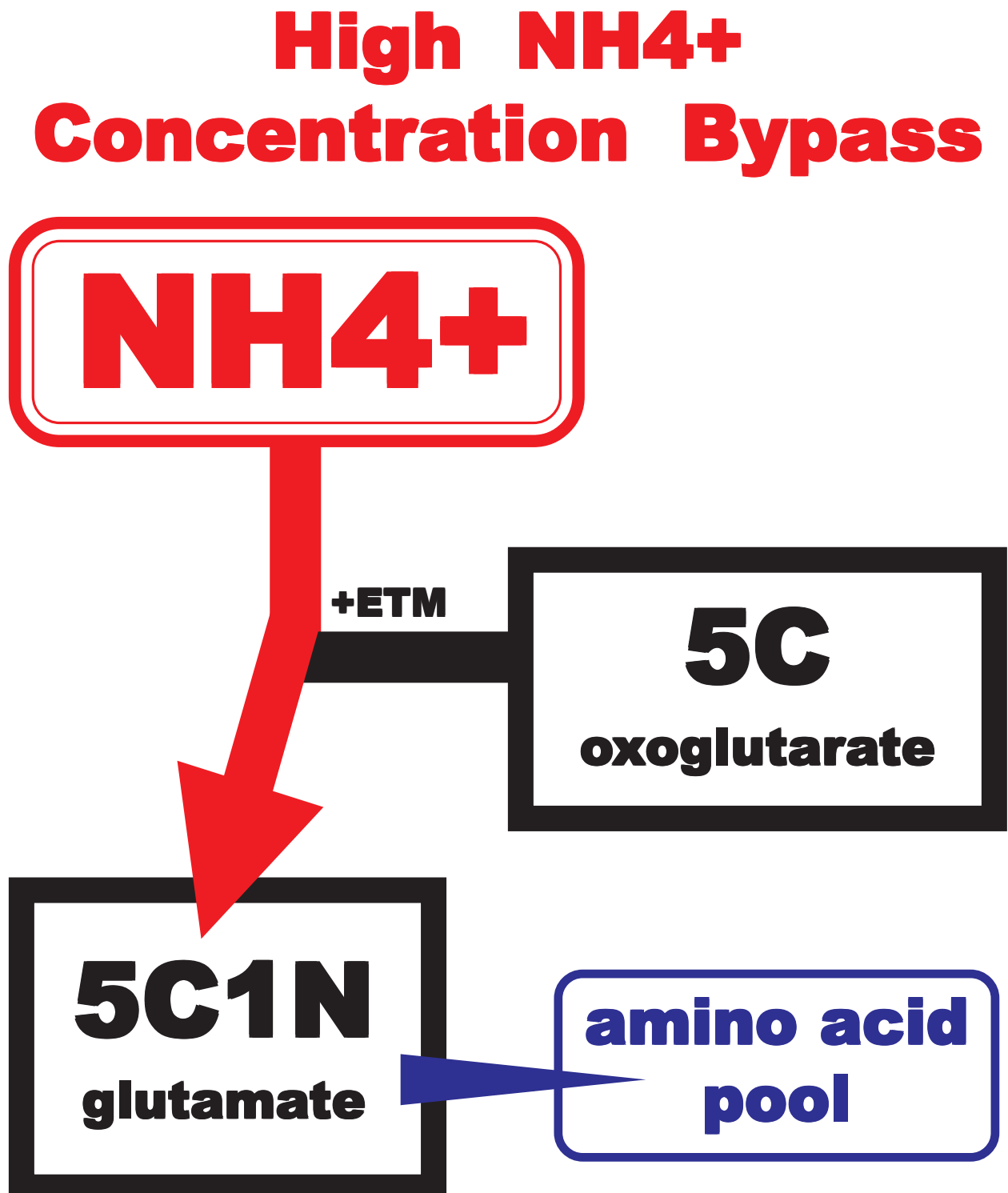
Figure 19: Pathway inside tree cells for high concentrations or excess ammonium ions (NH4+) accumulation being consolidated into a carbon framework generating one amino acid. (i.e. high NH4+ concentration bypass)

29

HIGH NH4+ LOADS

1N **+ 5C => 5C1N**

NH4+   **oxoglutarate**   **glutamate**

5C1N   **+**   **4C**   **=>**

glutamate   **oxaloacetate**

4C1N   **+**   **5C**

aspartate   **oxoglutarate**
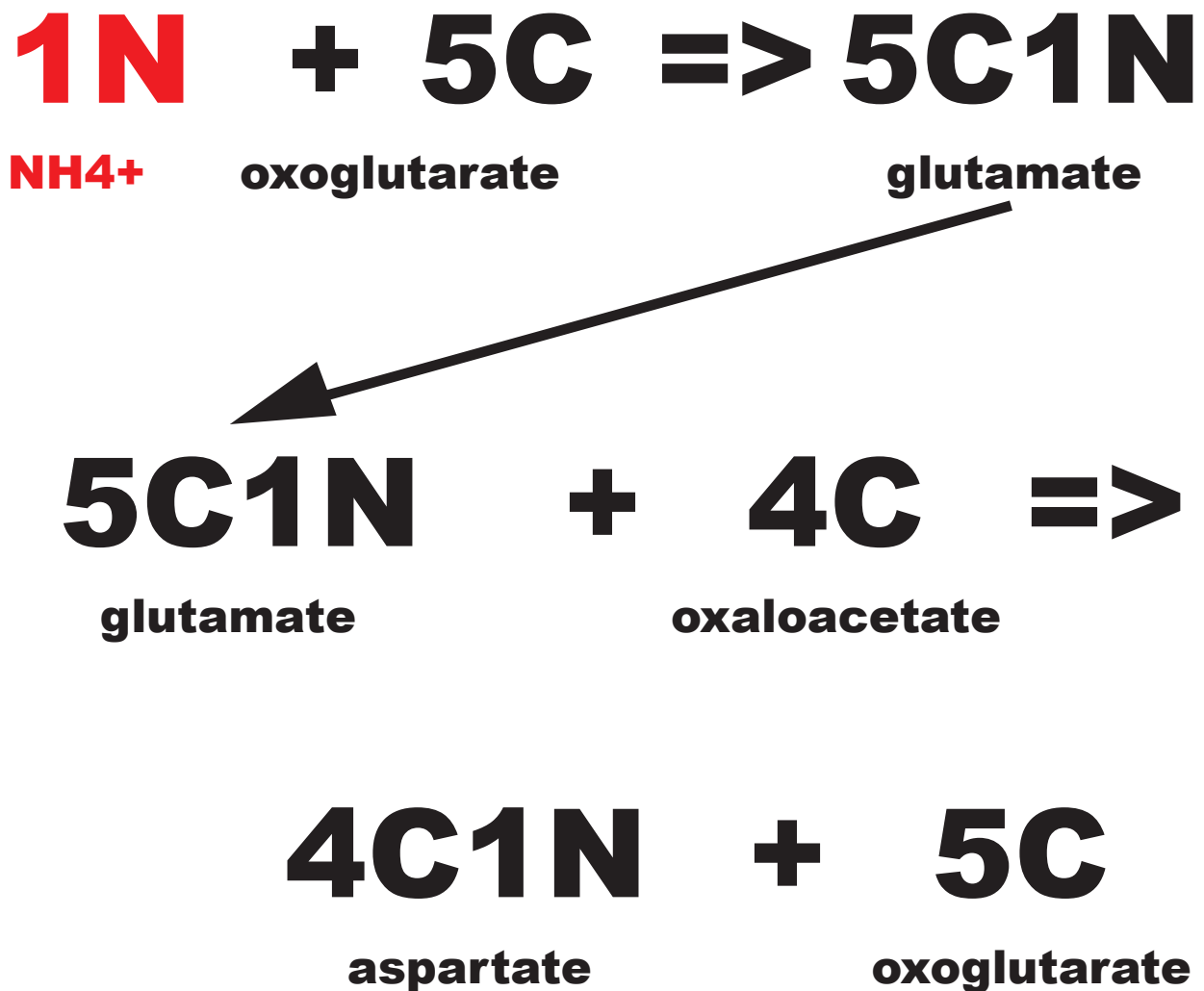
Figure 20: Ammonium assimilation under high concentration loads directly to glutamate using a carbon chain (5C), and shifting of nitrogen to aspartate using a glutamate source combined with a carbon chain (4C).
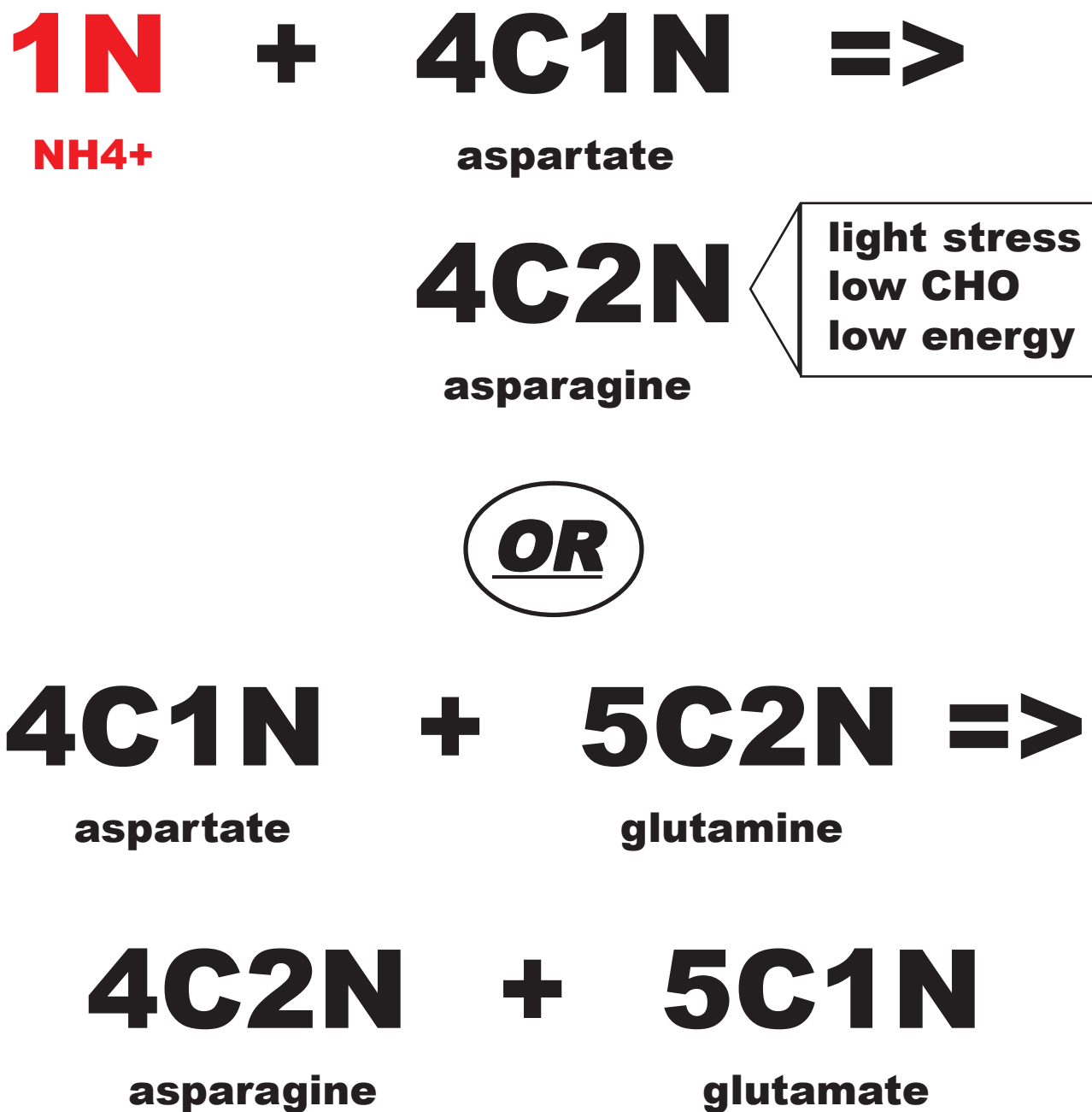
Figure 21: Ammonium assimilation to generate asparagine, a major transport form of nitrogen, and recombination of nitrogen to generate asparagine and glutamate. Asparagine is generated under low light, low carbohydrate levels, and low energy levels.

nitrogen gained. In other words, a 2% nitrogen assimilation level in tree tissues required 10% of the tree's carbohydrate to build.

Reduction Location

Many herbaceous and rapidly growing annual plants ship captured nitrate within their xylem stream to leaves for processing. Leaves have readily available energy for nitrate reduction and incorporation of ammonium into amino acid frameworks. In trees, temperate species tend to process nitrate in roots, and tropical species tend to process nitrate in roots, stems, and leaves. Nitrate can be stored and transported. Ammonium can become easily toxic and is not usually stored or transported. Increasing ammonium concentrations inside cells dissipates the pH gradients responsible for ATP (energy) production.

There is great variability in processing location partially because increasing nitrate concentrations are moved farther along the transpiration stream. The more nitrate available to, and taken-up by, a tree -- the quicker root reduction ability is exceeded and the more nitrate is shipped upward to be reduced where energy sources are available. Xylem parenchyma serve as auxiliary nitrogen reduction centers. With excessive nitrogen sources in xylem transport, nitrates could reach leaves where direct light reduction products can be used.

In Roots

For most landscape trees in temperate areas, assume nitrate is reduced almost exclusively in root tissues.   Nitrogen reduced in roots is then added to the transpiration stream and sent up to the leaves. The cost for nitrogen reduction is paid by current phloem carbon contents (food shipped from leaves), and stored root carbon (food taken from local storage). Glutamate, glutamine, asparagine, and aspartate are amino acid storage and transport forms for nitrogen in trees. The interconversion web is complex but assures nitrogen assimilation under a variety of conditions. Figure 22. Of these, asparagine and glutamine are the most effective and efficient. Both have a high nitrogen / carbon ratio (asparagine = 2N:4C; glutamine = 2N:5C). Figure 23.

Root Plight

The dependence upon tree roots to reduce nitrates, except in times of excess, is of concern from an oxygen supply standpoint. Nitrate reduction is an energy-expensive and complex process. Good oxygenation around tree roots is required for effective processing. Under flooded, compacted, or water saturated soil conditions, oxygen can be quickly depleted in the rooting zone. Oxygen diffuses across water-filled soil 10,000 times slower than across a soil with 25% air-filled macro-pores. In addition, microbes can easily use any available oxygen quickly under oxygen limiting conditions, leaving tree roots under full anaerobic conditions.

Respiration (stored carbon and oxygen use) doubles for every 18^oF increase in temperature. Warm summer nights under wet conditions, low oxygen, and nitrate presence can cause massive quantities of stored carbon in roots to be used. Figure 24. Intermediate products like ethanol and lactate build-up under these conditions. Under low oxygen levels in the rooting zone and moderate nitrate levels, 20 times more stored carbon must be used for processing nitrate and for root respiration than under normal oxygen conditions.

Control System

The control system within a tree for regulating nitrogen uptake is based upon cycling of amino acids formed in ammonium assimilation, and cycling of organic acids generated in photosynthesis and

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
Warnell School of Forestry
& Natural Resources
1785

ASSI WEB
1N = ★

1N	**=**	**ammonium**
4C	=	oxalacetate
5C	=	oxogluterate
4C1N	=	aspartate
4C2N	=	asparagine
5C1N	=	glutamate
5C2N	=	glutamine
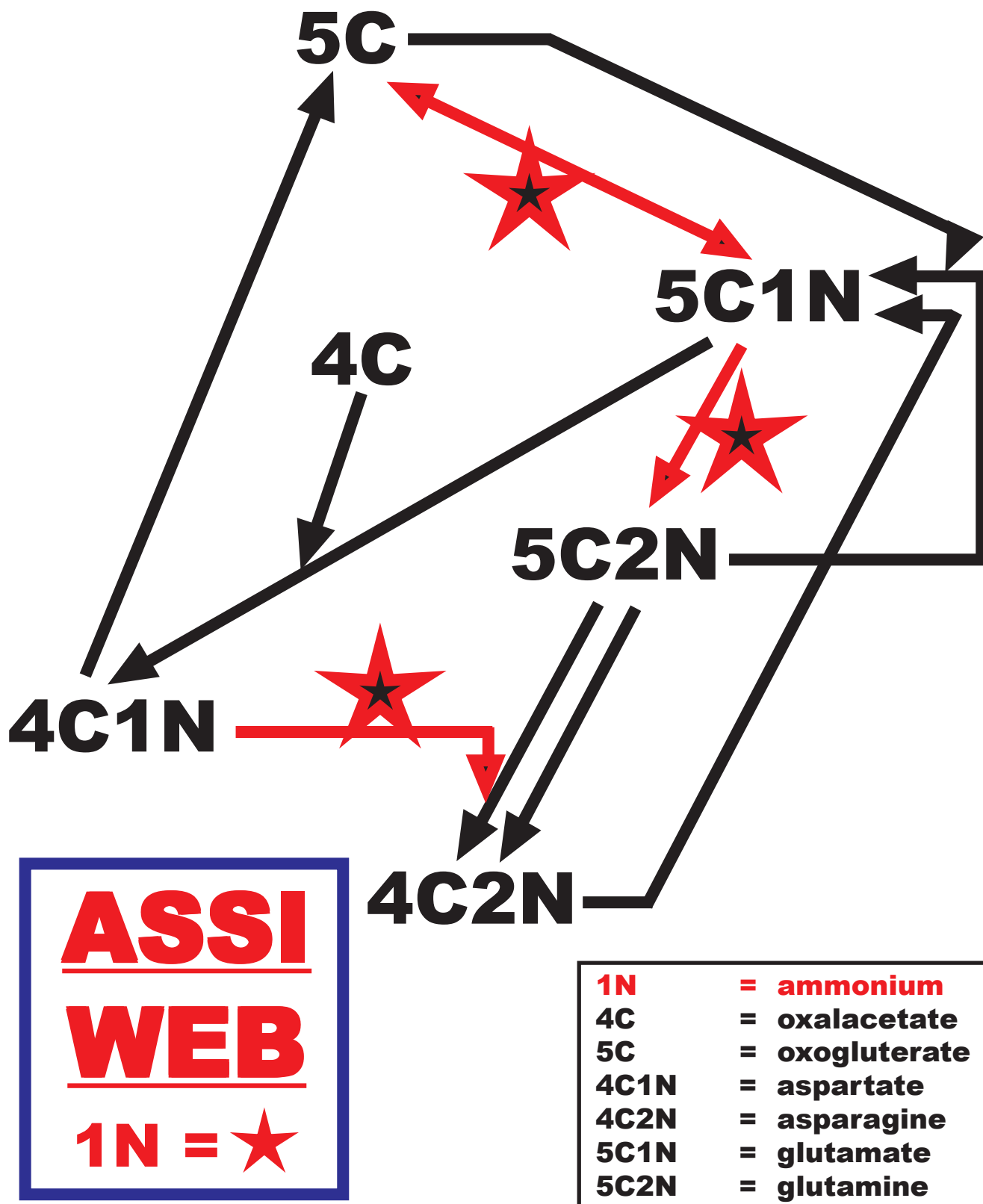
Figure 22: Ammonium ion (+1N) assimilation web in trees with transport and storage amino acids, and carbon feedstocks.

TRANSPORT !

4C1N
aspartate

4C2N
asparagine

5C1N
glutamate

5C2N
glutamine

Figure 23: Primary transport and storage forms of nitrogen with the number of carbons and nitrogens given.

temperature	relative amount of carbohydrate used in respiration (+N, +O$_2$)	relative amount of carbohydrate used in respiration (+N, -O$_2$)
40°F (4°C)	1X	20X
58°F (14°C)	2X	40X
76°F (24°C)	4X	80X
94°F (34°C)	8X	160X

Figure 24: Temperature effects on carbohydrate use in tree
 roots under ideal conditions and carbohydrate use in
 tree roots under oxygen poor (near anaerobic) conditions
 when moderate nitrate levels are present in soil.
 ("2X" means two times the respiration rate at 40°F (4°C) under aerated conditions.)

respiration. Amino acids and organic acids are the primary signal / products cycling between shoot and root in xylem and phloem. Figure 25.

If too much nitrogen is present in the system, amino-acids from the glutamate cycle begin piling-up. Figure 26. Alternatively with tree stress, growth slows and protein synthesis declines, leaving additional amino-acids available. Increasing amino-acid levels deliver a message to roots that tree nitrogen needs are satisfied. Given this amino-acid signal (generated locally and as transported in the phloem), nitrate uptake is slowed. Overabundance of nitrogen and tree stress that slows growth, generate the same signal in slowing nitrate uptake.

More Control

Increasing organic acid concentrations initiate nitrate up-take due to the release of carboxylate anions (HCO_3^-). Figure 27. An increasing level of organic acids signify a decrease in amino-acid production and/or a strong carbon production source. Carboxylate anions are essential for the primary carrier of nitrate uptake to function. The key feature of nitrate up-take control systems is the integration of whole tree nitrogen and carbon status in determining a tree's response. Several amino-acids have been cited in this control process. Of the organic acids playing a role, malate is a good example.

Malate is an organic acid that can be stored in cell vacuoles, can generate carboxylate anions for co-transport of nitrate, or can be used to balance electrostatic charges (malate carries two negative charges). Malate (not glucose or sucrose) from local sources moving into root cells from the phloem transport pathway, stimulates nitrate up-take.

Circulation

With increased nitrate uptake, nitrate reduction is stimulated and amino-acids are produced. The amino-acids are feed stock for protein synthesis. When growth slows and protein synthesis declines, unused amino-acids circulate and slow nitrate uptake. The nitrogen demand in a tree is the difference between the nitrogen reduction rate and the protein synthesis rate.

Control Scenarios

Inside trees is a feed-back control system using amino acids (transportable nitrogen) and organic acids. If one product recirculates and accumulates inside a tree back to its inception point, it will slow further production. To appreciate nitrate uptake control, the following bullets provide five basic results:

A) If amino-acids are used for protein synthesis (concentrations fall), then nitrate uptake increases.

B) If amino-acids concentrations increase in roots, then nitrate uptake decreases.

C) If organic acids increase, then nitrate uptake is stimulated.

D) If organic acids are reduced (less HCO3-), then nitrate uptake is reduced.

E) As trees become more stressed, growth rate is reduced, less amino acids are used in protein synthesis, and more amino-acids recycle in a tree, causing nitrate uptake reduction.
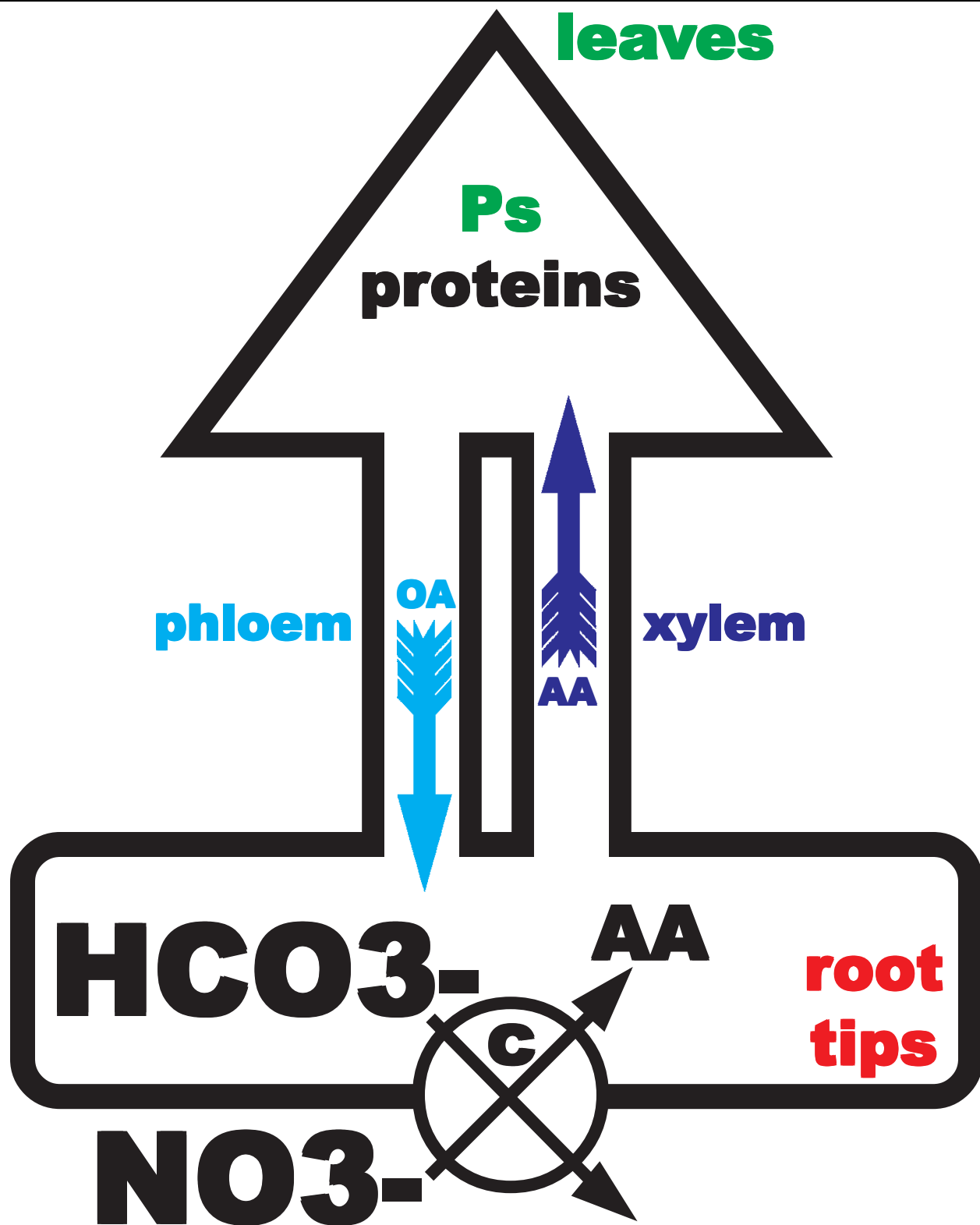
Figure 25: Nitrate uptake and control model inside a tree generating amino acids (AA) and using carboxylate ions from organic acids (OA).
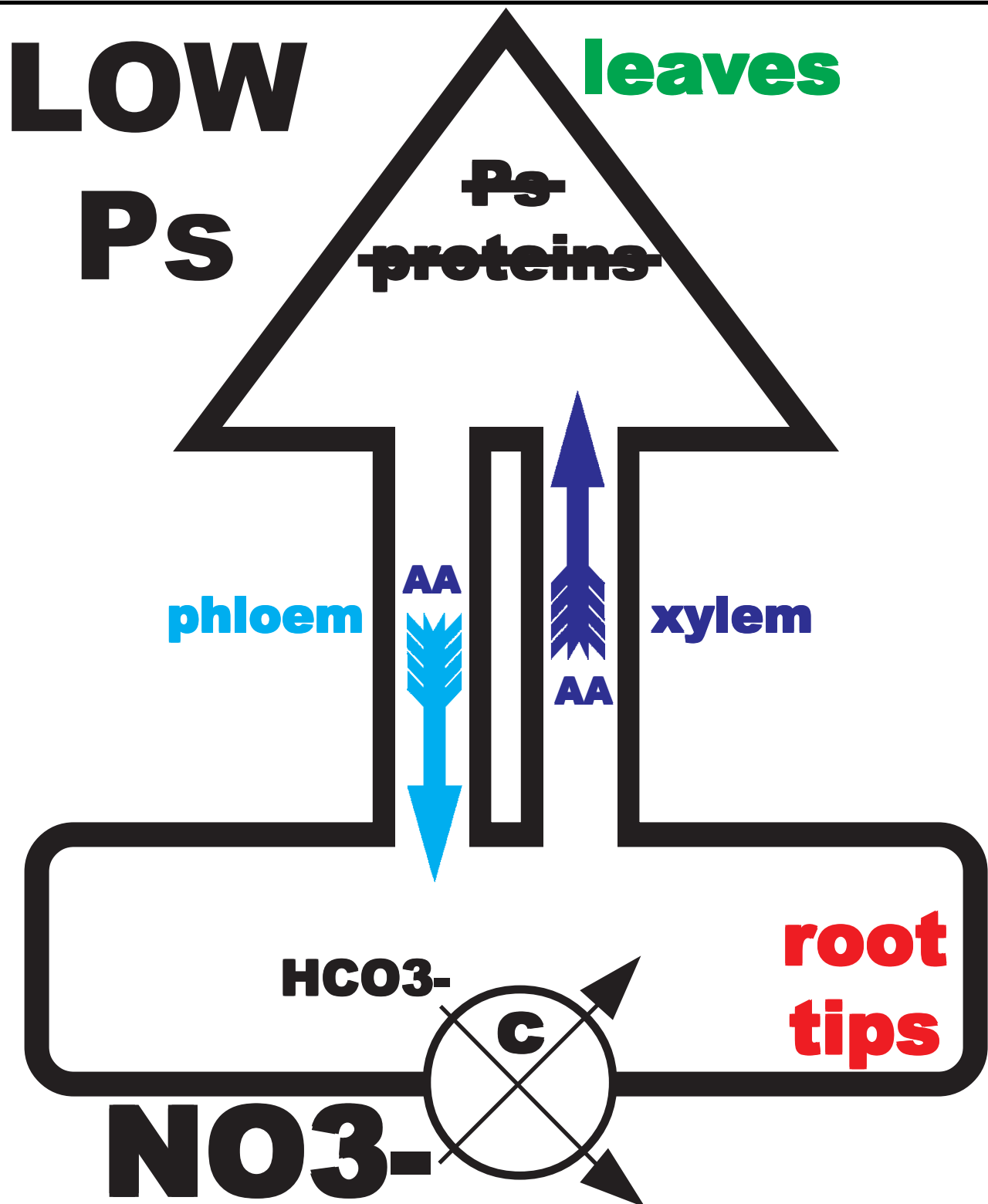
Figure 26: Nitrate uptake and control model inside tree under photosynthetic and protein synthesis constraints or stress causing recycling of unused amino acids (AA) slowing nitrate uptake.
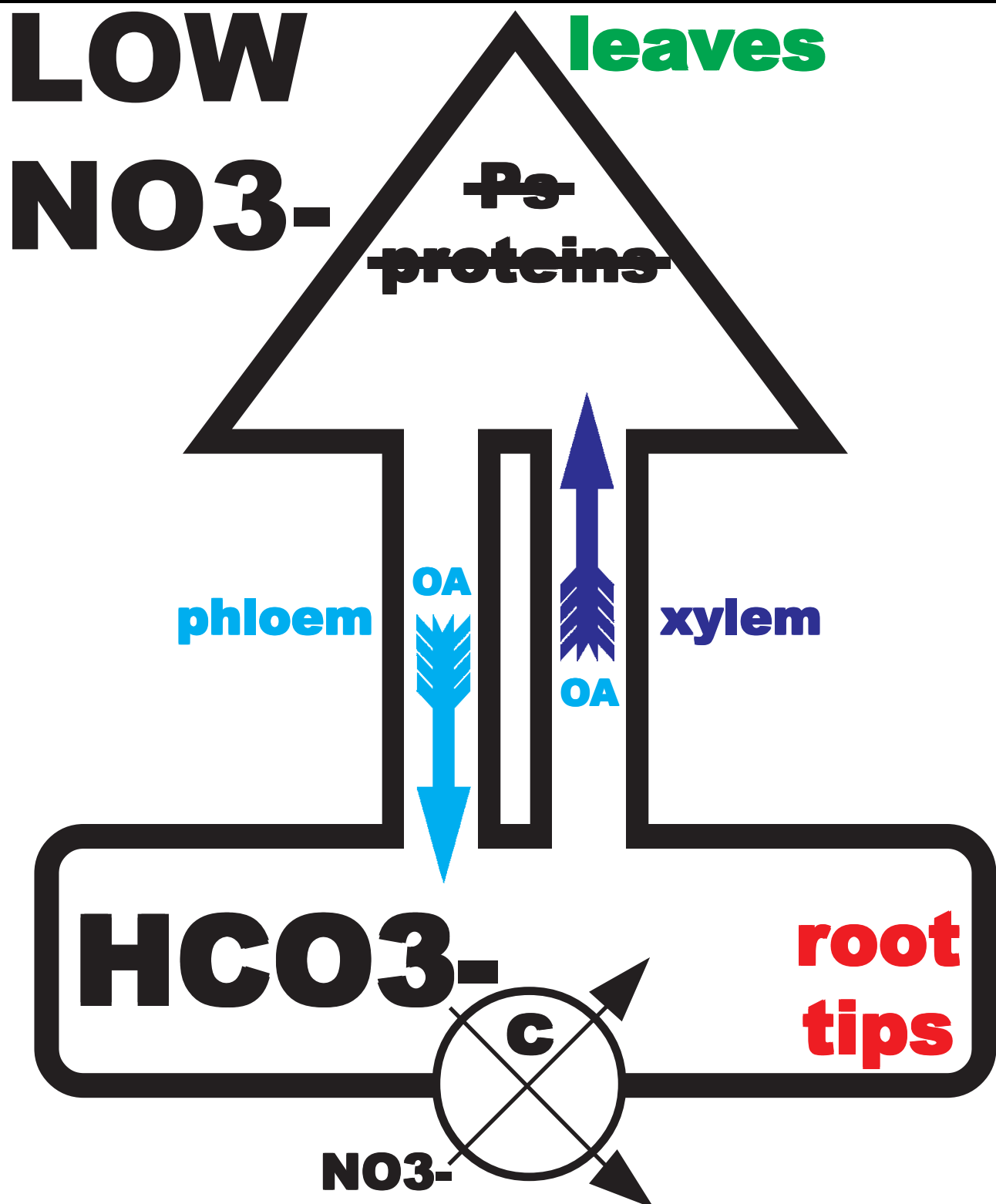
Figure 27: Nitrate uptake & control model inside tree under nitrate availability constraints / stress causing recycling of organic acids (OA) slowing photosythesis & protien synthesis.

Nitrogen Conclusions

Reduced (energized) nitrogen in several external forms is essential for trees to collect and control. Internally, a large amount of energy and carbon chains are used to corral and transport nitrogen. Nitrogen is the glue which holds tree life together. Tree health care providers must understand the essential element nitrogen in trees.

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
1785
Warnell School of Forestry
& Natural Resources

Essential Element Conservation & Appearance In Trees

Trees require 19 elements from the environment, plus large amounts of water, to survive and thrive. Figure 28 demonstrates in a soil, weathering of minerals and organic matter are two key sources for sustaining essential element balance in trees, while enriching essential elements on a site may be needed for adequate or better performance.

At one time or another, each essential element could be at a deficient level, toxic level, or at a biologically and therapeutically adequate level. Trying to balance all 19 elements is difficult, for both a tree and for a tree health care provider. Only a few elements generate short term (i.e. noticeable) growth gains. Some do not show significant visual symptoms until well into damaging deficiency. Some deficient essential elements show similar visual symptoms with many other essential elements deficiencies or toxicities, causing management by visual symptoms to be fraught with errors.

Conserving

Essential elements are valuable, and so, are conserved in trees by many processes. Key element conservation and recycling processes include heartwood generation, senescence, abscission, cladaptosis, and other forms of compartmentalization. Some elements are mobile inside a tree while others are immobile, locked into place once and not moved. Tree-mobile elements can be continually recycled. In soils some elements are mobile and some are immobile. The elements mobile in a soil environment may not be mobile inside a tree. For trees, rooting surface area, root density, and continued root growth are key to capturing both soil mobile and immobile elements.

Senescence

The living process in a tree conserving and recycling mobile resources, including essential elements, is called senescence. Senescence includes the pre-planned and orderly dismantling of light gathering machinery and associated elements inside a deciduous or declining tree leaf, retracting mobile essential elements from within a woody or absorbing root to be sealed off, and recalling mobile elements within a twig to be shed.

In senescence, a tree recalls valuable mobile essential elements, on-loan to temporary leaves, roots, and twigs. Approximately 77% of nitrogen (N), potassium (K), and phosphorus (P) in deciduous tree leaves are remobilized and returned to the tree. Less than 45% of magnesium (Mg) is returned from senescing leaves. There is usually a slight loss of heavier metals with falling leaves. Tissues killed quickly by pathogens, or damaged by animals or climatic extremes, do not have time to senesce. In these cases, a tree can not recall and reuse any of the essential elements in tissues except through ecological recycling. Figure 29.

Doing The Job

Many elements are essential to tree life. All of these essential elements are needed in different proportions. Each element has a unique job(s) to perform in a tree. Too much or too little of any single element disrupts tree life. Figure 30 provides a list of life sustaining categories in which different
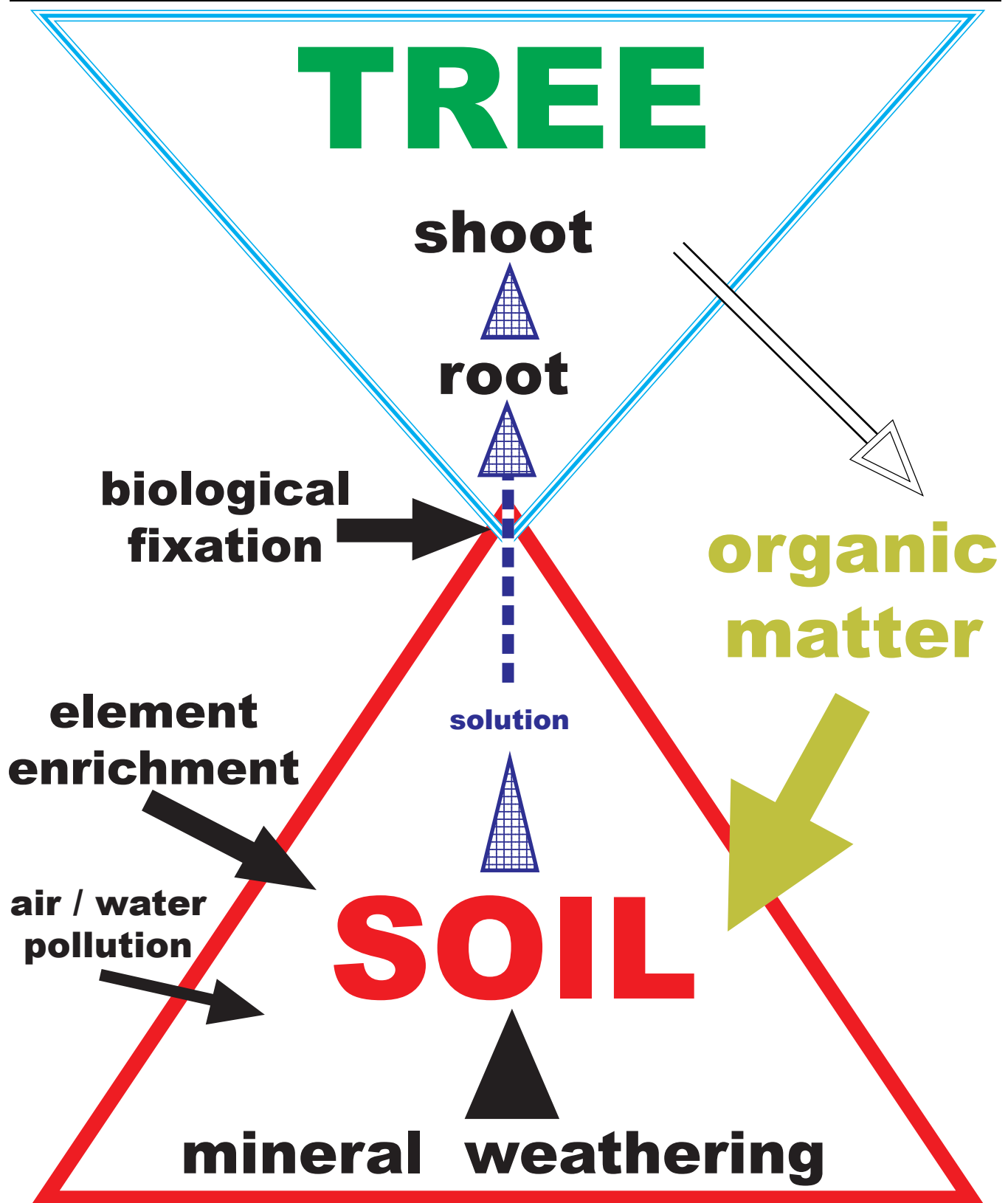
Figure 28: Primary sources of essential elements in a soil / tree association.

all elements
to growing
tissues

tree mobile
elements
recovered /
immobile
elements lost

growth   senescence

**ESSENTIAL
ELEMENTS**
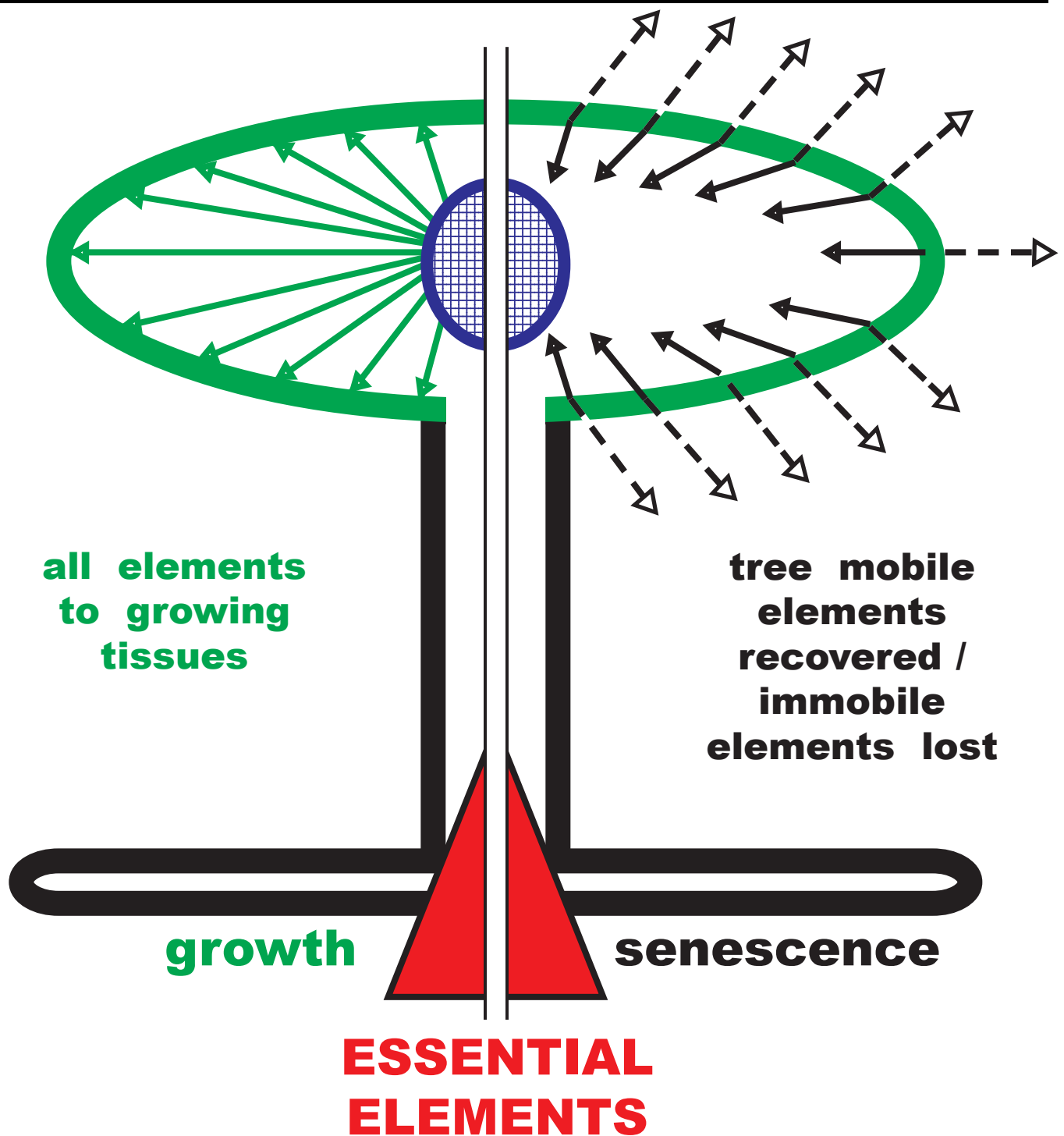
Figure 29: General view of element mobility in tree
symplast with growth and senescence.

Carbon Activators

Energy Production

Genetic Control

Cell Wall & Membrane Structure

Parts of Enzymes & Metabolites

Activator / Modifier of Enzymes

Counter Ionic Charge

Counter Osmotic Pressure

Figure 30: Function categories within a tree for essential elements

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
1785
Warnell School of Forestry
& Natural Resources

elements participate. Note these are general areas representing tens-of-thousands of individual processes and structures. Some elements define all of life like nitrogen and phosphorus. Other elements are utilized in a single process or structural role. For all these many categories of use, maintaining essential elements at an appropriate balance is key to tree health and sustainability.

Element Roles

Figure 31 shows the major players in moving life forward -- nitrogen, sulfur, and phosphorus all within a carbohydrate (CHO) framework. By definition, amino acids and the proteins they build are carbon scaffolds holding nitrogen atoms. Phosphorus represent the batteries of the tree cells, assuring continuing use of captured sunlight energy in all work within living cells. Carbon represents the static organic materials, while nitrogen, sulfur and phosphorus make life dynamic.

Figure 32 represents specialized parts of working proteins / enzymes where the value of a specific element is essential to its function. From magnesium in the center of chlorophyll to nitrogen processing using molybdenum and nickel, all these metals are used for their unique chemistry. Figure 33 addresses elements not as part of a working structure, but making the working structure function. These elements adjust and hold enzymes in a position to effectively function.

Figure 34 shows the framework of walls and membranes within which all life functions occur. Some of these element structural roles are outside the living cell membrane in the apoplast. For trees, these nails and stitching are as vital to survival as symplastically used elements. Also, the chemistry rules of ionic charge and hydration must be met in order for any life function to proceed. Potassium plays a key role in assuring chemical energy is conserved.

Specific Roles

Another way to look at essential elements is by the variety of essential tasks completed within a tree. Figure 35 is a multi-page figure providing the key functions and participation for each tree essential element, in alphabetical order.

Checking Element Levels

For generations many tree health care providers have depended upon visual symptoms and simple identification guides for anticipating and treating element deficiencies and toxicities. Unfortunately, element interactions and limited tree symptom presentation allow for many diagnosis errors. To determine the actual biological concentration of an element, tree tissue samples should be pulled and analyzed primarily for deficiencies, and soil samples collected and analyzed for availability and toxicities.

Go TEAIM

Figure 36 provides the Coder Tree Element Availability Interaction Matrix (TEAIM). The TEAIM shows major interactions between tree essential element availabilities on tree sites. As one element is enriched (added) on a site, another element's functional availability could be increased, decreased, or not impacted at all. Adding an element requires ecological tuning and balancing of other elements.

For example, the availability of calcium (Ca), cobalt (Co), potassium (K), magnesium (Mg), molybdenum (Mo), and sulfur (S) improves with enrichment of nitrate on a site. At the same time, nitrate enrichment disrupts availability of chlorine (Cl), iron (Fe), manganese (Mn), silicon (Si), and zinc

Carbon Activators

N   all amino acids
         & proteins
S   stress amino acids,
         proteins, & coenzymes

Energy Production

P   capture, storage & use
         of cellular energy,
         sugar phosphates,
         adenosine phosphates
         (ATP)

Genetic Control

N   nucleic acids
P   nucleic acids

Figure 31: General description of the most important
functions in trees for essential elements.

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
Warnell School of Forestry
& Natural Resources
1785

Parts of Enzymes & Metabolites

Mg   chlorophyll

Fe   heme pigments, ferredoxin & iron-sulfur proteins

Mn   water splitting enzyme in LHCII & superoxide dismutase enzyme

Zn   several enzymes

Cu   several enzymes

Ni   urease enzyme

Mo   nitrogenase, nitrate reductase

Figure 32: General description of the most important functions in trees for essential elements.

Enzyme Activator / Modifier

K	**many enzymes activated**
Cl	**LHCII water splitting & oxygen release**
Mg	**phosphate transfers, many (most) enzymes**
Ca	**binds to calmodulin (an enzyme regulator) & other enzymes**
Mn	**citric acid cycle enzymes, many enzymes**
Fe	**activates several enzymes**
Zn	**activates several enzymes**
Cu	**activates several enzymes**
Co	**stabilizes and activates enzymes**

Figure 33: General description of the most important functions in trees for essential elements.

Cell Wall & Membrane Structure

Ca   binds polysaccharides in cell walls

B   binds pectic polysaccharides in & between walls

P   cell membranes

Si   stability in cell walls

Counter Ionic Charge

K   Cl Ca   Mg

Counter Osmotic Pressure

K   Cl

Figure 34: General description of the most important functions in trees for essential elements.

Figure 35: Key functions and process participation
for tree essential elements.

B   boron

chlorophyll synthesis, cell wall integrity, RNA base synthesis, cell division & maturation, phophogluconates, CHO synthesis, nucleic acid synthesis, phosphate utilization

Ca   calcium

cell wall stability, membrane structure, membrane permeability, growth regulation, signals, activates enzymes for cell division & elongation, protein synthesis, CHO transport, heavy metal detoxification

Cl   chlorine

water splitting step in photosynthesis, osmotic pressure control, stomate function, hydration control

Cu   copper

plastocyanin, cytochrome functions, antioxidants, lignin synthesis, electron transport systems, protein & CHO metabolism, nitrogen fixation, fatty acid metabolism

(continued)

Figure 35: Key functions and process participation
for tree essential elements. (continued)

Co   cobalt

cobamide coenzyme, synthesis of chlorophyll, protein synthesis, symbiotic nitrogen fixation

Fe   iron

cytochromes, iron-sulfur energy transfer compounds, electron transfer system, terminal respiration step, ferredoxin, nitrogen & sulfur processing, NADP energy system, chlorophyll synthesis, protein synthesis, hemoproteins, non-heme proteins, dehydrogenases

K   potassium

protein synthesis, water balance / turgor, electric charge balance, stomate function, transport of CHO

Mg magnesium

chlorophyll, essential ion for many enzyme configurations & functions, integrity of ribosomes, protein synthesis, bridge between ATP energy activation & enzymes

(continued)

Figure 35: Key functions and process participation
for tree essential elements. (continued)

Mn manganese

amino acids, water splitting step in photosynthesis, antioxidant, bridge for ATP activation of enzymes, growth regulation, multiple enzyme systems, nitrate reduction

Mo molybdenum

symbiotic relationships with nitrogen fixation, nitrate processing, sulfur processing, dehydrogenases, antioxidants, oxidases, nitrogenases, molybdoferredoxin

N   nitrogen

proteins, nucleic acids, chlorophyll, alkaloids, synthesis of amino acids, growth regulators

Ni   nickel

nitrogen processing & transport, urease, hydrogenases

(continued)

Figure 35: Key functions and process participation
for tree essential elements. (continued)

P   phosphorus

links nucleotides, nucleic acids RNA / DNA, energy metabolism, structure of ATP, protein synthesis, carbohydrate phosphorylation, phospholipid membranes, signals

S   sulfur

amino acids, proteins, coenzymes, metallothioneins, iron-sulfur energy transfer compounds, sulfolipids, antioxidants, stress response

Si   silicon

structural integrity, lignin synthesis

Zn   zinc

RNA DNA synthesis, dehydrogenases, antioxidants, chlorophyll synthesis, enzyme activation, anhydrase, proteins, CHO metabolism, lipid synthesis

Figure 36: Coder Tree Element Availability Interaction Matrix.

	Zn	Si	S	P	Ni	N-	N+	Mo	Mn	Mg	K	Fe	Cu	Co	Cl	Ca
B	A	A		S		AS	AS	A	A	A	A	A	A			A
Ca	AS			A	A	S	A	AS	AS	A	A	A	AS	A		
Cl					A	S										
Co	AS				A	S	S	A	A	A		A				
Cu	A		A	A	AS	AS	AS	A	AS	A	A	A				
Fe	A	A	AS	A	A	A	S	A	A	A	A					
K	A					S	S	A	A	A						
Mg	AS		S	S	A	S	A	S	A							
Mn	A	AS		AS	A	A	S	A								
Mo		S	A	AS		S	A									
N+	A	A	S													
N-	A	A	S													
Ni	A	A		A												
P	AS	AS	A													
S	A															
Si																

N- = nitrate
N+ = ammonium

TEAIM

A = antagonistic ▲▼

S = synergistic ▲▲

--Element which is increased in availability while decreasing another element availability is considered antagonistic (A).
--Element which is increased in availability while also increasing another element's availability is considered synergistic (S).
--Some elements have been cited by research to be antagonistic in some processes and found to be synergistic in others. This table contains all interactions reported.

Tree Essential Elements (part 3) -- Dr. Kim D. Coder

UNIVERSITY OF
GEORGIA
1785
Warnell School of Forestry
& Natural Resources

(Zn). Another example of availability interactions is when calcium (Ca) and magnesium (Mg) liming products are applied to a soil where each is deficient. In this case, dolomitic limestone enrichment will initiate disruption of phosphorus (P) availability caused by calcium (Ca) and increase phosphorus (P) availability caused by magnesium (Mg), but not in a balanced off-setting process over time.

Symptom Meanings
        There have always been deficiency and toxicity symptom keys, many from annual agriculture field crops or fast growing greenhouse crops, which help people decide which elements are in short supply based upon visual symptoms. For many elements, once symptoms are clearly apparent, significant physiological disruption has already occurred. It is always preferable to head-off element problems early before strong symptoms are generated.
        In keeping with traditional views of symptomology, Figure 37 provides deficiency symptom identification for trees using visual clues. Symptoms across the entire tree or concentrated in the root and above ground areas have been identified with a number of element deficiencies. Note one symptom can have many elemental causes, as well as pest interactions.
        Figure 38 provides element deficiency symptoms visible on secondary meristems (periderm and cambial areas), and in buds and new leaves. The numerous elements leading to similar visual symptoms are clear from the literature.
        Figure 39 is most telling regarding leaf tissue being very suspectable to small deficiencies and quickly showing symptoms. Across all various leaf symptoms, 13 different elements can generate symptoms when deficient. A number can show multiple symptoms when deficient in leaves. For example, a zinc deficiency can manifest itself as a blue-green coloration, dark veins, yellowing, and stunted and distorted leaf blades. At the same time, several other element deficiencies cause the same symptoms.

Breaking Down
        Besides the traditional visual symptoms of physiological changes in a tree from element deficiency, a number of observers have found changes in a tree's tolerance and resistance to abiotic and biotic stress and strain. Figure 40 provides a number of element interactions with pests, abiotic stressors, and nitrogen processing in trees. For example, drought stress is accentuated by cobalt (Co) deficiencies. A number of leaf pathogens are facilitated for entrance and successful attack by element deficiencies.

Old vs. New
        Within the literature on visual deficiency symptom catalogs, one component used is whether symptoms are in old tissue or new tissue. This symptomology goes back, supposably, to mobility in trees of different elements. Figure 41 provides symptoms of element deficiency based upon the location within a tree where symptoms first develop, and age of tree tissues. Symptom identification systems using mobility of elements in a tree as a general means of identifying which elements were deficient show large potential for errors. Because the same tree symptom can have multiple causes, applying element mobility concepts can lead to inconsistent and inaccurate diagnosis in the field.
        Figure 42 presents a gradient of element mobility among select tree essential elements. All the essential elements have varying degrees of mobility within a tree, and this mobility changes with time, tissue age, tissue type, and environmental interactions. When some truly immobile elements are defi-

tree part	primary symptom element deficiency responsible
whole tree	**complete disruption** **N, P, K, S**
roots	**stunted / damaged** **B, Cl, Cu, Mn, N, Ni, P, K, S, Si, Zn** **gum exuded** (exanthema) **Cu, Zn**
shoots	**stunted, damaged, killed** **B, Ca, Cl, Cu, Fe, Mn, Mo, N, Ni, P, K, S, Zn** **gum exuded** (exanthema) **Cu, Zn**

Figure 37: Primary visual deficiency symptoms in trees.
Note many elements elicit the same limited set
of symptoms from various species of trees. These
are symptoms and associated deficiencies
specifically for tree species, not other plant forms.

tree part	primary symptom
	element deficiency responsible
secondary meristems	**periderm cracks, atypical patches, localized growths**
	B, Cu, Ni
	cambium death / lesions
	Ca
buds	**released buds, brooms**
	Cu, Ni
	distorted / death
	B, Ca, Cu, Ni
new leaves	**wilting**
	B, Cl, Cu, K, Mo, Zn

Figure 38: Primary visual deficiency symptoms in trees.
Note many elements elicit the same limited set of symptoms from various species of trees. These are symptoms and associated deficiencies specifically for tree species, not other plant forms.

tree part	primary symptom element deficiency responsible
leaves	**color – bleaching white** Fe **color – blue-green / dark** Cl, K, P, Zn **color – dark viens** Cu, Mn, P, Zn **color – yellow-brown** Cl, Cu, K, N, P **color – purpling / reddish** Mg, P **color – general chlorosis** B, Cl, Cu, Fe, K, Mg, Mo, Mn, Ni, S, Zn **marginal chlorosis / death** B, Ca, Cl, Cu, K, Mg, Mo, Ni **intervienal chlorosis / death** Fe, Mg, Mo, Mn, Ni, S, Zn **stunted / distorted blades** B, Cl, Cu, K, Mg, Mn, Mo, N, Ni, Zn

Figure 39: Primary visual deficiency symptoms in trees.

interaction type	causal element deficiency
increase pest effectiveness whole tree	B, Cl, K, Mg, Mn, Ni, Si
increase pest effectiveness in roots	Ca, K, Mg, Mn, Si
increase abiotic stress in whole tree	Ca, Co, Si
decrease metal toxicity	Ca, Si
nitrogen processing disrupted	Co (legume trees), Mo, K, S
growth regulator disruption / dysfunction	Co, Zn

Figure 40: List of element deficiency problems interacting with other biotic and abiotic problems in trees.

symptom tissue location	element mobility inside tree element deficiency
new tissues	**immobile** B, Ca, Co, Cu, Fe, Mn, Ni, S, Zn
old tissues	**mobile** K, Mg, Mo, N, P, S
all tissues	**mobile** Cl, Cu, K, Ni, N, P, Si, Zn
intermediate	**mobile / immobile** Mn, Mo, S, Zn

Figure 41: Examination of visual symptoms of element deficiency across the whole tree with associated internal mobility expectations. Note multiple element deficiencies are responsible for visual symptoms in all tree areas.

deficiency symptoms

**older
tissue**   **newer
tissue**

N K P Mg | S Mo Zn Mn | Co Cu Ni Fe B Ca

mobile | **partially
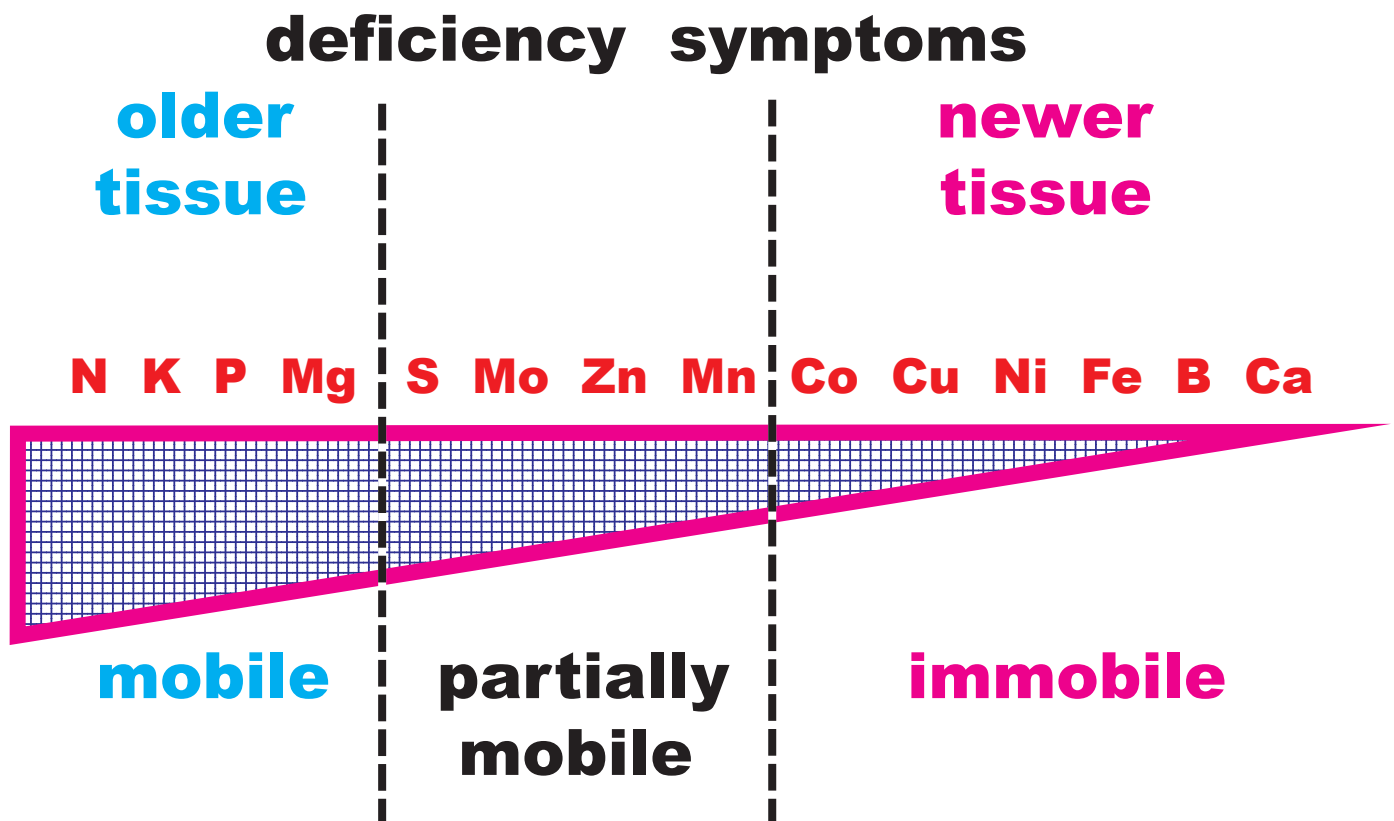mobile** | **immobile**

Figure 42: Gradient view of cited tree essential element
mobilities inside a tree ranging from elements with
great mobility to elements with little mobility.

cient, depending upon the depth and extent of the deficiency, new tissue may show symptoms first. Unfortunately, other elements can show the same symptoms in the same tissues and not be associated with element mobility. Generally, old versus new tissue symptom recognition is not reliable in understanding deficiency.

Trees Are Different

Because of the great mass of information in agronomic and horticulture crops, deficiency symptoms have been cataloged and defined by season and crop. For trees, little of this type of information has been determined. Transferring element symptom information from other cropping systems, especially annuals, has proven inaccurate and wasteful. In trees deficiency has been looked at in a few species, but essential element toxicity has had little study. Toxicity visual symptoms provide a critical aspect in essential elements.

Toxic

Figure 43 provides a list of visual essential element toxicity symptoms in roots, shoots, and cambium / periderm of trees. There are fewer elements, but still multiple element toxicity per symptom. Figure 44 examines leaf visual symptoms of essential element toxicity. Again, there are a few element toxicity symptoms presented by many essential elements, and some elements cause multiple symptoms, though never exclusively.

Figure 45 is a summary of both essential element deficiency and toxicity symptoms. The elements listed, boron (B), chlorine (Cl), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), and nickel (Ni), present significantly similar tree visual symptoms at both deficient and toxic levels. For these elements, visual symptoms can not determine whether an element is at a deficient or toxic level because symptoms are the same. In addition, for most of these elements, the pinnacle between adequate / optimum, and too much or too little, is very sharp and narrow.

The Point!

Because the same visual symptoms of element deficiency and toxicity can have many different causes, over simplified visual assessment guides lead to misdiagnosis and serious errors in treatments. Visual symptoms should not be relied upon for assessing essential element problems. Only through tissue testing for deficiency and soil testing for availability and toxicity can a tree health care provider accurately determine essential element concentration levels, attempt to correct antagonistic / synergistic essential element interactions, and prescribe beneficial treatments.

tree part	primary symptom element toxicity responsible
roots	**stunting** **Cu, Mg** **root browning / death** **Fe, Mn, Ni** **carbohydrate depletion** **N**
shoots	**tip dieback** **Cl** **stunting / damage / death** **N, Mg** **golden yellow new shoots** **Mo**
periderm	**lesions** **Mn, Ni** **cambium death / lesions** **Mg**

Figure 43:   List of visual toxicity symptoms in tree tissues.
Note B, Cl, Cu, Fe, Mg, Mn, Mo, and Ni present significantly
similar tree symptoms at both toxic and deficient levels.

tree part	primary symptom element toxicity responsible
leaves	**chlorosis** B, Ca, Cl, Co, Cu, Mn, Ni **darkened yellow-brown** Fe, Mg **dark green** N **wilting** Cl, N **curling / cupping / distorted** Cl, Mn, Mo, Ni **marginal burn / scorch** B, Cl, Mn, Ni **brown lesions** Fe, Mn **brown / death** B **premature senescence / abscision** Cl, S

Figure 44:   List of visual toxicity symptoms in tree tissues.
Note B, Cl, Cu, Fe, Mg, Mn, Mo, and Ni present significantly similar tree
symptoms at both toxic and deficient levels.

DEFICIENCY & TOXICITY

B	**boron**
Cl	**chlorine**
Cu	**copper**
Fe	**iron**
Mg	**magnesium**
Mn	**manganese**
Mo	**molybdinum**
Ni	**nickel**

Figure 45:   List of tree essential elements causing similar visual deficiency and toxicity symptoms in the same tissues.

CONCLUSION

All tree essential elements, plus water, are needed to keep a tree healthy and structurally sound. Essential proportions and balance between elements are key tree health care issues for sustainability. A tree health care provider must carefully tune the ecological system of a tree and site to provide adequate elements.

Tree life depends upon the "essential 20!"

Selected Literature

Blackmer, A.M. 2000. Bioavailability of nitrogen. Pp.D3-D17 in M.E. Sumner (editor). 2000. **Handbook of Soil Science**. CRC Press, BocaRaton, FL.

Barker, A.V. & D.J. Pilbeam. 2007. **Handbook of Plant Nutrition**. CRC Press, Taylor & Francis, Boca Raton, FL. Pp.613.

Camberato, J.J. & W.L. Pan. 2000. Bioavailability of calcium, magnesium, and sulfur. Pp.D53-D69 in M.E. Sumner (editor). 2000. **Handbook of Soil Science**. CRC Press, BocaRaton, FL.

Coder. Kim D. 2011. Misdiagnosing essential elements: One tree symptom -- multiple element causes. Arborist News 20(2):61-64.

Epstein, E. & A.J. Bloom. 2005. **Mineral Nutrition of Plants: Principles & Perspectives** (2nd edition). Sinauer Associates, Sunderland, MA. Pp.400.

Havlin, J.L., J.D. Beaton, S.L. Tisdale, & W.L. Nelson. 2005. **Soil Fertility and Fertilizers** (7th edition). Pearson-Prentice Hall, Upper Saddle River, NJ. Pp.515.

Helmke, P.A.. 2000. The chemical composition of soils. Pp.B3-B24 in M.E. Sumner (editor). **Handbook of Soil Science**. CRC Press, BocaRaton, FL.

Jones, J.B. 2012. **Plant Nutrition and Soil Fertility Manual.** (2nd edition), CRC Press, Boca Raton, FL. Pp.282.

Jones, R., H. Ougham, H. Thomas, & S. Waaland. 2013. **The Molecular Life of Plants.** Wiley-Blackwell. Hoboken, NJ. Pp.742.

Kabata-Pendias, A. 2011. **Trace Elements In Soil and Plants** (4th edition). CRC Press, Boca Raton, FL. Pp.520.

Lide, D.R. (editor). 1998. **Handbook of Chemistry and Physics** (79th edition). CRC Press, Boca Raton, FL

Marschner, P. 2012. **Mineral Nutrition of Higher Plants.** (3rd edition). Academic Press, Waltham, MA. Pp.651.

Meuser, H. 2010. **Contaminated Urban Soils.** Environmental Pollution Series Volume 18. Springer, New York, New York. Pp.318.

Mortvedt, J.J. 2000. Bioavailability of micronutrients. Pp.D71-D88 in M.E. Sumner (editor).
        Handbook of Soil Science. CRC Press, BocaRaton, FL.

Sharpley, A. 2000. Phosphorus availability. Pp.D18-D37 in M.E. Sumner (editor). 2000.
        Handbook of Soil Science. CRC Press, BocaRaton, FL.

Sparks, D.L. 2000. Bioavailability of soil potassium. Pp.D38-D52 in M.E. Sumner (editor). 2000.
        Handbook of Soil Science. CRC Press, BocaRaton, FL.

Stwertka, A. 2002. **A Guide to the Elements**. (2nd edition). Oxford University Press. New York,
        NY. Pp.246.

Wilkinson, S.R., D.L. Grunes, & M.E. Sumner. 2000. Nutrient interactions in soil and plant nutrition.
        Pp.D89-D111 in M.E. Sumner (editor). 2000. **Handbook of Soil Science**. CRC Press,
        BocaRaton, FL.

Dr. Kim D. Coder   Warnell School   University of Georgia   2021

PERIODIC TABLE OF ELEMENTS

(natural elements / human created elements)

* = radioactive

family groups

periods

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1																	**He** 2
Li 3	**Be** 4											**B** 5	**C** 6	**N** 7	**O** 8	**F** 9	**Ne** 10
Na 11	**Mg** 12											**Al** 13	**Si** 14	**P** 15	**S** 16	**Cl** 17	**Ar** 18
K 19	**Ca** 20	**Sc** 21	**Ti** 22	**V** 23	**Cr** 24	**Mn** 25	**Fe** 26	**Co** 27	**Ni** 28	**Cu** 29	**Zn** 30	**Ga** 31	**Ge** 32	**As** 33	**Se** 34	**Br** 35	**Kr** 36
Rb 37	**Sr** 38	**Y** 39	**Zr** 40	**Nb** 41	**Mo** 42	Tc 43*	**Ru** 44	**Rh** 45	**Pd** 46	**Ag** 47	**Cd** 48	**In** 49	**Sn** 50	**Sb** 51	**Te** 52	**I** 53	**Xe** 54
Cs 55	**Ba** 56	**La** 57	**Hf** 72	**Ta** 73	**W** 74	**Re** 75	**Os** 76	**Ir** 77	**Pt** 78	**Au** 79	**Hg** 80	**Tl** 81	**Pb** 82	**Bi** 83	**Po** 84*	**At** 85*	**Rn** 86*
Fr 87*	**Ra** 88*	**Ac** 89*	Rf 104*	Db 105*	Sg 106*	Bh 107*	Hs 108*	Mt 109*	Ds 110*	Rg 111*	Cn 112*	Nh 113*	Fl 114*	Mc 115*	Lv 116*	Ts 117*	Og 118*

Lanthanides

Ce 58	**Pr** 59	**Nd** 60	Pm 61*	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68	**Tm** 69	**Yb** 70	**Lu** 71

Actinides

Th 90*	**Pa** 91*	**U** 92*	Np 93*	Pu 94*	Am 95*	Cm 96*	Bk 97*	Cf 98*	Es 99*	Fm 100*	Md 101*	No 102*	Lr 103*