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*Warnell School of Forestry & Natural Resources*

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# **Tree Essential Elements Manual (Part 2)**

**(element attributes, proportions & descriptions)**

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**Scope & Disclaimer:** This training manual is part 2 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.

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# Tree Essential Elements Manual (Part 2)

## Element Attributes

To make it easier to keep track of essential elements needed in tree life, the entire periodic table of elements can be modified and truncated. Figure 1. This figure of tree essential elements demonstrate element relationships. Although each essential element in a family (each table column has similar electron shells and reactivity, each element is unique physically, as well as how its chemical properties in soil and within a tree are manifested. Essential element attributes make each usable for providing structures and biochemical functions in a tree. Basic chemical differences of essential elements are utilized by a tree to perform many essential functions.

### Interactions

Figure 2 shows possible oxidation states (i.e. electron hoarding status) and electron shell configurations for each essential element. These two items are related. The electron configuration shows exterior electrons participating in interactions with other atoms. The oxidation states show the number of electrons potentially shared or given-up in bonding, or represents charge values when an element is in ionic form. Some elements like oxygen (O), magnesium (Mg), potassium (K), and calcium (Ca) have only a single oxidation state or valence with which to chemically interact and be used by a tree. Several elements like nitrogen (N), chlorine (Cl), manganese (Mn), and molybdenum (Mo) have a great variety of potential states for interactions, and this character allows for their unique uses in a tree. Note, metals tend to have either a +2 or +3 oxidation state.

Many elements interact with the most exterior electron shell -- the boxed numbers farthest to the right side of the electron configuration list in Figure 2. Each shell can only hold a set number of electrons before it is filled and a new shell begins to fill. For example, the second shell (called the "L" shell), can hold a maximum of eight electrons. A number of heavier elements (manganese (Mn) through nickel (Ni) and molybdenum (Mo) ) interact with two outer electron shells. This is a peculiar (and vital) attribute of these metals.

### Dominant Form

Figure 3 provides a list of the dominant or most stable oxidation state of each element and its normal physical form in a pure state. Although many elements can exist in many electronic states there is usually a most stable state based on internal particle interactions. Many elements have a stable oxidation state of 2, some reactive elements have a stable oxidation state of 1, and massive molybdenum and lighter sulfur reside at an oxidation state of 6. Notable is the lone representative of oxidation state 5, phosphorus (P) which is a critical component of the cellular power grid and a structural component of genetic materials. All these individual oxidation states can be changed through incorporation into biological (organic) housings or bindings.

<b>1</b>																
<b>H</b> 1												<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>
												<b>B</b> 5	<b>C</b> 6	<b>N</b> 7	<b>O</b> 8	
	<b>Mg</b> 12	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>		<b>Si</b> 14	<b>P</b> 15	<b>S</b> 16	<b>Cl</b> 17			
<b>K</b> 19	<b>Ca</b> 20		<b>Mn</b> 25	<b>Fe</b> 26	<b>Co</b> 27	<b>Ni</b> 28	<b>Cu</b> 29	<b>Zn</b> 30								
		<b>Mo</b> 42														

Figure 1: Periodic Table of Elements For Trees:  
Heavy Elements, Non-Essential Families, and  
Non-Essential Elements Truncated

#	element	average weight	oxidation state(s)	electron configuration
1	H	1 <sub>amu</sub>	+1 -1	1
5	B	11	+3 -3	2-3
6	C	12	+2 +4 -4	2-4
7	N	14	+2 +3 +4 +5 -1 -2 -3	2-5
8	O	16	-2	2-6
12	Mg	24	+2	2-8-2
14	Si	28	+4 -4	2-8-4
15	P	31	+3 +4 +5 -3	2-8-5
16	S	32	+2 +4 +6 -2	2-8-6
17	Cl	36	+1 +3 +5 +7 -1	2-8-7
19	K	39	+1	2-8-8-1
20	Ca	40	+2	2-8-8-2
25	Mn	55	+2 +3 +4 +6 +7	2-8-13-2
26	Fe	56	+2 +3	2-8-14-2
27	Co	59	+2 +3	2-8-15-2
28	Ni	59	+2 +3	2-8-16-2
29	Cu	64	+1 +2	2-8-18-1
30	Zn	65	+2	2-8-18-2
42	Mo	96	+2 +3 +4 +5 +6	2-8-18-13-1

(maximum in each shell – 1(K) = 2; 2(L) = 8; 3(M) = 18; 4(N) = 32, 5(O) = 32).

Figure 2: Comparison of principal atomic properties for tree essential elements, listed in order of increasing atomic weight. Given for each element are its number, symbol, rounded average atomic weight (amu), possible oxidation states, and filling sequence of electron shells (K-L-M-N-O configuration). The small boxes show the electron shell unfilled and most responsible for chemical interactions. Electron configuration shows the number of electrons in each shell.

most stable oxidation state					
1e	2e	3e	4e	5e	6e
<b>Cl</b> <sub>gn</sub>	<b>Ca</b> <sub>sm</sub>	<b>B</b> <sub>sl</sub>	<b>C</b> <sub>sn</sub>	<b>P</b> <sub>sm</sub>	<b>Mo</b> <sub>sm</sub>
<b>H</b> <sub>gm</sub>	<b>Co</b> <sub>sm</sub>	<b>Fe</b> <sub>sm</sub>	<b>Si</b> <sub>sl</sub>		<b>S</b> <sub>sn</sub>
<b>K</b> <sub>sm</sub>	<b>Cu</b> <sub>sm</sub>	<b>N</b> <sub>gn</sub>			
	<b>Mg</b> <sub>sm</sub>				
	<b>Mn</b> <sub>sm</sub>				
	<b>Ni</b> <sub>sm</sub>				
	<b>O</b> <sub>gn</sub>				
	<b>Zn</b> <sub>sm</sub>				

**s = solid; g = gas**  
**m = metal; n = non-metal;**  
**l = metalloid**

Figure 3: The most stable oxidation states (+ or -) for essential elements in trees, and each element form at biological temperatures and in pure form.

Figure 4 provides further information about the range of oxidation states, both positive and negative, for tree essential elements. The range of oxidation states are shown for a tree essential element as it reacts as part of a compound, and as it reacts centered within an organic framework. Carbon (C), chlorine (Cl), nitrogen (N), phosphorus (P), sulfur (S), and silicon (Si) all have tremendous numbers of oxidation states possible, and so can serve many possible biological roles. Six elements can only exist in a single oxidation state regardless of surroundings and bonding.

### Light Metal

Different tree elements exist in different forms at biological temperatures in the natural world. Chlorine (Cl), hydrogen (H), nitrogen (N), and oxygen (O) are (diatomic) gases in pure forms. The rest of the elements are solids. Tree elements can also be divided by appearance and reactivity in pure form. Calcium (Ca), cobalt (Co), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), potassium (K), and zinc (Zn) are all metals. Metals usually are dense with a high melting point, good heat conductors, and tend to combine easily with nonmetal elements, but seldom with each other. Metals tend to lose electrons in chemical reactions.

Carbon (C), chlorine (Cl), nitrogen (N), oxygen (O), phosphorus (P), and sulfur (S) are nonmetals. Nonmetals can be either solid or gas, usually with low density and melting points. Nonmetals tend to easily combine with both nonmetals and metals. Metalloids are intermediate in characteristics between metals and nonmetals. Metalloids tend to gain electrons in reactions. Boron (B) and silicon (Si) are example metalloids.

### Size Matters

Elements have different chemical attributes depending upon their chemistry and physical size. Figure 5 shows relative size of tree essential elements based upon atomic radius and divided into small, medium, and large. Metals are large while nonmetals are small to medium in size. Atomic weight is not directly correlated with size as calcium (Ca), potassium (K), and magnesium (Mg) are extra-large while heavier elements, like other metals, are smaller. Figure 6 uses a graphical means to differentiate relative element sizes.

Almost all elements moving into a tree are in ionic form (i.e. are ions, either cations or anions). Instead of atomic radius, ionic radius can better demonstrate effective size of each tree essential element. Figure 7 show relative ionic radius of elements divided into size classes. The heavier metal ions occupy medium size classes while chlorine and sulfur are the largest ions. Figure 8 represents the graphical form of ionic radius in tree essential elements. Here just three class sizes were pulled out with carbon (C), nitrogen (N), and phosphorus (P) at small size, and chlorine (Cl), oxygen (O), potassium (K), and sulfur (S) at large size. Atomic weight (i.e. mass) plays little role in ion size of an element.

Atomic radius of a tree essential element is graphed against its own ionic radius in Figure 9. This figure presents four major size groups. The small group has relative small atomic radius and extremely small ion size. The heavier metals in the medium group tend to have ion size at half their atomic radius. Some elements appear similar to each other physically, although not in the same element family chemically.

### Electron Matters

Figure 10 shows the first ionization energy of an element, or the amount of energy required to manipulate the first electron, divided into low, medium, and high energy requirements. Most metals have medium to low ionization energy requirements, easily losing an electron in a chemical reaction. Zinc (Zn) is unique because it lies at the boundary of medium and high. Magnesium (Mg) is also unique as it is a light element which has an ionization energy similar to heavier metals. These energy require-

element symbol	element name	within compounds		organic center			state range
		+	-	+	-	0	
<b>B</b>	<b>boron</b>	<b>3</b>		<b>3</b>			<b>1</b>
<b>C</b>	<b>carbon</b>	<b>2-4</b>	<b>4</b>				<b>9</b>
<b>Ca</b>	<b>calcium</b>	<b>2</b>		<b>2</b>			<b>1</b>
<b>Cl</b>	<b>chlorine</b>	<b>1-7</b>	<b>1</b>				<b>9</b>
<b>Co</b>	<b>cobalt</b>	<b>2-3</b>		<b>1</b>	<b>0</b>	<b>1</b>	<b>3</b>
<b>Cu</b>	<b>copper</b>	<b>1-2</b>		<b>1</b>	<b>0</b>	<b>1</b>	<b>3</b>
<b>Fe</b>	<b>iron</b>	<b>2-3</b>		<b>1</b>	<b>0</b>	<b>2</b>	<b>4</b>
<b>H</b>	<b>hydrogen</b>	<b>1</b>	<b>1</b>				<b>2</b>
<b>K</b>	<b>potassium</b>	<b>1</b>		<b>1</b>			<b>1</b>
<b>Mg</b>	<b>magnesium</b>	<b>2</b>		<b>2</b>			<b>1</b>
<b>Mn</b>	<b>manganese</b>	<b>2-7</b>		<b>1</b>	<b>0</b>	<b>3</b>	<b>5</b>
<b>Mo</b>	<b>molybdenum</b>	<b>6</b>		<b>1</b>	<b>0</b>	<b>2</b>	<b>4</b>
<b>N</b>	<b>nitrogen</b>	<b>1-5</b>	<b>1-3</b>				<b>9</b>
<b>Ni</b>	<b>nickel</b>	<b>2-3</b>		<b>1</b>	<b>0</b>	<b>1</b>	<b>3</b>
<b>O</b>	<b>oxygen</b>		<b>2</b>			<b>2</b>	<b>1</b>
<b>P</b>	<b>phosphorus</b>	<b>3-5</b>	<b>3</b>				<b>9</b>
<b>S</b>	<b>sulfur</b>	<b>4-6</b>	<b>2</b>				<b>9</b>
<b>Si</b>	<b>silicon</b>	<b>2-4</b>	<b>4</b>				<b>9</b>
<b>Zn</b>	<b>zinc</b>	<b>2</b>		<b>2</b>			<b>1</b>

Figure 4: Oxidation states (negative & positive) of tree essential elements in compounds or as a center of an organic structure. Potential oxidation state ranges are provided.



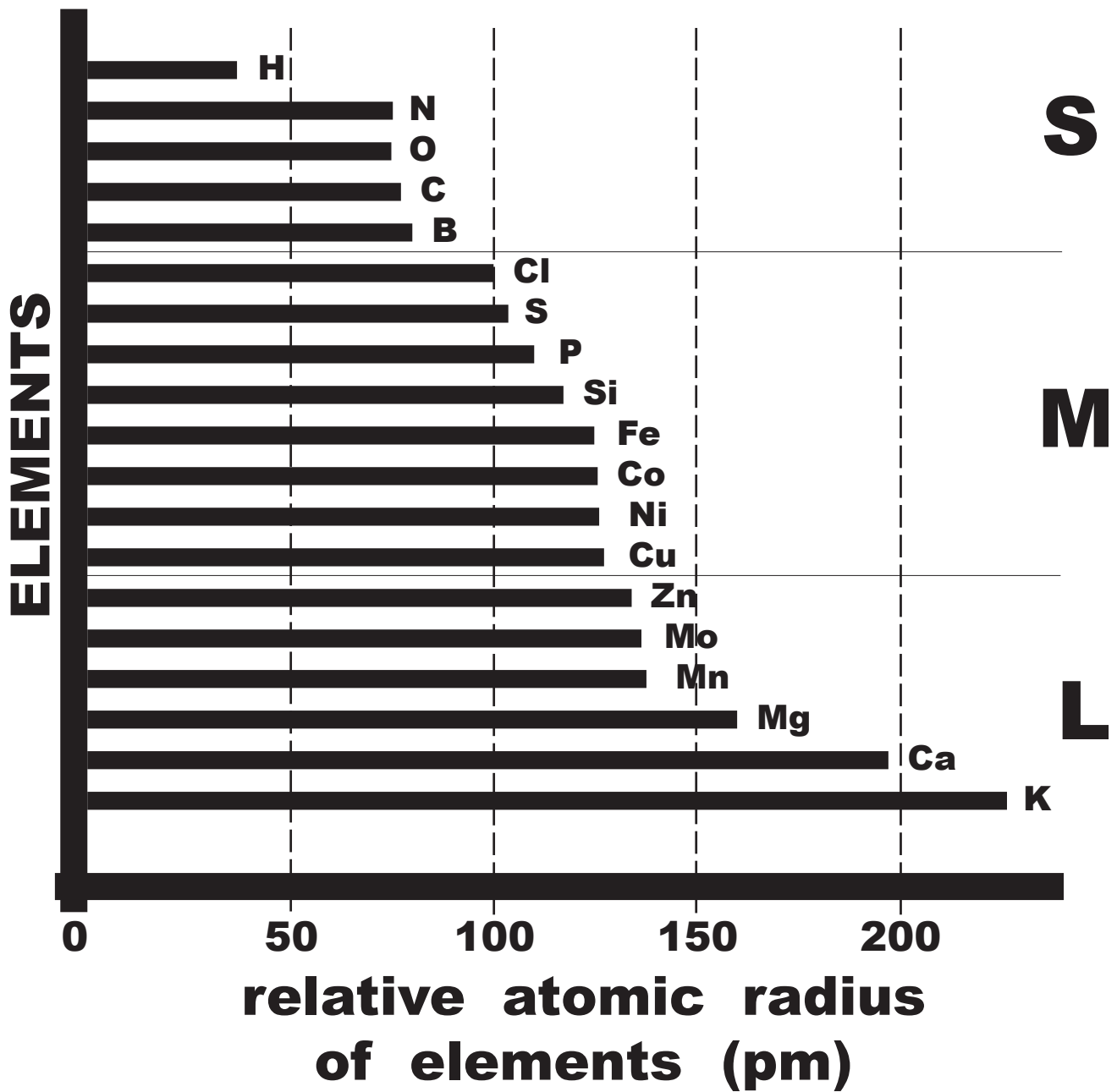


Figure 5: Relative atomic radius of tree essential elements with small, medium, and large size classes. (1 pm = 1 picometer = 100 angstrom)

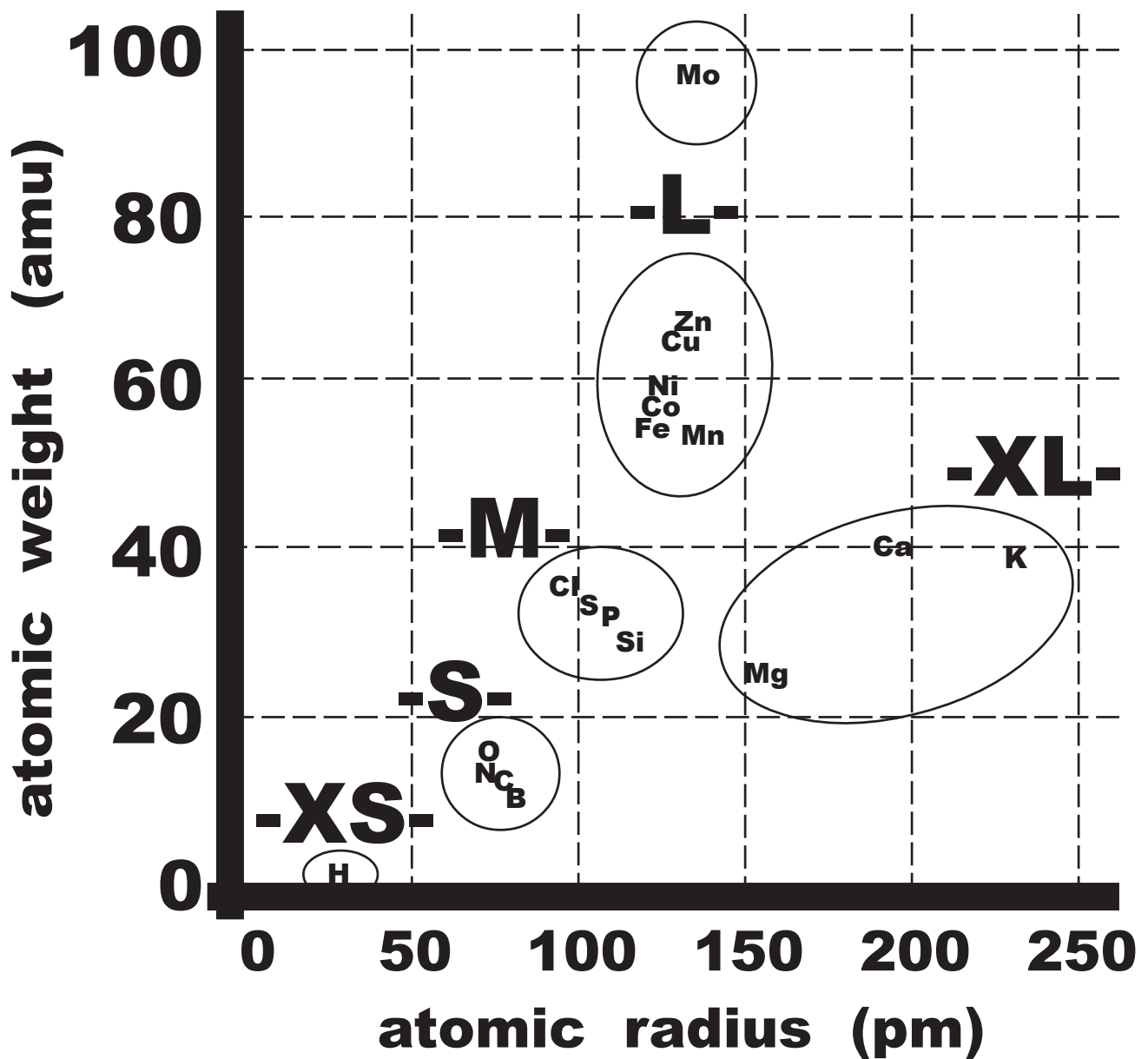


Figure 6: Comparison of tree essential element atomic weights (in amu) and atomic radii (in pm). There are six size groupings with hydrogen (H) and molybdenum (Mo) as single element groups.

(1 pm = 1 picometer = 100 angstrom)

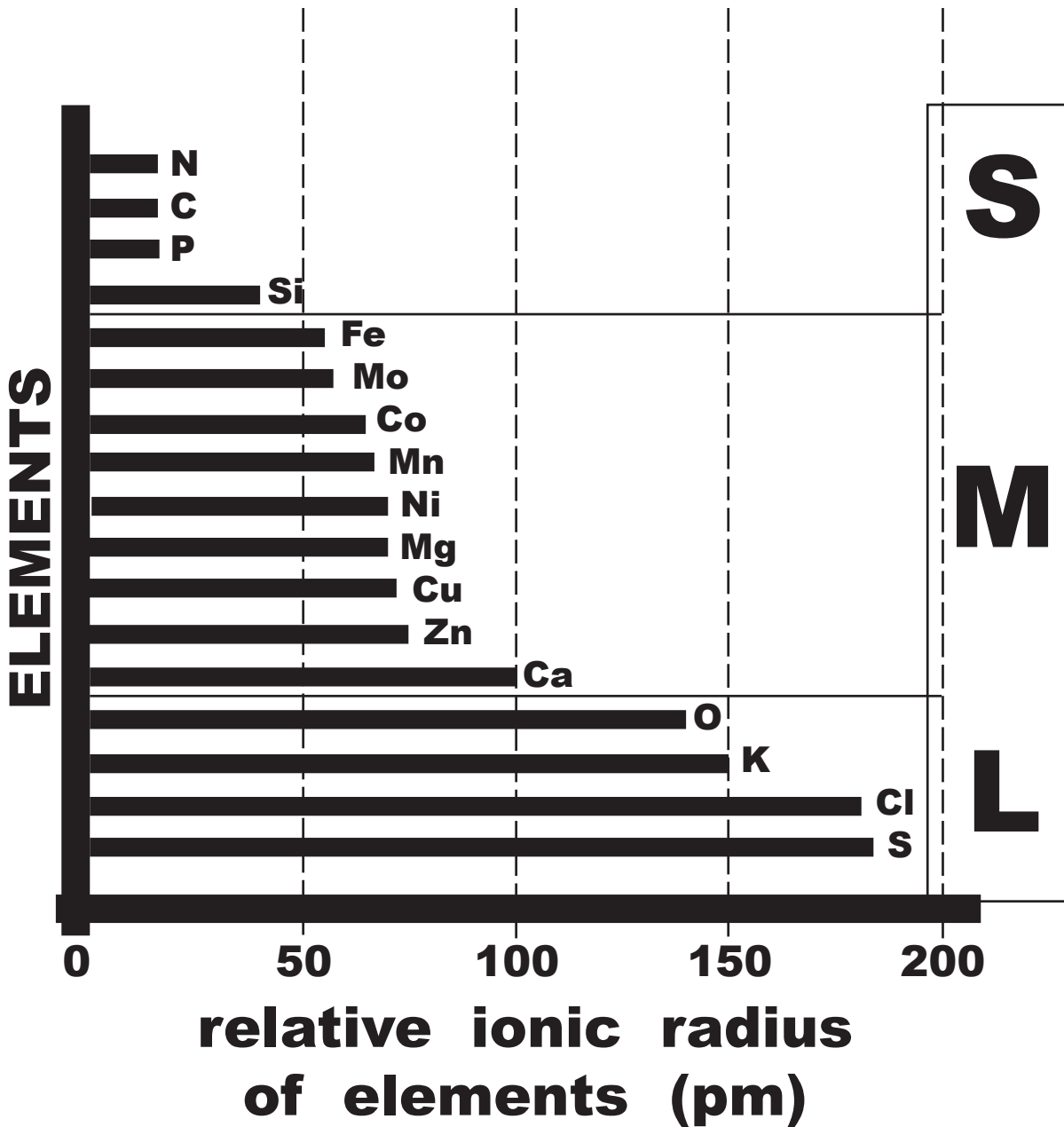


Figure 7: Relative ionic radius of tree essential elements with small, medium, and large size classes. (1 pm = 1 picometer = 100 angstrom)

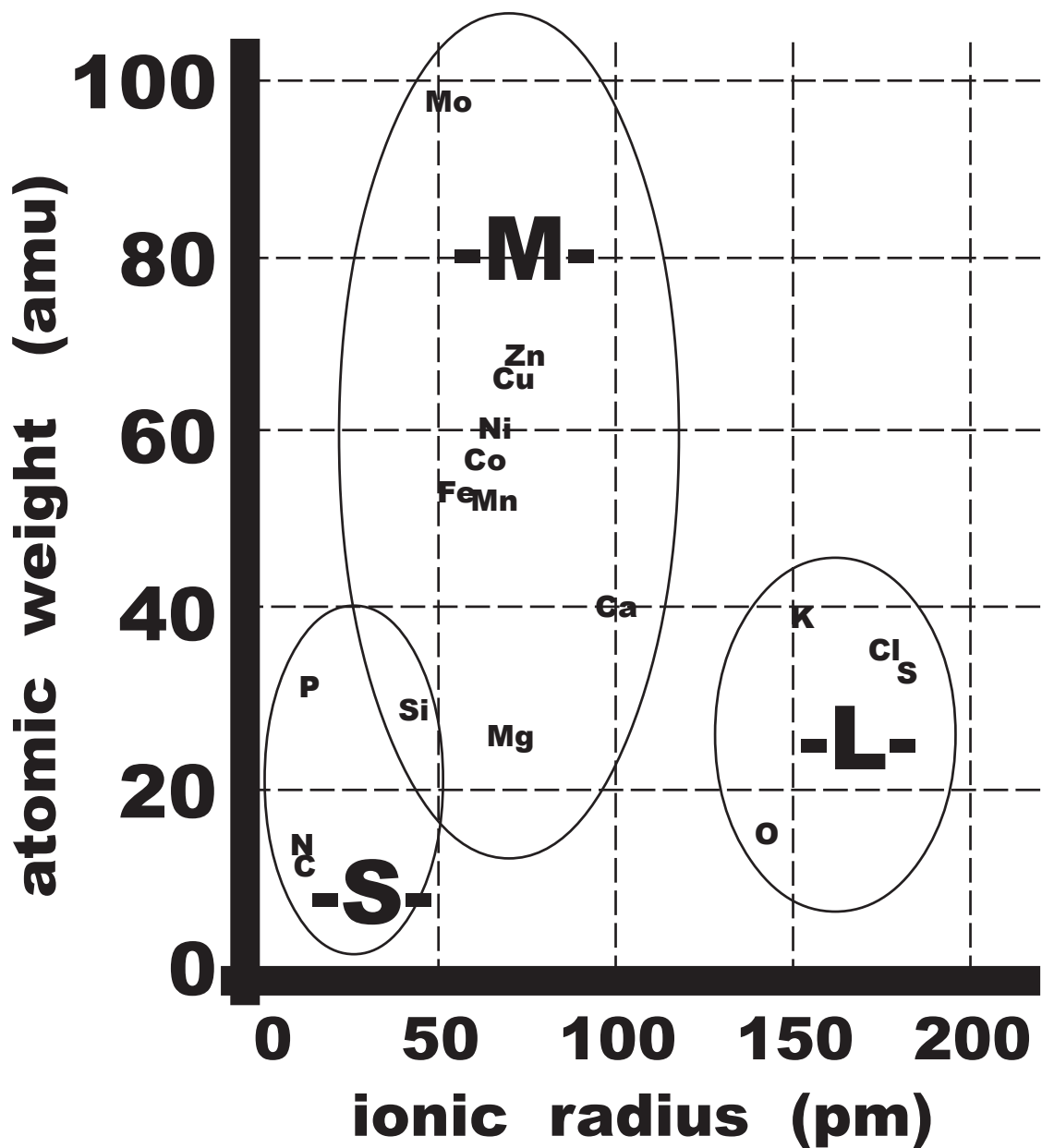


Figure 8: Comparison of tree essential element atomic weights (in amu) and ionic radii (in pm). Graphically there are three size groupings.  
 (1 pm = 1 picometer = 100 angstrom)

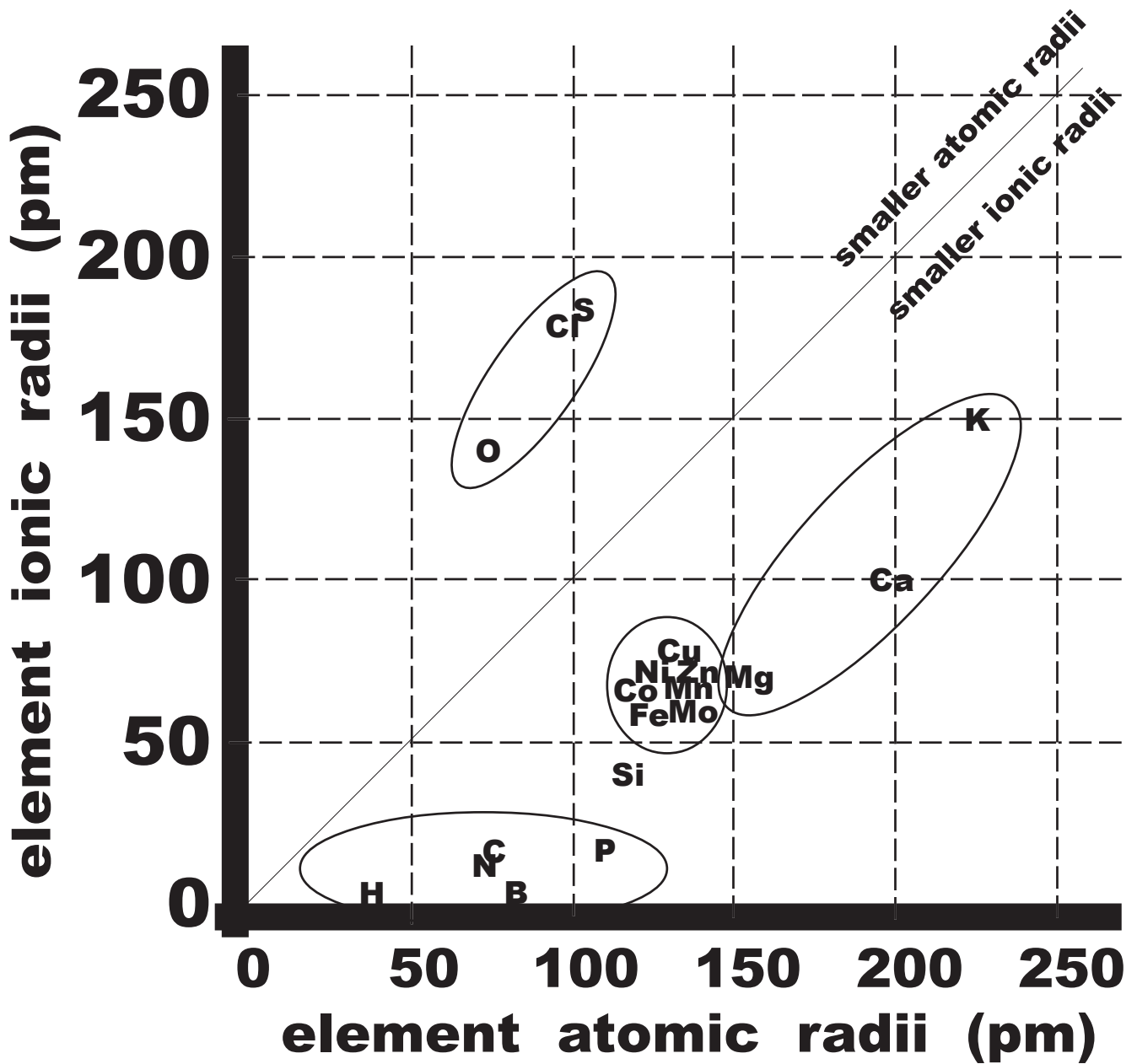


Figure 9: Tree essential element atomic and ionic radius values. (1 pm = 1 picometer = 100 angstrom)

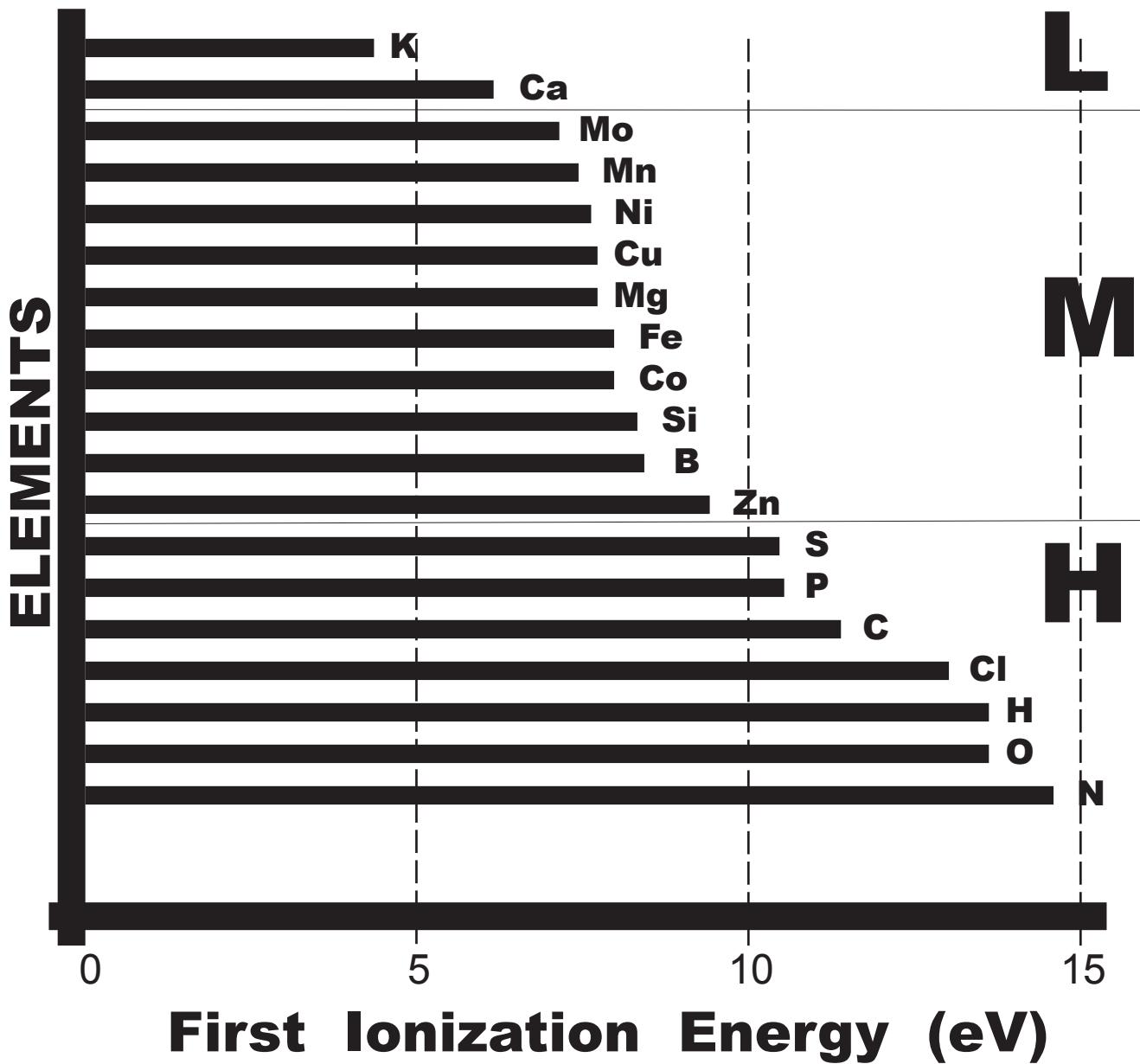


Figure 10: First ionization energy (energy to remove first electron) for tree essential elements divided into low, medium, and high energy classes.

ments for first ionization give each element unique chemical properties. Figure 11 uses a graphical means to differentiate first ionization energy values. The medium group is further divided in this graphical representation by atomic weight.

### Being Dense

Density of an element plays a role in how it can be used in biological systems. Figure 12 provides tree essential element density in grams per cubic centimeter at 68°F. There is a great density split between elements on either side of the zinc (Zn) / chlorine (Cl) line. Figure 13 is a graphical representation of element density. There are clearly two density groups as atomic weight increases. Note how unusually low density potassium (K) is for its weight.

### Abridged View

All essential elements have many diverse characteristics which can be used in a tree. Some groups of elements seem clumped close together and some are clearly wildly unique. Over time unique properties of some elements have been made part of tree life, while others have been avoided. Figure 14 provides a summary of tree essential element attributes. Elements with similar characteristics are grouped together. Note there are two separate metal groups, and the unique chlorine (Cl) / sulfur (S) group.

Figure 15 provides a number of element characteristic trends as you move across from left to right and downward through the modified periodic table of elements. These trends help show the unique characters of each element and suggest why some elements are used in trees and some are not.

### Basically Acid

One of the most commonly used appraisals of element availability is soil pH. The pH value is a logarithmically transformed ( $\text{pH} = -\log [\text{H}^+ \text{ concentration}]$ ) concentration of protons in a solution. As pH falls or the pH value becomes smaller (i.e. more acid), more protons exist in solution. As pH climbs or the pH number gets larger (i.e. more alkaline or basic), fewer protons exist in solution. The pH around an element helps determine its availability. The difference between each whole number pH value in concentration of protons  $[\text{H}^+]$  is 10 times.

For example, Figure 16 provides availability or activity of different tree essential elements across a pH gradient. Availability of many heavier metal elements decline with increasing pH, and increase as pH falls (i.e. become more available as the solution becomes more acidic.) Molybdenum and phosphorus provides a contrasting availability track with changing pH. Figure 17 represents element availability thresholds in soils across various pH levels. Figure 18 shows select metal ion mobility in soil for a range of pH values. For a wide range of pH values, element availability for trees is adequate.

Soil water pH does impact how effective an applied fertilizer can be. Figure 19 shows how pH effects a traditional NPK fertilizer. Note phosphorus (P) is always more impacted below neutral pH ( $\text{pH} = 7$ ) than either nitrogen (N) or potassium (K).

### pH Red Flags

There are a few pH markers primarily at the edges of biological values which should be recognized as leading to element deficiencies and toxicities in trees. Element availability below: pH 2.8 for molybdenum (Mo); pH 3.8 for iron (Fe); pH 4.2 for copper (Cu); and, pH 5.2 cobalt (Co), manganese (Mn), nickel (Ni), and/or zinc (Zn), can be toxic. Phosphorus availability below pH 5.5 is severely limiting. Element availability above: pH 8.2 for zinc (Zn); pH 7.5 for copper (Cu); pH 7.2 for iron (Fe) and manganese (Mn); and, pH 6.5 for boron (B) and nickel (Ni), can be limiting.

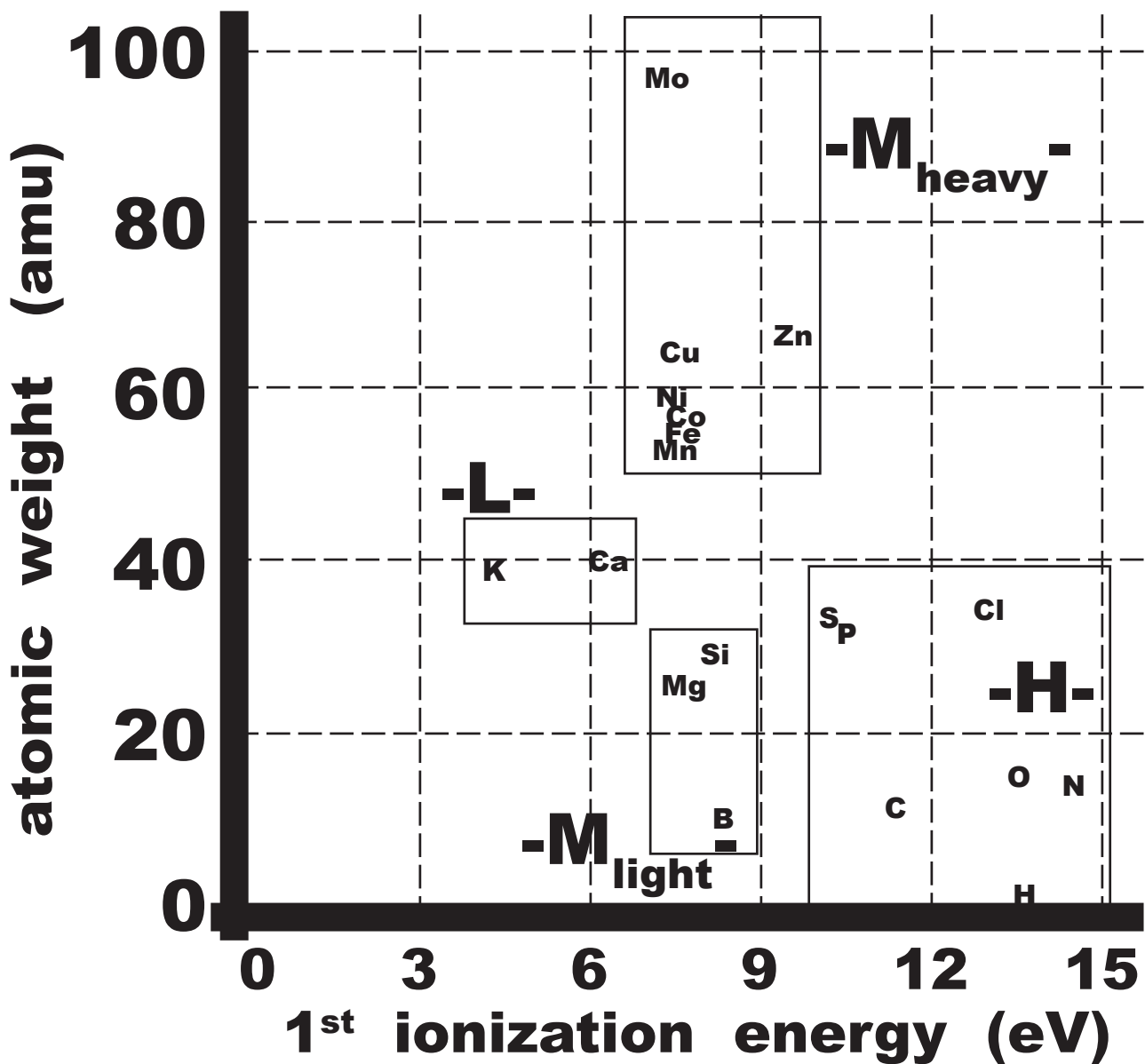


Figure 11: Comparison of tree essential element atomic weights (in amu) and first ionization energy (in eV). There are four energy groupings with medium ionization energies divided between a heavier metal dominant group and a light weight mixed group.



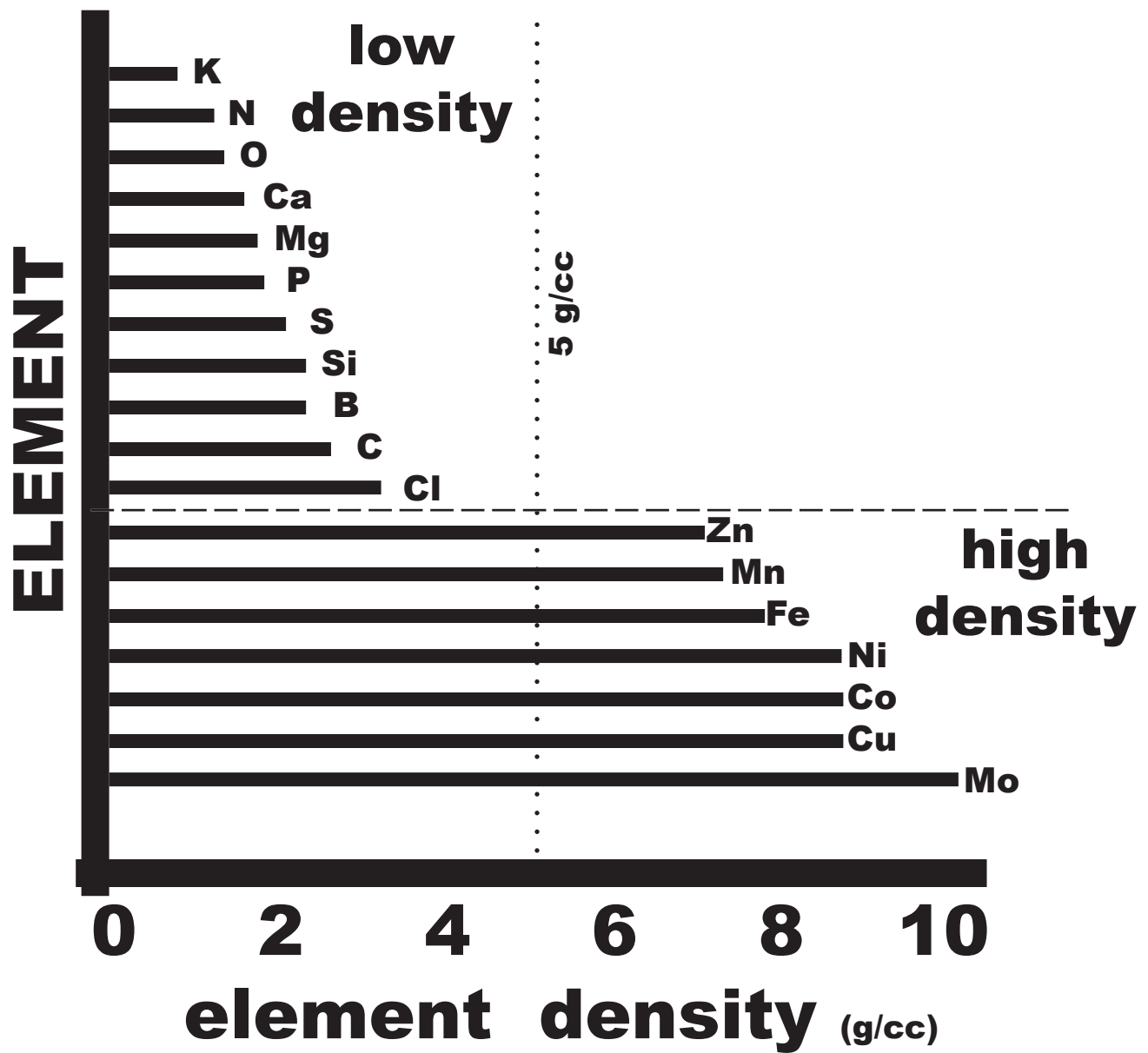


Figure 12: Tree essential element density (grams per cubic centimeter at 68°F).

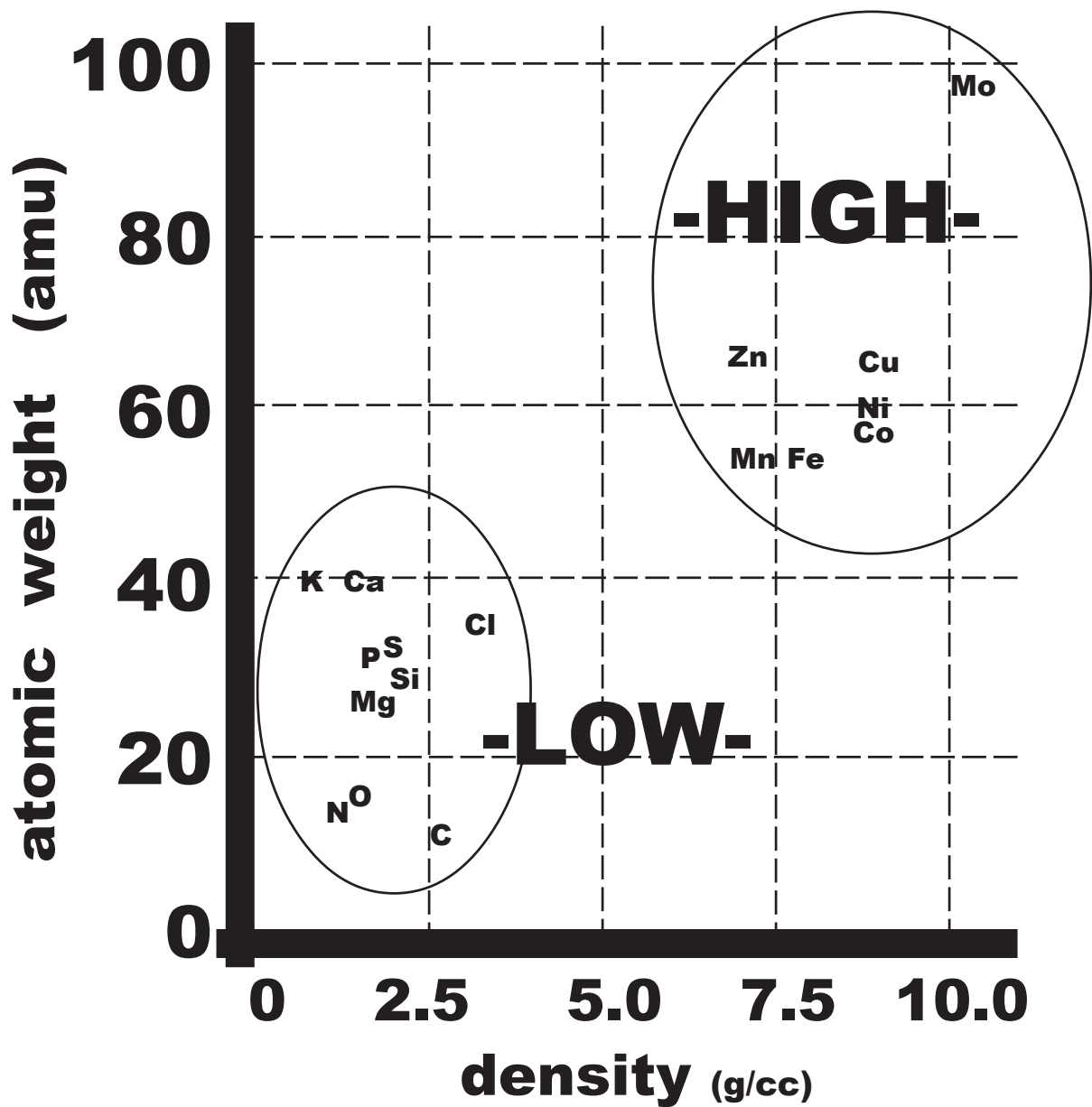


Figure 13: Comparison of tree essential element atomic weights (in amu) and element density (grams per cubic centimeter at 68°F).

# PHYSICAL / CHEMICAL GROUPS

symbol	atomic radius	ionic radius	first ionization energy	density	oxidation range
<b>B</b>	<b>small</b>	<b>--</b>	<b>medium</b>	<b>low</b>	<b>1</b>
<b>N</b>	<b>small</b>	<b>small</b>	<b>high</b>	<b>low</b>	<b>9</b>
<b>Si</b>	<b>med</b>	<b>small</b>	<b>medium</b>	<b>low</b>	<b>9</b>
<b>P</b>	<b>med</b>	<b>small</b>	<b>high</b>	<b>low</b>	<b>9</b>
<b>Co</b>	<b>med</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>3</b>
<b>Cu</b>	<b>med</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>3</b>
<b>Ni</b>	<b>med</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>3</b>
<b>Fe</b>	<b>med</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>4</b>
<b>Cl</b>	<b>med</b>	<b>large</b>	<b>high</b>	<b>low</b>	<b>9</b>
<b>S</b>	<b>med</b>	<b>large</b>	<b>high</b>	<b>low</b>	<b>9</b>
<b>Ca</b>	<b>large</b>	<b>med</b>	<b>low</b>	<b>low</b>	<b>1</b>
<b>Mg</b>	<b>large</b>	<b>med</b>	<b>med</b>	<b>low</b>	<b>1</b>
<b>Zn</b>	<b>large</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>1</b>
<b>Mn</b>	<b>large</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>5</b>
<b>Mo</b>	<b>large</b>	<b>med</b>	<b>med</b>	<b>high</b>	<b>6</b>
<b>K</b>	<b>large</b>	<b>large</b>	<b>low</b>	<b>low</b>	<b>1</b>

Figure 14: Summary of tree essential element atom characteristics.

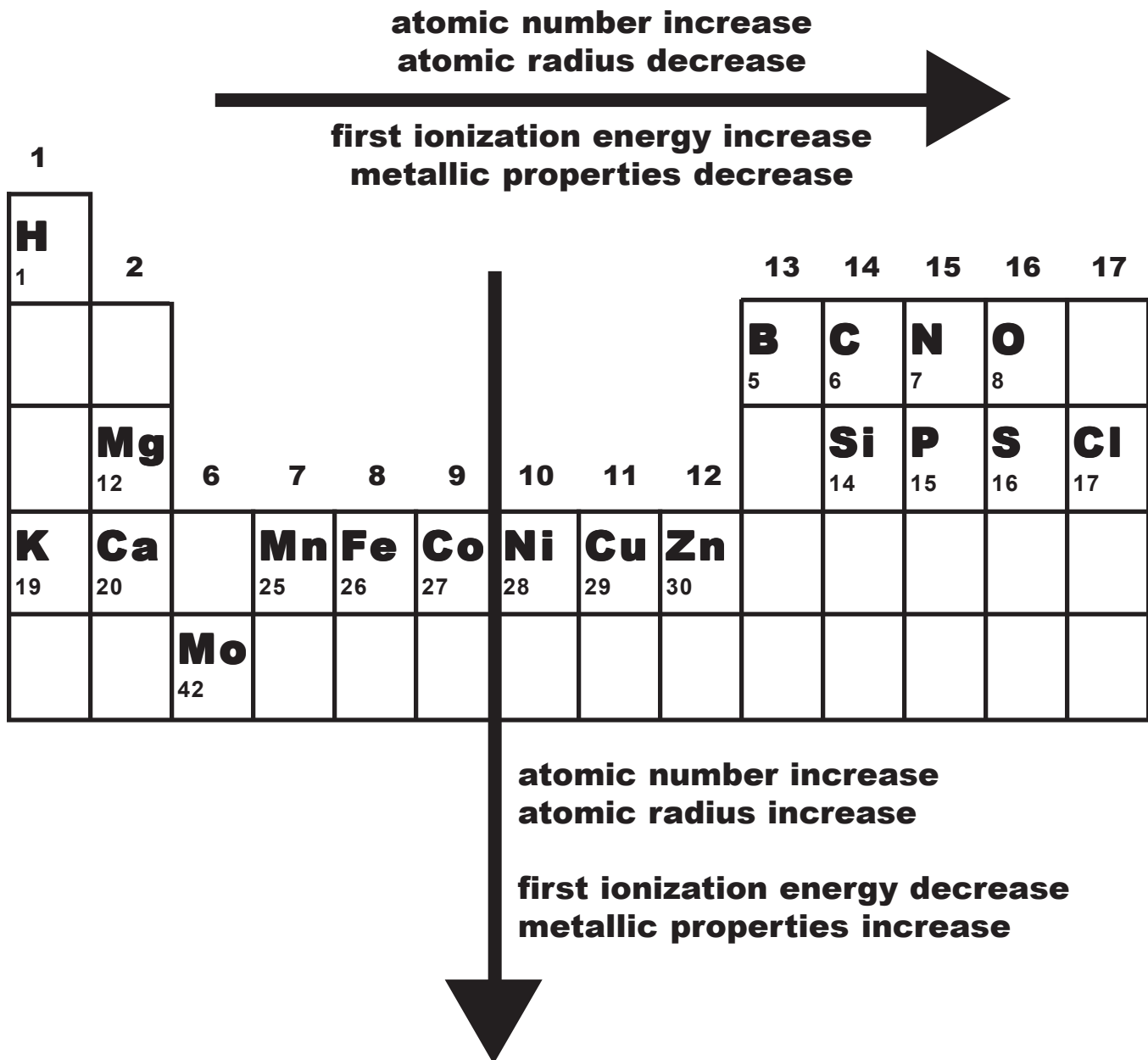


Figure 15: Element attribute trends across modified periodic table of elements. Heavy elements and element families without a tree essential element have been truncated.

**relative  
availability  
(percent)**

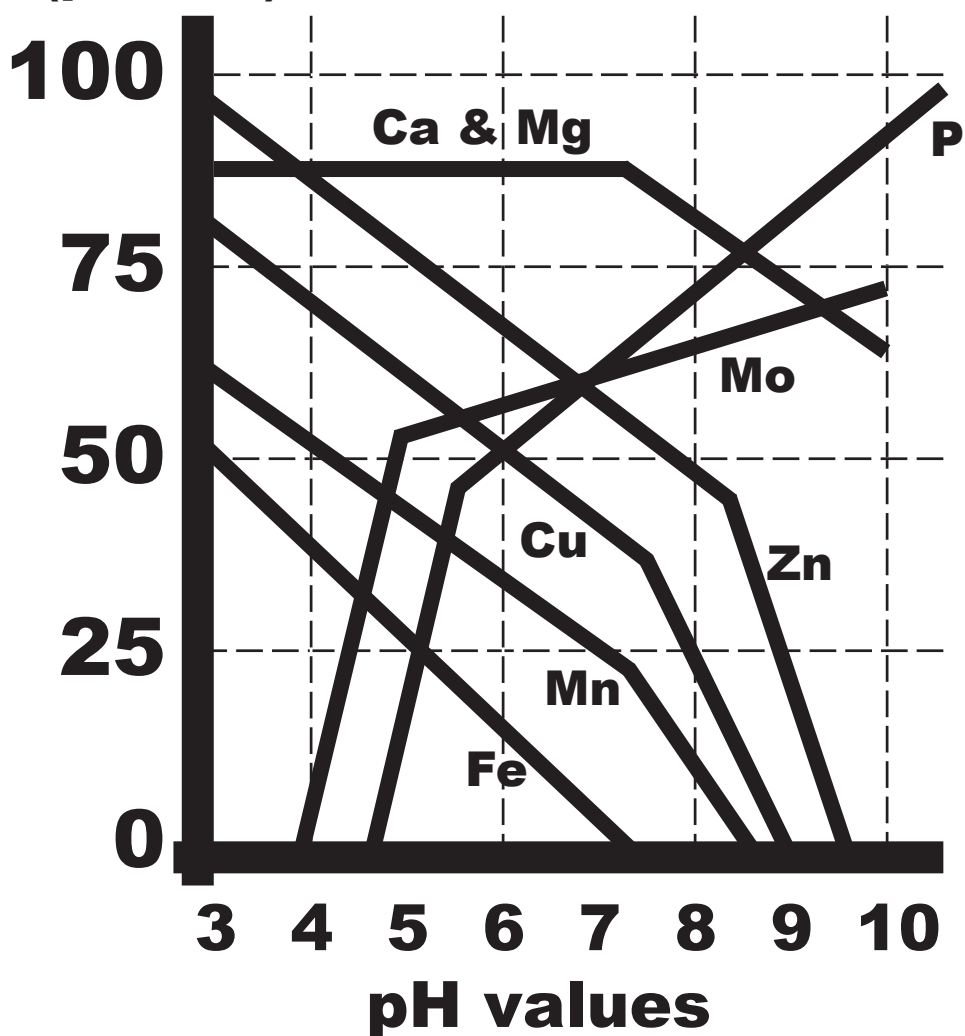


Figure 16: Average relative availability of elements in soil with changing pH.

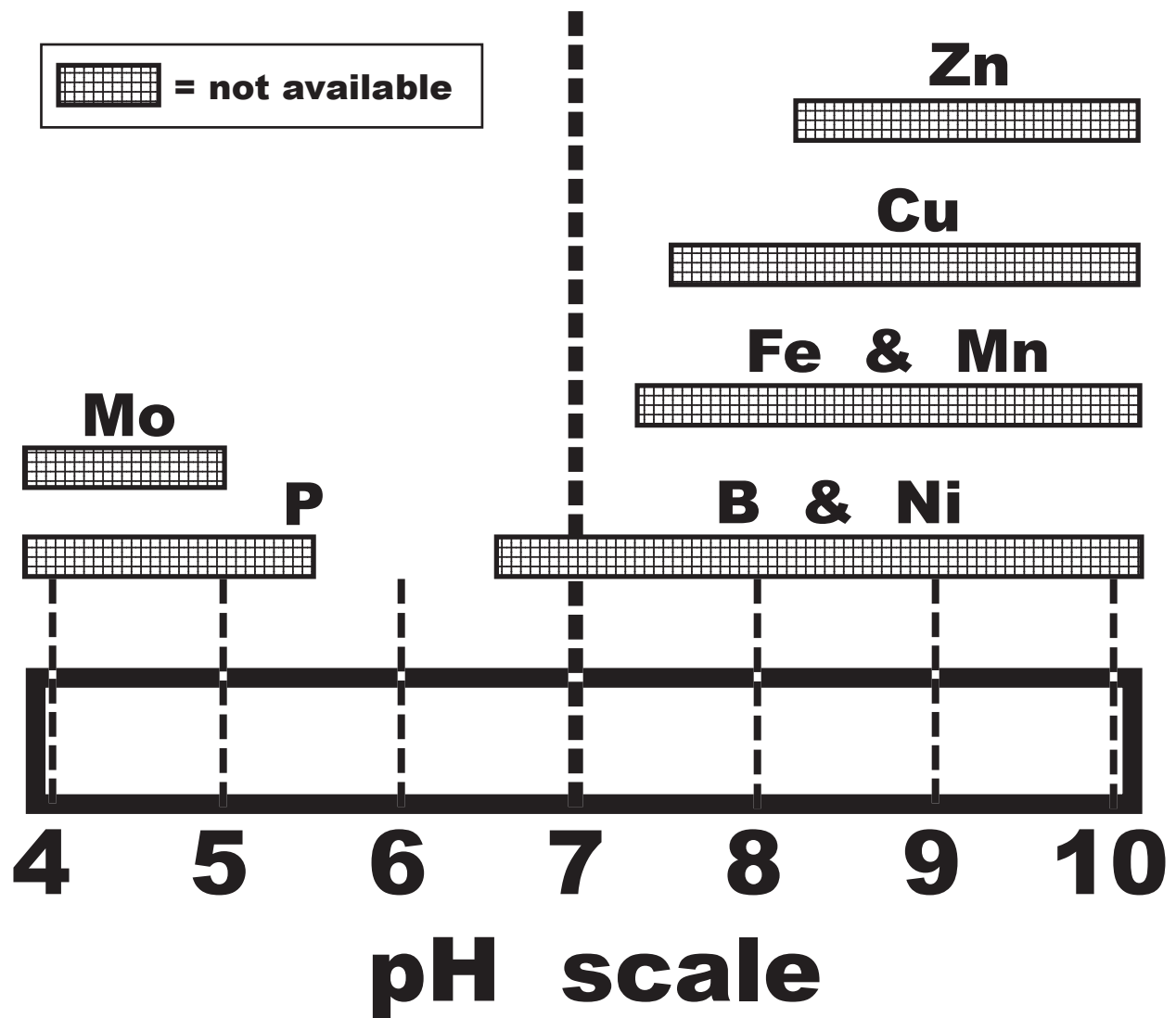


Figure 17: Most critical pH limitations and thresholds of select tree essential elements. Shaded bars represent soil pH levels where listed elements are poorly available or not available to trees.

# relative ion mobility

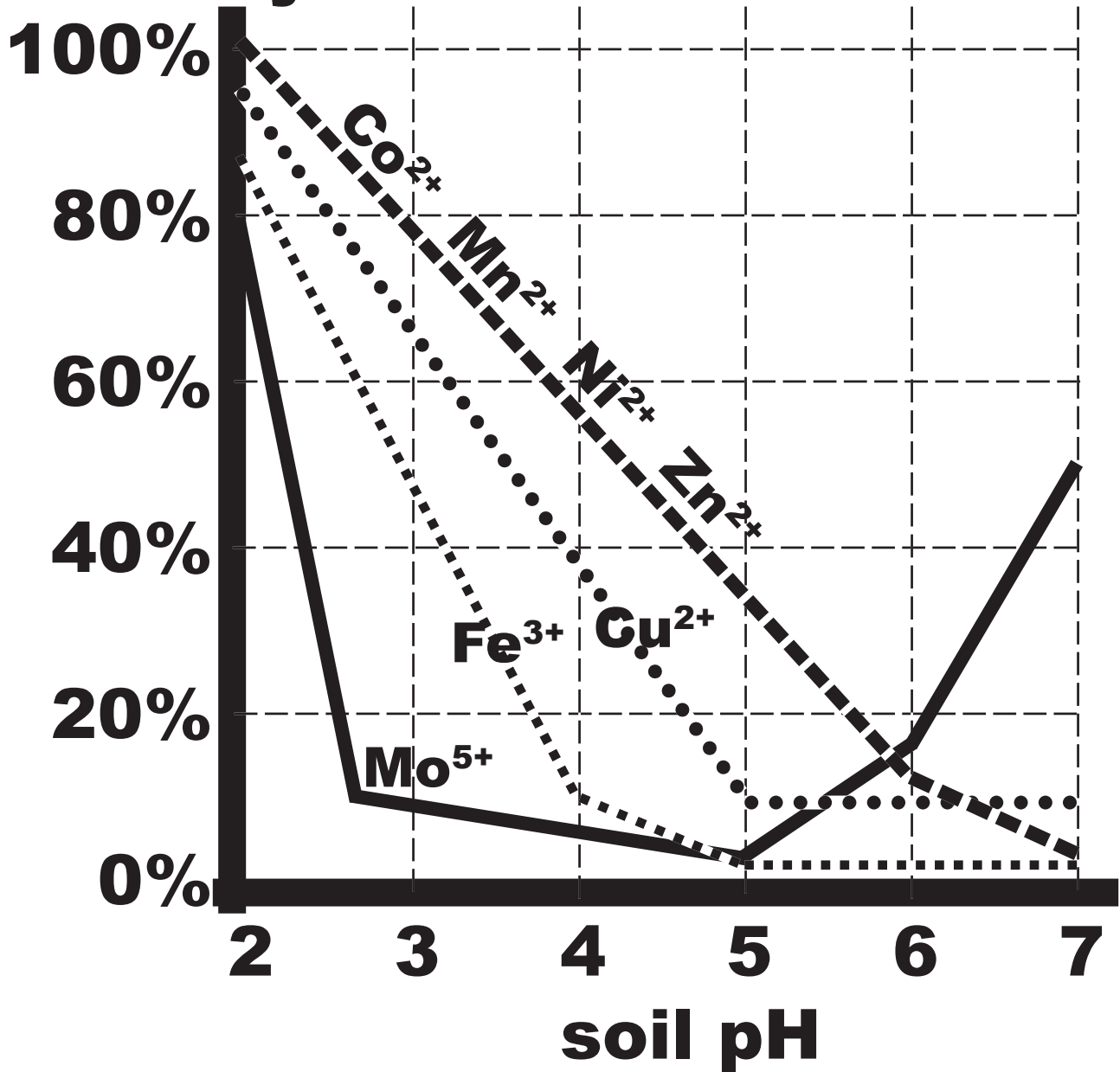


Figure 18: Relative soil mobility of metal ions across pH levels. (derived from Kabata-Pendias, 2011)

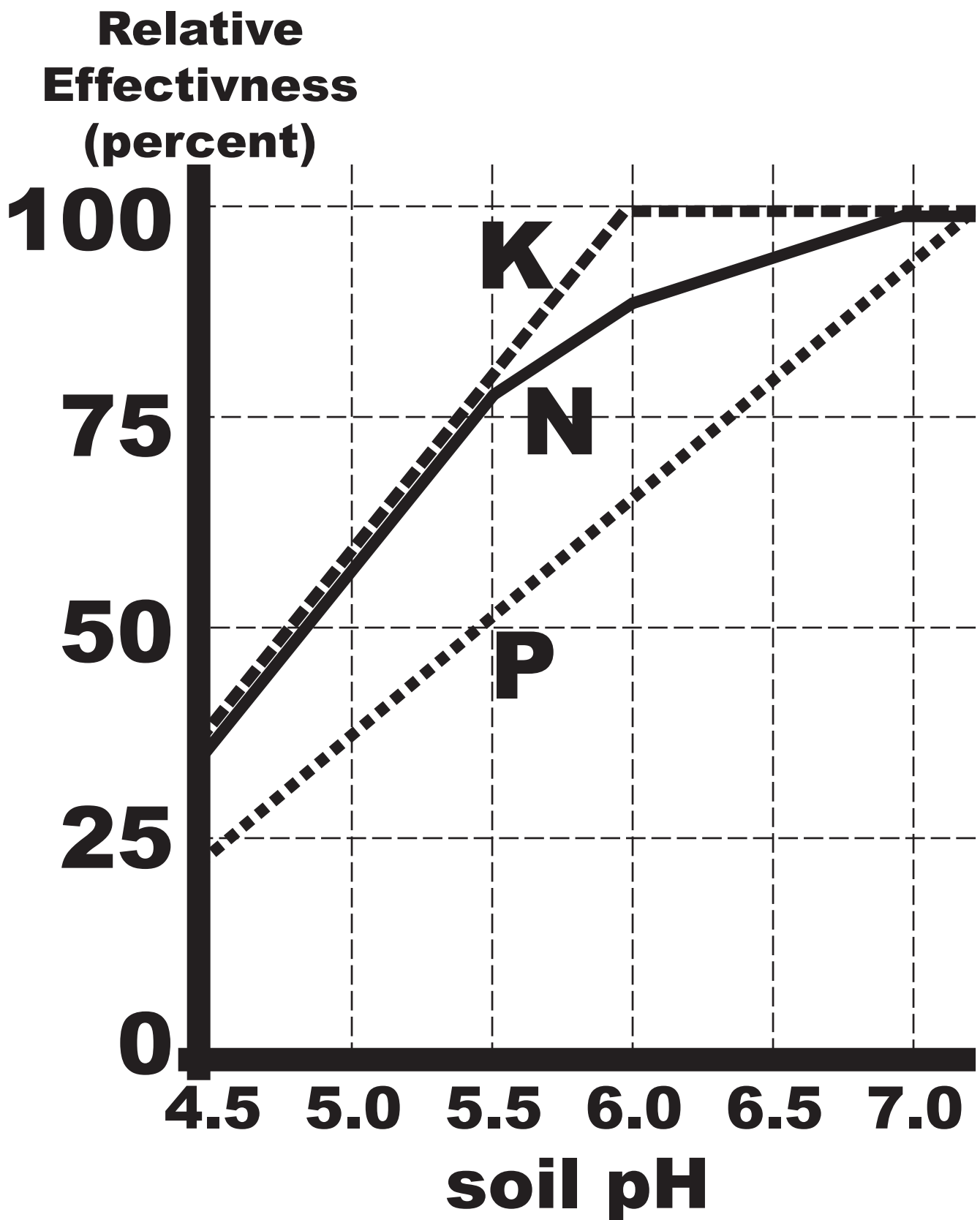


Figure 19: Relative traditional NPK fertilizer effectiveness over a range of soil water pH values. (from Jones, 2012)



## Nucleus Parts

Elements are defined by the number of protons in each atom. The number of protons and neutrons comprise, in essence, all atomic mass for each atom. For each element with a given number of protons, there can be a various number of neutrons present yielding different isotopes. On average, extra neutrons found in each element are given in Figure 20. As elements become heavier, there is a tendency to deviate from one proton / one neutron ratio. Heavier elements tend to carry more neutrons and so, more mass per atom.

Figure 21 provides for each essential element, the potential number of native isotopes found within a tree. Listed are isotope weights and percent of each isotope found in nature. Short-lived, unstable, radioactive, and extremely low concentration isotopes are not listed. A number of elements have isotopes with overlapping weights. There is a tendency for element isotopes with odd numbered weights to be less abundant. Among all isotopes of a single element, it is usually the lightest and most abundant which is most effectively used by the biochemical system of a tree. Notable exceptions are zinc (Zn) and molybdenum (Mo) where several isotopes are interchangeably utilized.

## Tree Recipe

Although only 1% of tree life materials are derived from essential elements taken from a soil, failure to secure all essential items lead to primary deficiencies, secondary symptoms, compounding problems, and metabolic dysfunction. The recipe for building a healthy and structurally sound tree depends upon adequate soil availability and precise concentrations, of essential elements. Figure 22 provides the relative proportion of essential elements in trees along with their functional names. Traditional micro- and macro-element designations / classes should be discarded as inaccurate, imprecise, and functionally meaningless. Too much or too little of any essential element can lead to minor health issues at least, or catastrophic failure and death at most.

## Proportion

One means to appreciate essential element proportions in a tree is to use a box diagram. Figure 23 provides a large box representing the proportion of elements based upon the relative amount of carbon (C) and oxygen (O) in a healthy tree. This box figure shows the mega-elements and myri-elements. Other elements in trees are represented by other boxes whose areas represent their proportions in a tree. Note the letter “X” is placed within a box whose size is proportional to all the remaining essential elements in a tree. This “X” box is blown up to a larger size to represent each subsequent box figure.

Figure 24 shows the relative proportion of the kilo-elements and hecto-elements in trees, with the “X” box representing the remaining elements found in smaller proportions. Figure 25 shows the deka-elements, with the “X” box representing the remaining elements found in smaller proportions. Figure 26 shows the deci-elements essential in trees.

## Adequate is Good

Tree essential elements are described in six concentration groups: mega, myri, kilo, hecto, deka, and deci. These groups represent general concentration needs for healthy trees. Figure 27 shows a generic curve with specific regions of each element’s concentration versus tree health. At low concentrations any essential element is deficient. As concentrations increase, an adequate zone is reached. Beyond adequate lies super-abundance and toxicity zones. Effective use of element resources is always dose dependent. As roughly 20% of relative element concentration is approached, relative tree health requirements reach 90%. As element concentration exceeds 20%, an adequate amount is usually attained by a tree.

#	element	average weight	number of protons	average neutrons	extra neutrons
<b>1</b>	<b>H</b>	<b>1<sub>amu</sub></b>	<b>1</b>	<b>1</b>	<b>0</b>
<b>5</b>	<b>B</b>	<b>11</b>	<b>5</b>	<b>6</b>	<b>1</b>
<b>6</b>	<b>C</b>	<b>12</b>	<b>6</b>	<b>6</b>	<b>0</b>
<b>7</b>	<b>N</b>	<b>14</b>	<b>7</b>	<b>7</b>	<b>0</b>
<b>8</b>	<b>O</b>	<b>16</b>	<b>8</b>	<b>8</b>	<b>0</b>
<b>12</b>	<b>Mg</b>	<b>24</b>	<b>12</b>	<b>12</b>	<b>0</b>
<b>14</b>	<b>Si</b>	<b>28</b>	<b>14</b>	<b>14</b>	<b>0</b>
<b>15</b>	<b>P</b>	<b>31</b>	<b>15</b>	<b>16</b>	<b>1</b>
<b>16</b>	<b>S</b>	<b>32</b>	<b>16</b>	<b>16</b>	<b>0</b>
<b>17</b>	<b>Cl</b>	<b>36</b>	<b>17</b>	<b>19</b>	<b>2</b>
<b>19</b>	<b>K</b>	<b>39</b>	<b>19</b>	<b>20</b>	<b>1</b>
<b>20</b>	<b>Ca</b>	<b>40</b>	<b>20</b>	<b>20</b>	<b>0</b>
<b>25</b>	<b>Mn</b>	<b>55</b>	<b>25</b>	<b>30</b>	<b>5</b>
<b>26</b>	<b>Fe</b>	<b>56</b>	<b>26</b>	<b>30</b>	<b>4</b>
<b>27</b>	<b>Co</b>	<b>59</b>	<b>27</b>	<b>32</b>	<b>5</b>
<b>28</b>	<b>Ni</b>	<b>59</b>	<b>28</b>	<b>31</b>	<b>3</b>
<b>29</b>	<b>Cu</b>	<b>64</b>	<b>29</b>	<b>35</b>	<b>6</b>
<b>30</b>	<b>Zn</b>	<b>65</b>	<b>30</b>	<b>35</b>	<b>5</b>
<b>42</b>	<b>Mo</b>	<b>96</b>	<b>42</b>	<b>54</b>	<b>12</b>

Figure 20: Comparison of principal atomic properties for tree essential elements, listed in order of increasing atomic weight.

#	element	average weight	native isotopes (weight / %)	#	element	average weight	native isotopes (weight / %)
1	H	1	1 / 100%	25	Mn	55	55 / 100%
5	B	11	10 / 20% 11 / 80%	26	Fe	56	54 / 6% 56 / 92% 57 / 2%
6	C	12	12 / 99% 13 / 1%	27	Co	59	59 / 100%
7	N	14	14 / 100%	28	Ni	59	58 / 68% 60 / 26% 61 / 1% 62 / 4% 64 / 1%
8	O	16	16 / 100%	29	Cu	64	63 / 69% 65 / 31%
12	Mg	24	24 / 79% 25 / 10% 26 / 11%	30	Zn	65	64 / 48% 66 / 28% 67 / 4% 68 / 19% 70 / 1%
14	Si	28	28 / 92% 29 / 5% 30 / 3%	42	Mo	96	92 / 15% 94 / 9% 95 / 16% 96 / 17% 97 / 9% 98 / 24% 100 / 10%
15	P	31	31 / 100%				
16	S	32	32 / 95% 33 / 1% 34 / 4%				
17	Cl	36	35 / 76% 37 / 24%				
19	K	39	39 / 93% 41 / 7%				
20	Ca	40	40 / 97% 42 / 1% 44 / 2%				

Figure 21: List of natural isotopes for tree essential elements listed in order of increasing atomic weight. Given are most common stable isotopes (percent) in nature rounded to nearest whole percent -- more isotopes occur, but at trace concentrations.

element	symbol	average in tree (parts-per-million)	relative proportion in trees
<b>group 1: (mega-)</b>			
carbon	C	450,000 ppm	1,000,000
oxygen	O	450,000 ppm	1,000,000
hydrogen	H	60,000 ppm	133,000
<b>group 2: (myri-)</b>			
nitrogen	N	17,000 ppm	38,000
potassium	K	12,500 ppm	28,000
calcium	Ca	10,000 ppm	22,000
<b>group 3: (kilo-)</b>			
magnesium	Mg	2,500 ppm	5,500
phosphorus	P	2,250 ppm	5,000
sulfur	S	1,500 ppm	3,300
<b>group 4: (hecto-)</b>			
chlorine	Cl	250 ppm	550
<b>group 5: (deka-)</b>			
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
<b>group 6: (deci-)</b>			
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 22: List of essential elements for tree life, average concentration in trees, and relative proportion in trees with carbon and oxygen set at 1 million (average values from multiple sources).

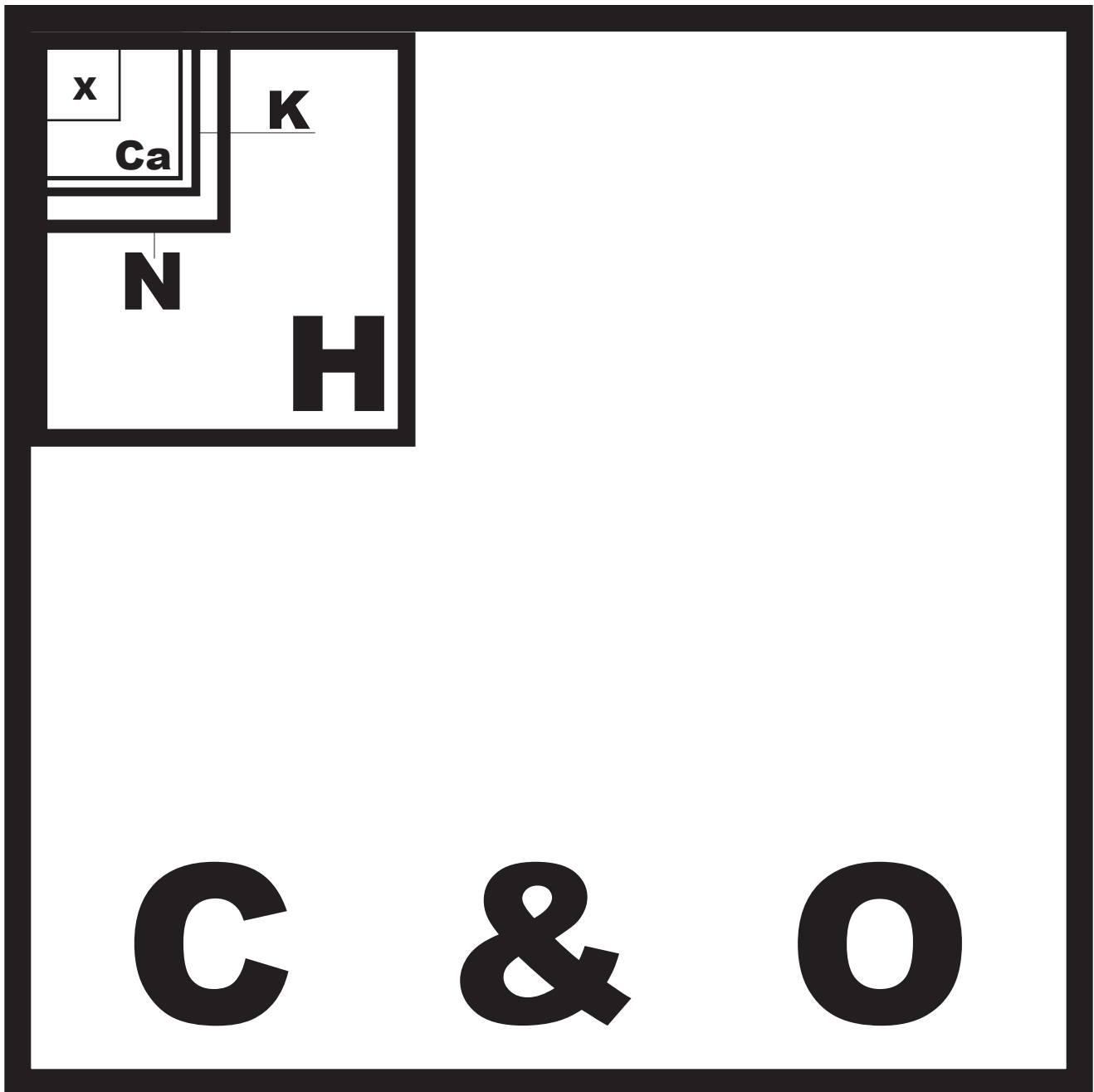


Figure 23: Relative proportion of tree essential elements (concentration groups 1 (3 mega-elements) & 2 (3 myri-elements)). “X” is the relative proportion of all remaining tree essential elements.

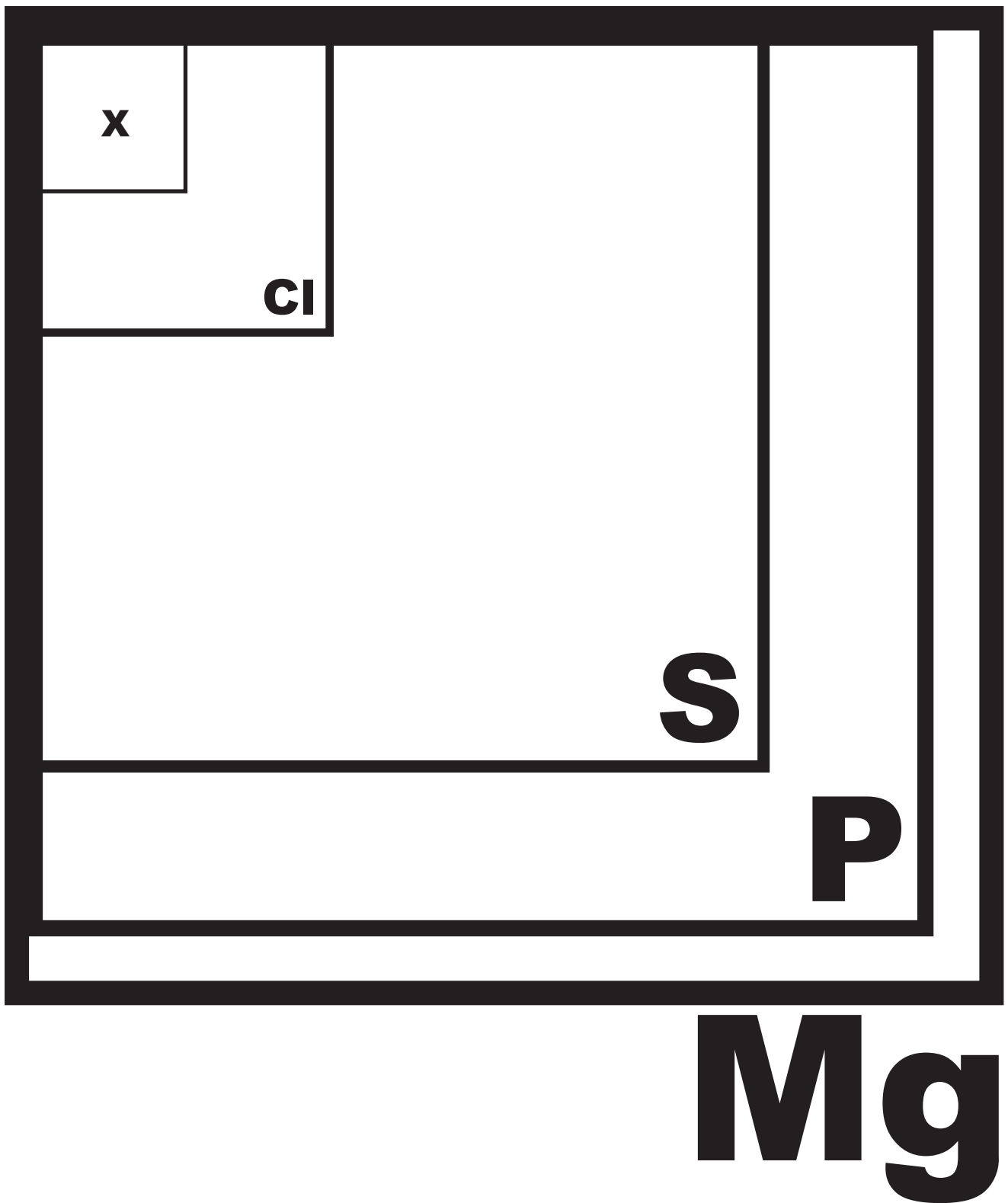


Figure 24: Relative proportion of tree essential elements (groups 3 (3 kilo-elements) & 4 (1 hecto-element)). “X” is the relative proportion of all remaining tree essential elements.

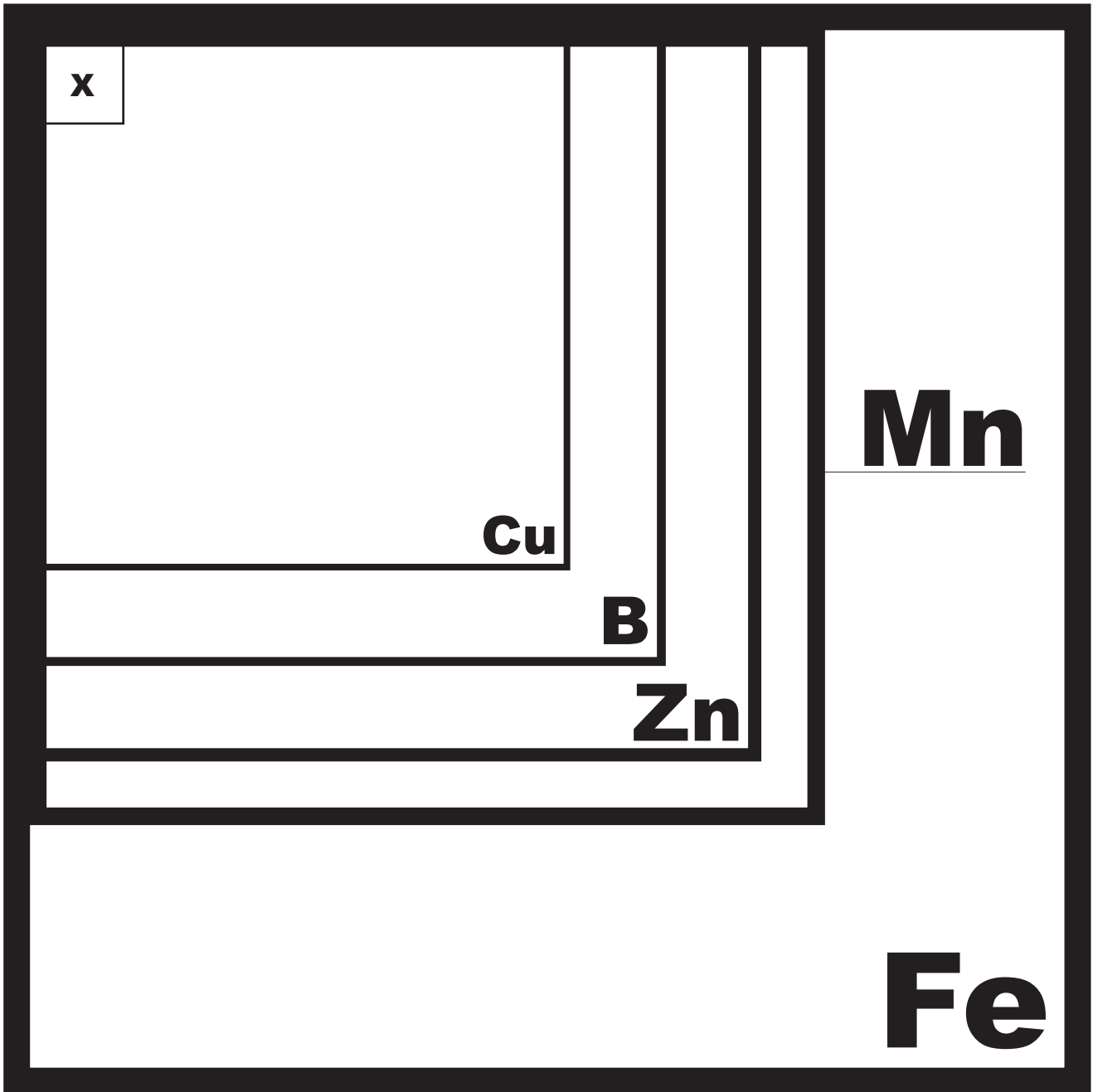


Figure 25: Relative proportion of tree essential elements (group 5 (5 deka-elements)). “X” is the relative proportion of all remaining tree essential elements.

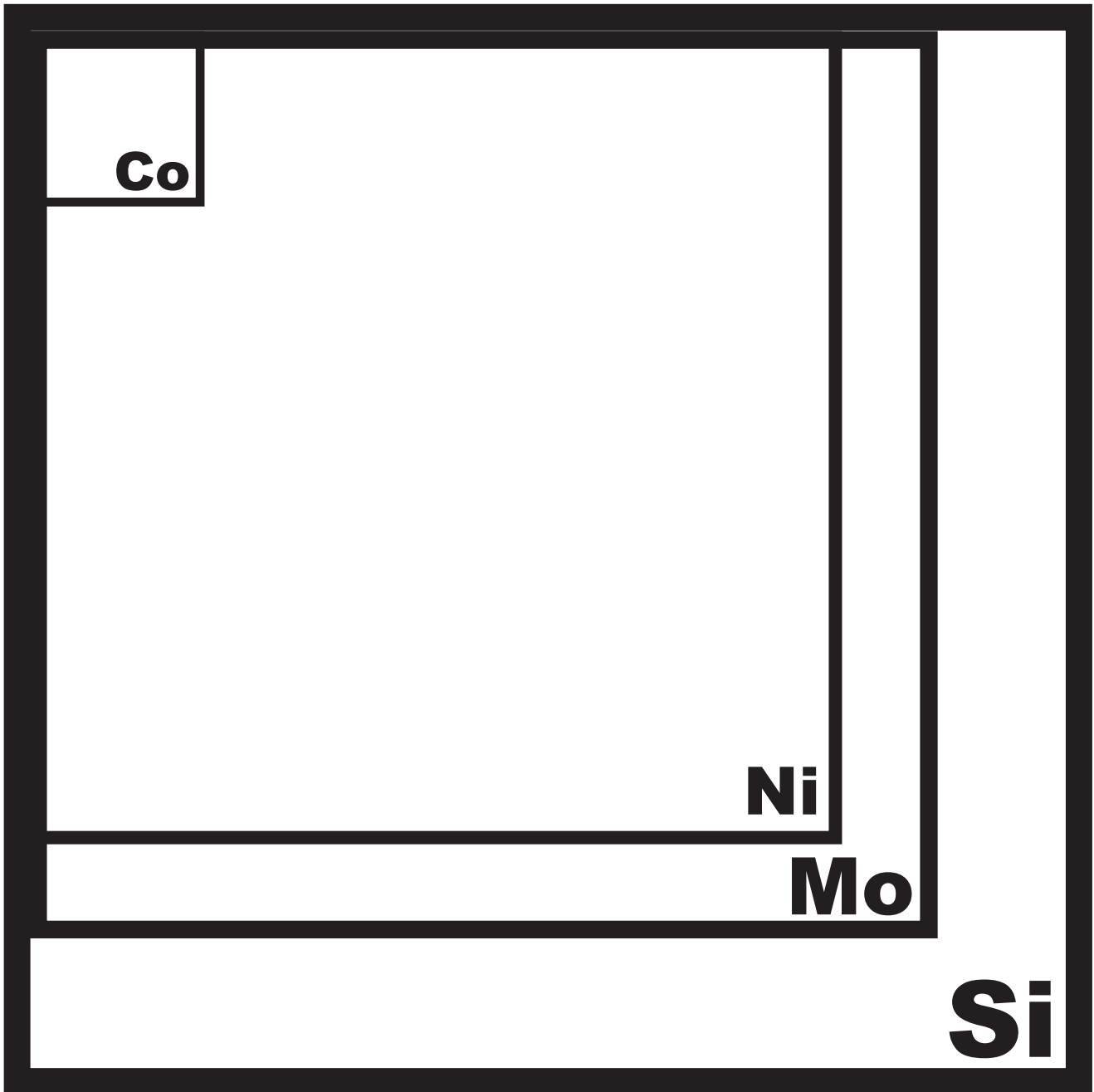


Figure 26: Relative proportion of tree essential elements (group 6 (4 deci-elements)).



# relative tree health

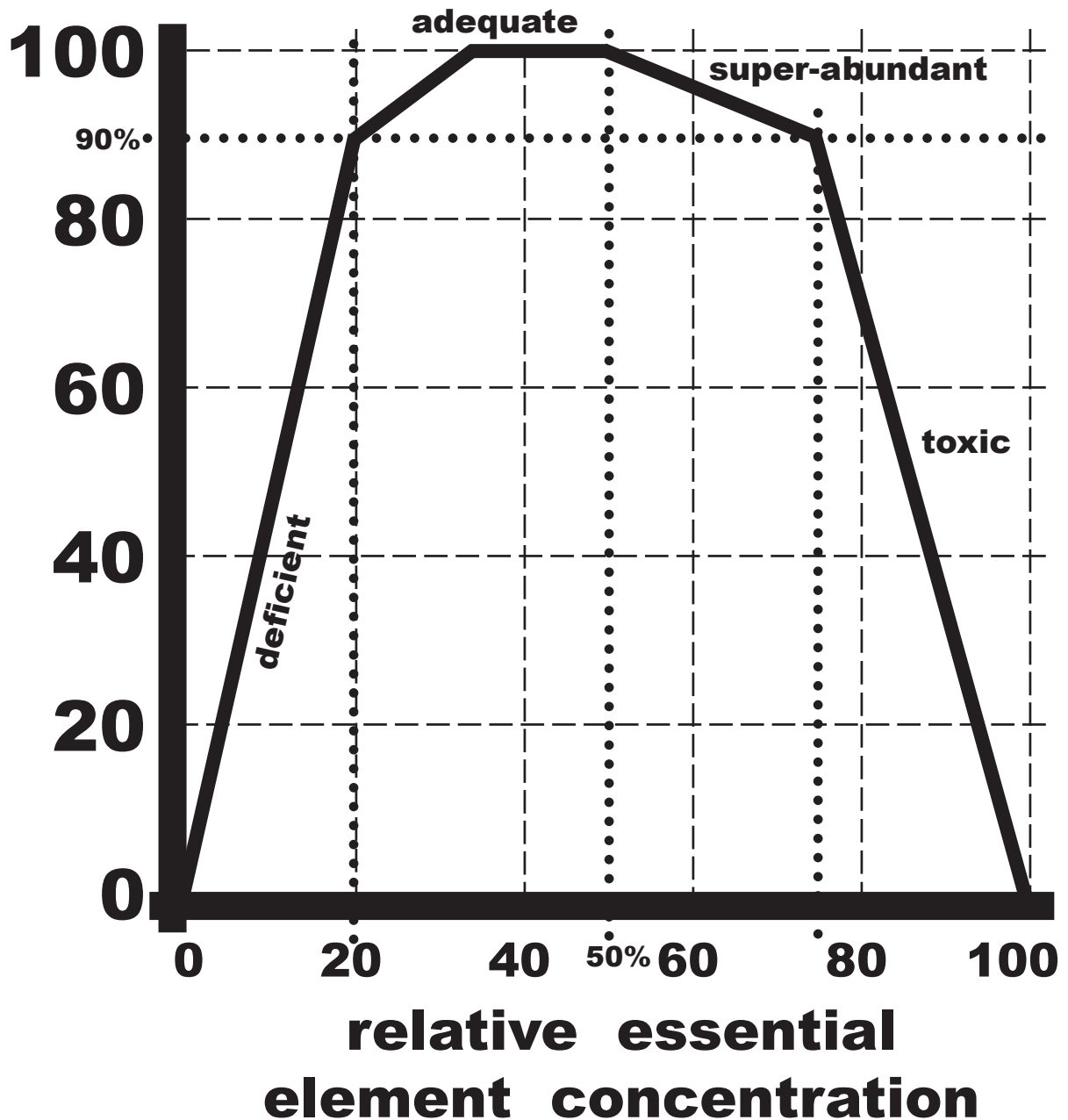


Figure 27: Generalized curve of an essential element concentration versus tree health. As element concentrations increase from zero, concentrations are classified as deficient, adequate, super-abundant, and toxic. Life in deficient and toxic areas will generate tree health problems.

Any element concentrations ranging too far away from adequate levels will damage a tree through toxicity (too much) or deficiency (too little). Some essential elements cannot vary much from adequate concentrations before they quickly lead to toxicity problems. Figure 28 shows an example of a much narrower adequate zone and a much quicker passage to toxicity. Some essential elements like metals follow more closely this narrowed curve where the line between deficient and toxic is thin. Enrichment activities with these essential elements, when a tree is deficient, can quickly reach toxic levels.

### Flexible Till Death

Tree genetics are constantly interacting with environmental messages of abundance, adequacy, deficiency, and toxicity. Genetic components of trees continually optimize growth, health, and structure depending upon immediate resources available and past resource legacies. There exists some flexibility / plasticity in optimizing tree life under environmental constraints currently present. This flexibility impacts essential element availability and interactions within a tree. Biological rules of growth and development decree element proportions, and amounts can not be modified by much for very long.

### Element Medallion

After having examined essential elements in trees -- attributes and organization -- a summary form is needed to keep track of essentiality. Because only a few elements out of all the native elements found on Earth are required for tree life, a new image of elements is presented here -- to eliminate unused elements from view and focus attention on tree-critical elements. This new figure of tree elements is given in Figure 29.

This image is called the **Coder Spiral of Tree Essential Elements**. Start in the middle and move outward and around the circles in a clockwise direction. Jump outward at the bottom (six-o'clock position) of each circle. This figure shows essential elements in order of decreasing concentrations needed for tree life. Water is listed here as an essential element surrounding all other tree elements. The intent with this figure is to visually represent tree essential element requirements.

### Growth & Health

Much management effort has been targeted at trees facilitating health and structure through water, light, and essential element modifications. The essential elements most commonly (i.e. traditionally) enriched around a tree are nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg). Additions of these elements have shown the greatest potential for improving tree growth if they are deficient on a site. Other essential elements may not initiate a significant acceleration in growth if enriched, but certainly improve or maintain tree health.

### Getting Elements

Essential elements are collected, captured, and conserved by trees. A small number and amount of essential elements are passively received in a gas phase, by precipitation interception, or through particulate deposition on tree surfaces. For most essential elements, trees expend energy to generate transpiration surfaces which are responsible for dragging elements into a tree dissolved in water (mass flow). Trees expend great energy to build absorption barriers and carriers to passively and actively pull in and push out elements. Trees also expend great energy to extract elements from the environment by generating roots (root interception). Figure 30 shows the three soil-centered processes a tree uses for collecting essential elements.

Roots collect and extract elements in five principal ways from soil:

**relative  
tree  
health**

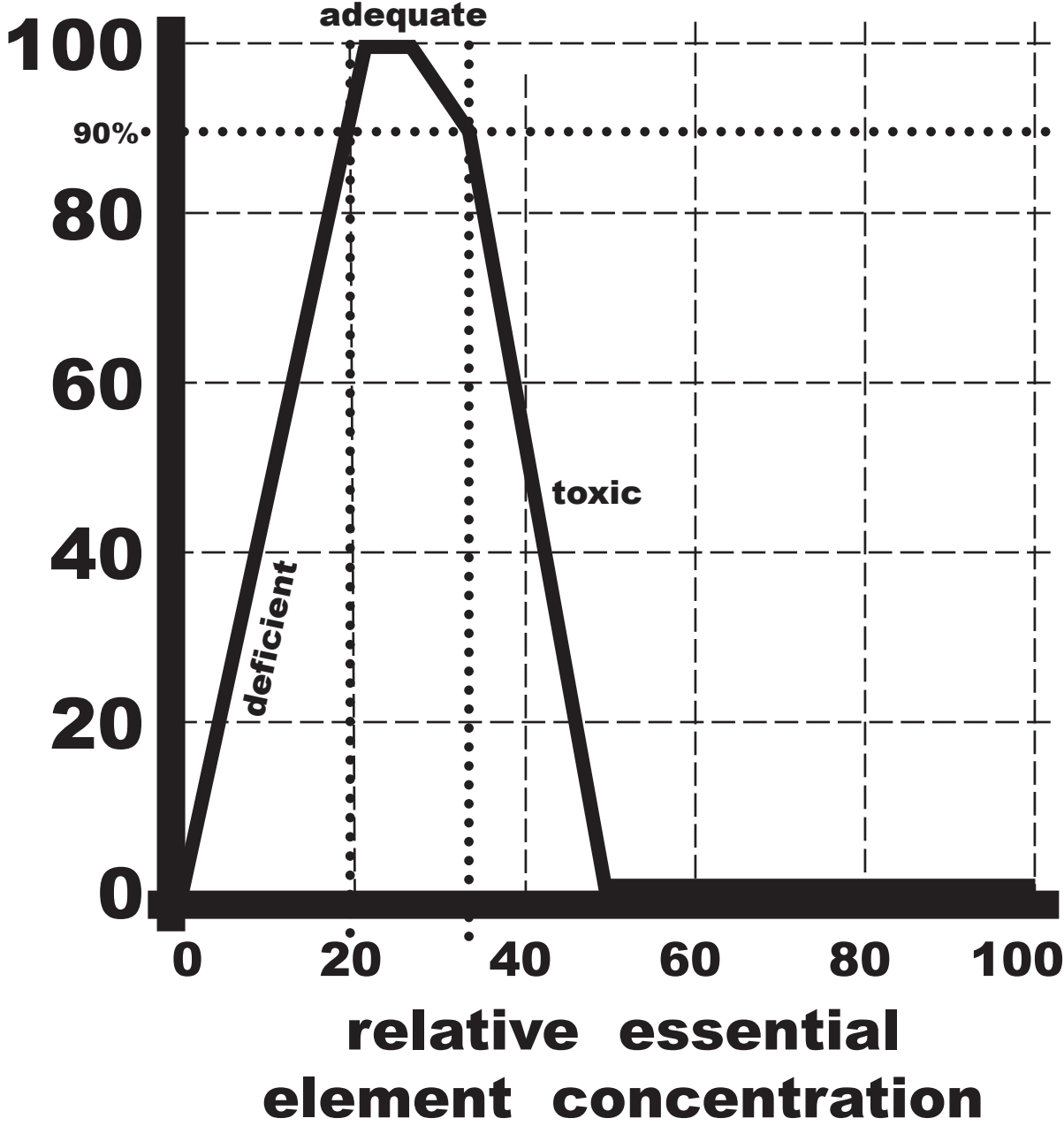


Figure 28: Generalized curve of an essential element concentration versus tree health. This essential element has a narrow concentration range between deficiency and toxicity.

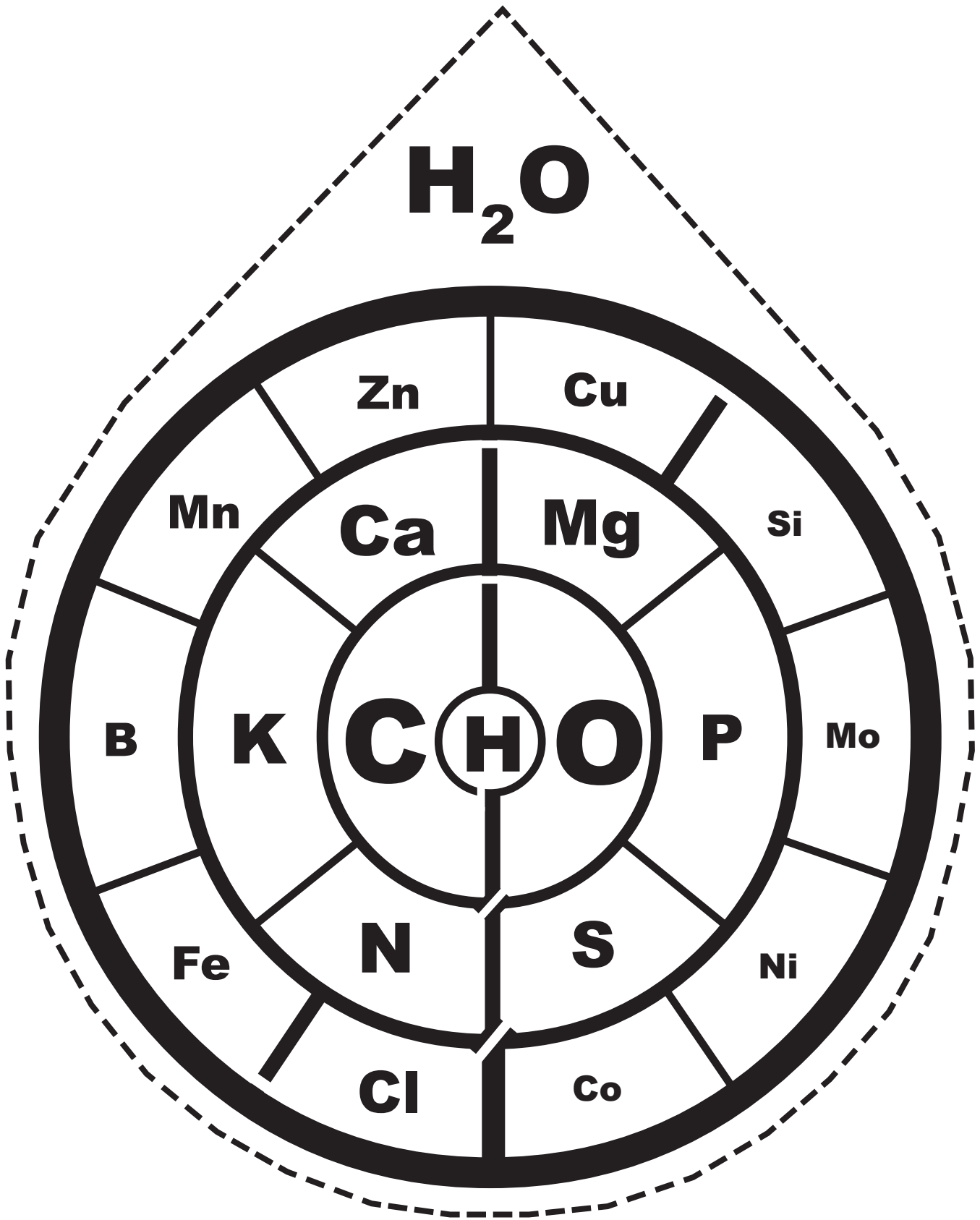


Figure 29: Coder Spiral of Tree Essential Elements.  
 The farther beyond center, the smaller concentrations required.

## **mass flow =**

**water flow in soil toward root  
caused by evapo-transpiration  
tensions with water carrying  
elements long distances.**

## **diffusion =**

**elements move from area of  
high concentration to area of  
low concentration over short  
distances near root surfaces.**

## **root interception =**

**roots continually initiated and  
elongated into soil generating  
increasing root surface area  
interface with soil (+ mycorrhizae)**

Figure 30: Mechanisms of element gathering by tree roots.  
(from Jones, 2012)

- 1) generate a large absorbing root surface area through new growing points and elongation;
- 2) continue to colonize and control soil resource space.
- 3) generate root exudates with specialized function for capturing and stabilizing elements;
- 4) generate root exudates for modifying rhizosphere ecology to facilitate element availability;  
and,
- 5) generate growth regulators and provide growth materials to support root  
symbionts (i.e. mycorrhizal fungi / bacteria) which extract elements from soil  
or atmosphere.

Environmental limitations generate many problems for proper root function. Figure 31 presents a number of major root issues in collecting essential element. Temperature, water, and physical injury prevent tree root functions.

### Root of It All

Figure 32 is a diagram of a primary tree root lengthwise. Element uptake is concentrated along an area behind the root tip where trichomes (root hairs) are being generated by the most exterior cell layers. Most element adsorption is through being dissolved in the mass flow of water into the vascular tissue area (vascular column) called the stele. In order for elements to enter the stele and be shipped throughout the tree, elements must pass within a living cell passing through its cell membrane. Until an element passes within a cell membrane (symplast), it is considered to be outside the living tree (apoplast).

Figure 33 presents a cross-section of a tree root where elements are taken within cells and passed along to the stele. There are two pathways elements move into a root: 1) flowing with water inbetween cells within cell walls and intercellular spaces of the cortex (apoplast); or, 2) moving across a living cell membrane (symplast). The apoplastic movement of elements is stopped by the last (most interior) layer of the root cortex called the endodermis. The endodermis is sealed from further element penetration outside living membranes by gaskets surrounding each endodermis cell (gasket called a casparian strip).

### Crossing the Membrane

Figure 34 emphasizes how elements can move in the symplast from cortical cell to cell, and through the endodermis to be placed into the xylem water stream. Elements can only move in dead and empty spaces of cell walls (apoplast) before being stopped at the endodermis. At this point the membrane proteins can allow or not allow access to any element.

Tree cell membranes are primarily double layers of phospholipids. The water loving head end of the lipid are turned outward toward the moisture of the apoplast and symplast. The fatty acid tails of the lipids are turned toward each other inward to avoid water. Figure 35. This membrane, although as frail as a soap bubble, keeps life contained inside and the oxidizing general environment outside. Essential elements are taken into cells using membrane mounted protein structures which transference elements across the membrane.

### Transporter Proteins

Membrane proteins are generated to passively assist or actively transport into (and out of) tree cells. These proteins come in four main forms: channels (pores); carriers; pumps; and co-transporters. Figure 36. Channels assist elements to gain access to inside a cell through the membrane limited primarily by size of the ion and size of the open pore / channel. Carriers actively move elements across the membrane. Pumps use direct cellular energy to force element (ions) across the membrane.

## **Root Limitations for Element Uptake**

- roots impaired or damaged by mechanical / physical problems**  
(compaction, crusting, trenching)
- low or high soil temperatures**
- low soil moisture content impairing mass flow**
- extremely low soil moisture content impairing diffusion**
- poor growing condition preventing root initiation & elongation**
- excessive soil water content**
- attack by biological systems**  
(disease, nematodes, insects, mites, parasites)

Figure 31: Causes of tree roots failing to find and collect essential elements. (from Jones, 2012)

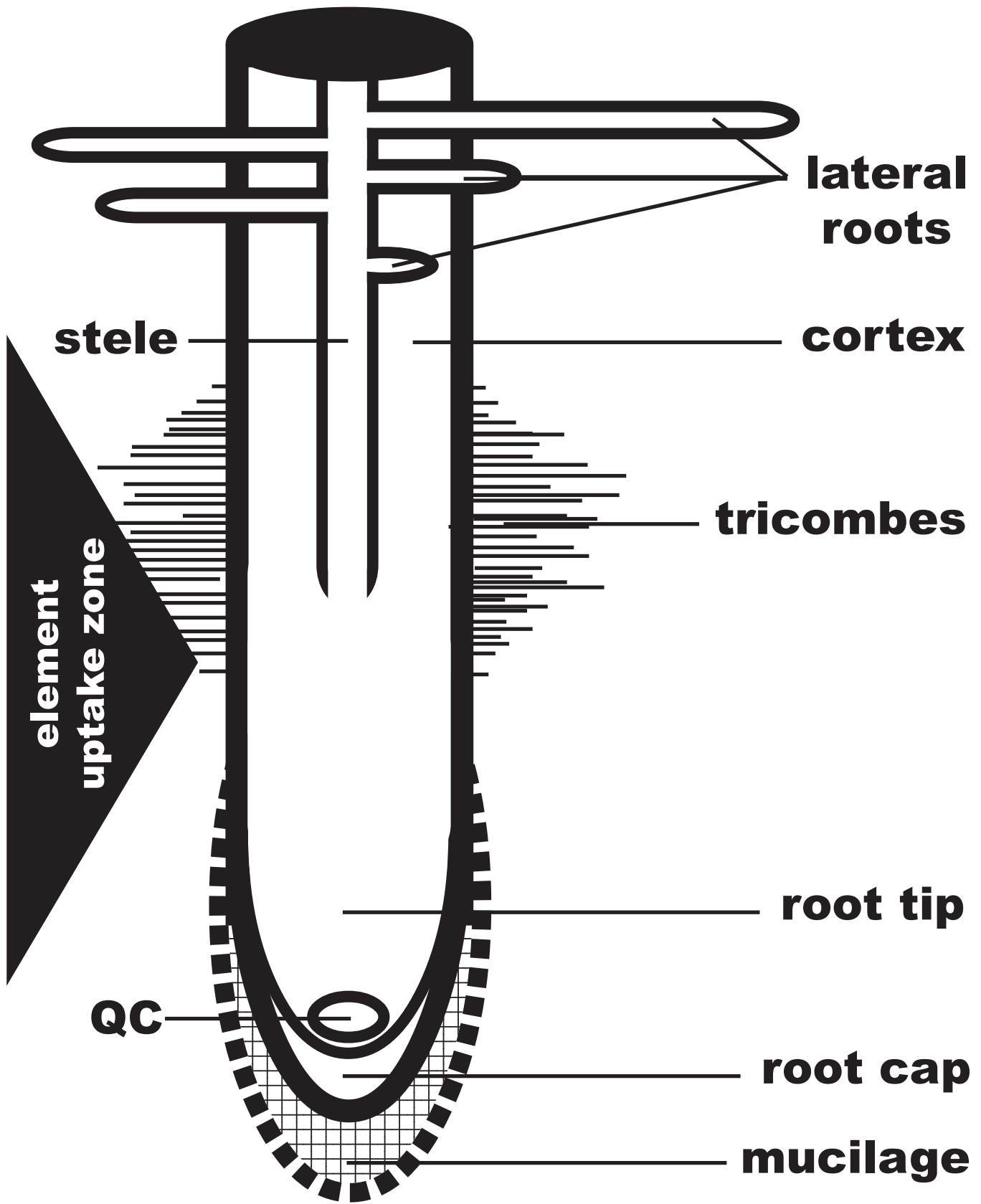


Figure 32: Longitudinal view of primary tree root showing area of element uptake.



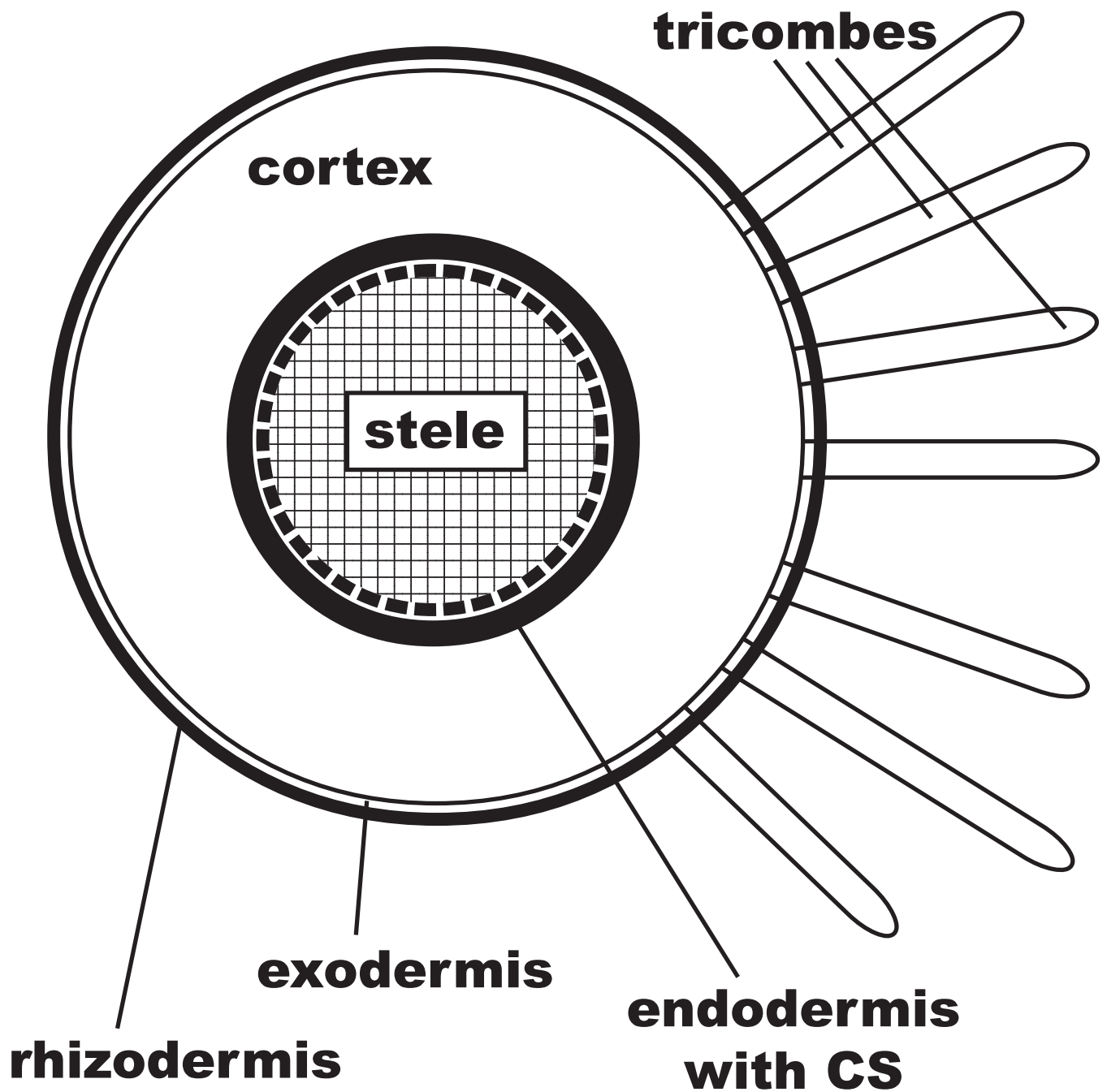


Figure 33: Cross-section of tree primary root before lateral roots develop from stele. Element transport through either apoplast to endodermis, or symplast through living cells.

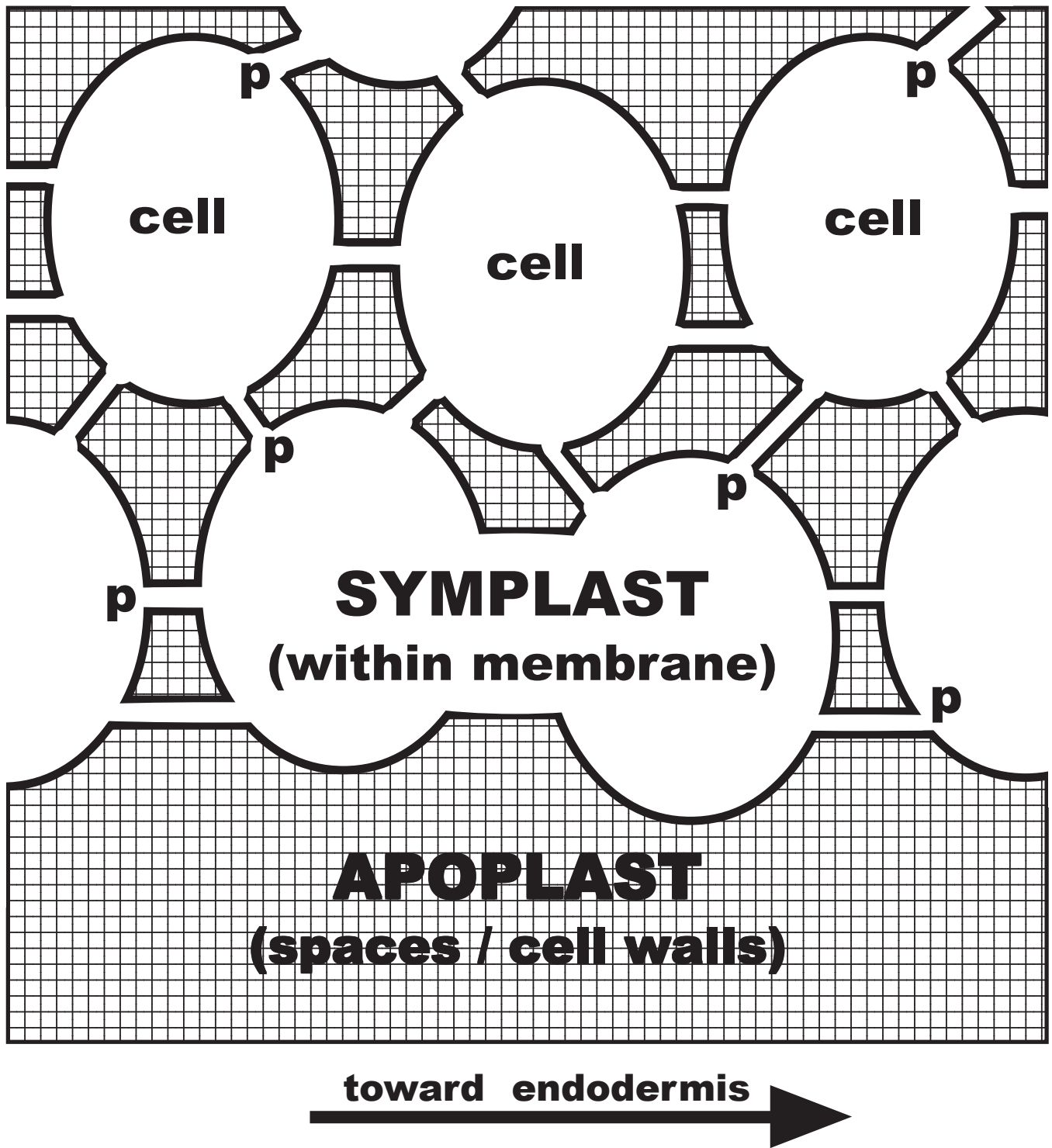


Figure 34: Elements move into tree through mass flow and diffusion in apoplast (cell walls & intercellular spaces), and symplast (passing through membrane and then from cell to cell by plasmodesmata (p) connections).

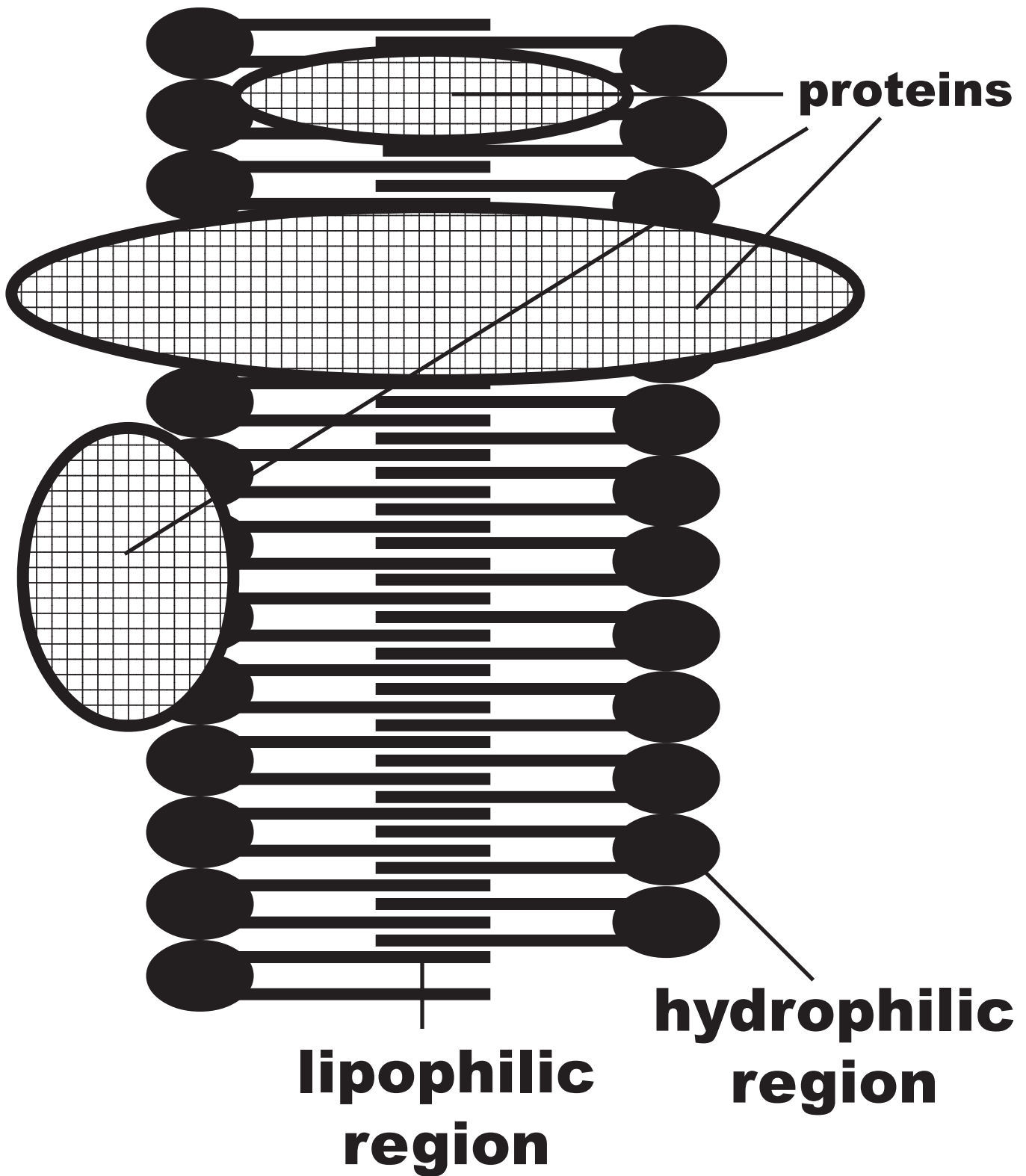


Figure 35: Diagram of a phospholipid membrane (double layer) with three protein locations.

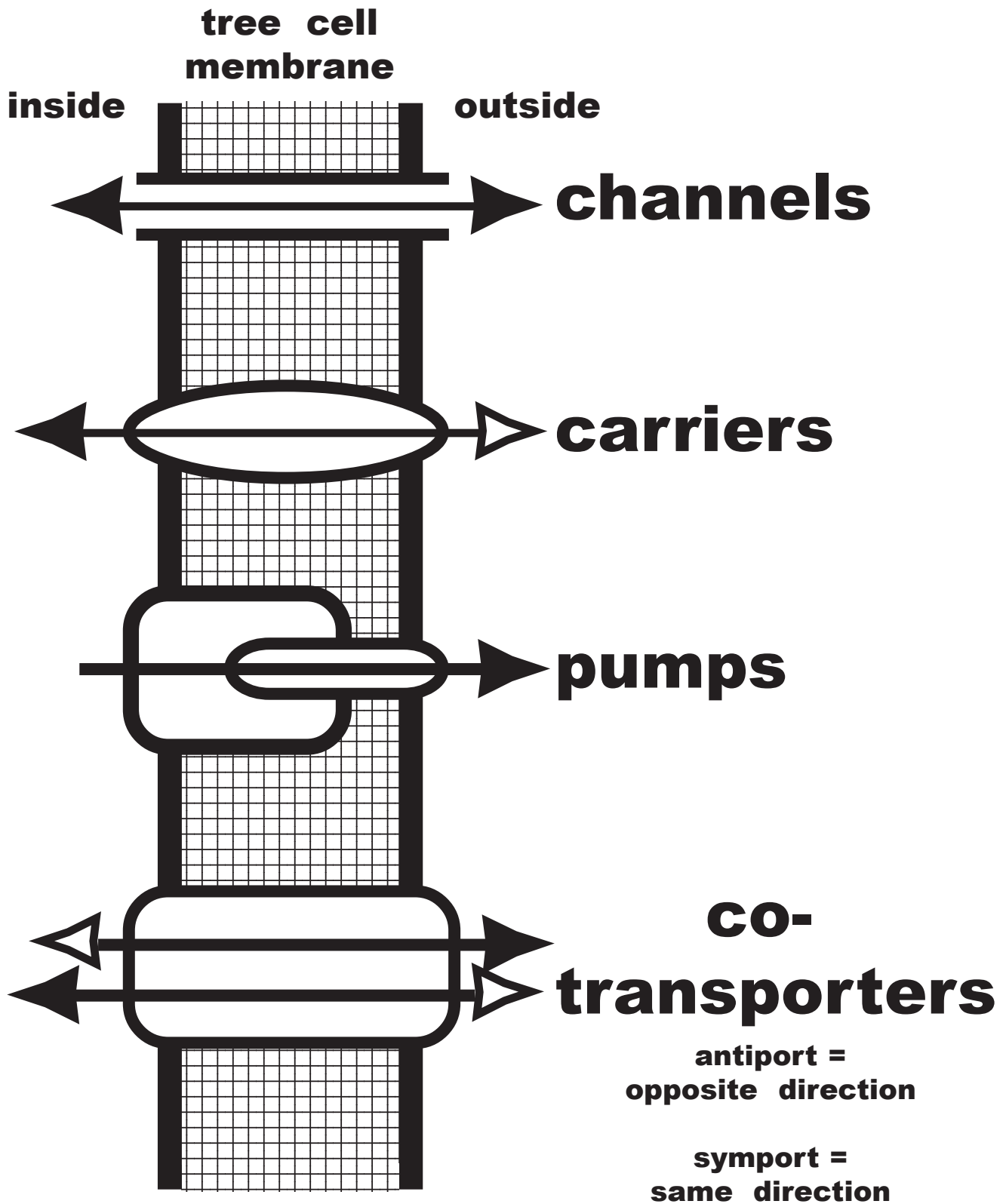


Figure 36: Transport proteins types on the plasma membrane.  
 (from Marschner, 2012)

Co-transporters allow elements to be shuttled across the membrane along with, or in exchange for, another ion. For co-transporters, if one element moves in and the other out at the same time, the co-transporter is called an antiport. If both elements / ions move in the same direction across the membrane, the co-transport protein is called a symporter. Figure 37. Remember channels, carriers, and co-transporters can all be used to either bring in elements, or to expell elements.

### Futility

In trees there is one peculiar, and potentially damaging, consequence of element transport systems on cell membranes. Because there are membrane transport proteins moving element in both directions (into and out of a cell), to sustain an adequate balance of concentrations and electrstatic charges, under some conditions these protein transporters work against each other.

“Futile” cycling occurs in some tree roots when  $K^+$ ,  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$  are present in moderate to high concentrations in soil surrounding tree roots, such as after fertilizer enrichment. Because transport proteins can be expensive to make and maintain, and because some use significant energy in moving elements in one direction or the other, taking up and releasing these select elements from cells costs a tree material and energy.

### Easy Elements

The ease of taking up essential elements is governed by how each element behaves at the soil / root interface. Figure 38 shows the difficulty of transporting select elements from soil to root symplast. Boron (B) is easy to move while iron (Fe) is difficult. Biological poisoning elements cadmium (Cd), mercury (Hg), bromine (Br), and cesium (Cs) are easy for a tree to take-up.

### Element Form

Figure 39 provides the most common forms of essential elements absorbed by tree roots. Almost all are in ionic forms dissolved in water. Notable are silicon (Si) and boron (B) which commonly enter a tree as a neutral molecule. Figure 40 provides select ion sizes when they are hydrated and surrounded by water molecules in soil and in tree tissues. Some ions can behave as if they are 5 times larger in a tree than ion size would suggest. Ion size in soil and trees impacts how each element interacts with other components of a tree and other essential elements.

Figure 41 is a summary graphic representing essential element proportionality in trees.

## channels

**B Ca Cl K NH<sub>4</sub> urea**  
**cations anions**  
**organic acids**

## carriers (uniport)

**Cu Fe Mg Mn Ni Co Zn**

## pumps (energy required)

**H Ca Cu Zn**

## co-transporters

(symport / antiport)

**H B Cl Fe K**  
**Mo P S Zn NO<sub>3</sub>**  
**amino acids**

Figure 37: Elements transported on membrane proteins.

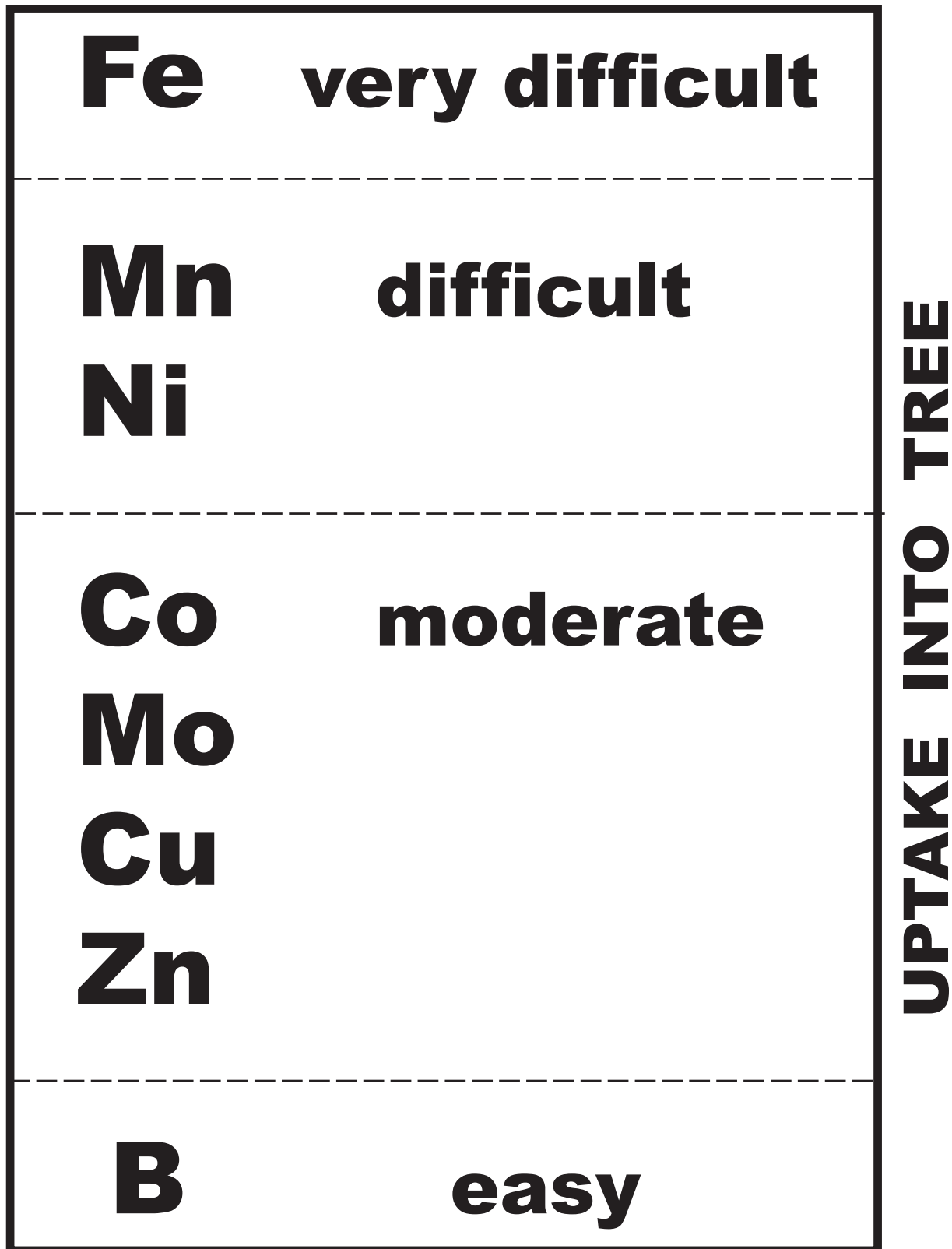


Figure 38: Ease of uptake of essential elements into trees. Note toxic elements Cd, Hg, Br, and Cs are all easily taken up by trees. (from Kabata-Pendias 2011)

element name	element symbol	most common form(s) available for tree
carbon	C	<b>HCO<sub>3</sub><sup>-</sup></b> , <b>CO<sub>2</sub></b> / carbon dioxide
oxygen	O	<b>O<sub>2</sub></b> / oxygen, H <sub>2</sub> O / water
hydrogen	H	<b>H<sub>2</sub>O</b> / water
nitrogen	N	<b>NO<sub>3</sub><sup>-</sup></b> / nitrate, <b>NH<sub>4</sub><sup>+</sup></b> / ammonium, CO(NH <sub>2</sub> ) <sub>2</sub> / urea
potassium	K	<b>K<sup>+</sup></b>
calcium	Ca	<b>Ca<sup>+2</sup></b>
magnesium	Mg	<b>Mg<sup>+2</sup></b>
phosphorus	P	<b>H<sub>2</sub>PO<sub>4</sub><sup>-</sup></b> , HPO <sub>4</sub> <sup>-2</sup> / phosphate
sulfur	S	<b>SO<sub>4</sub><sup>-2</sup></b> / sulfate, SO <sub>2</sub> / sulfur-dioxide
chlorine	Cl	<b>Cl<sup>-</sup></b> , Cl <sub>2</sub> / chlorine, ClO <sub>3</sub> <sup>-</sup> / chlorate
iron	Fe	<b>Fe<sup>+2</sup></b> , <b>Fe<sup>+3</sup></b>
manganese	Mn	<b>Mn<sup>+2</sup></b> , Mn <sup>+4</sup>
zinc	Zn	<b>Zn<sup>+2</sup></b>
boron	B	H <sub>3</sub> BO <sub>3</sub> / borate
copper	Cu	Cu <sup>+</sup> , <b>Cu<sup>+2</sup></b>
silicon	Si	H <sub>4</sub> SiO <sub>4</sub> / silicate
molybdenum	Mo	MoO <sub>4</sub> <sup>-2</sup> / molybdate
nickel	Ni	Ni <sup>+2</sup> , <b>Ni<sup>+3</sup></b>
cobalt	Co	<b>Co<sup>+2</sup></b> , Co <sup>+3</sup>

Figure 39: List of essential elements, in order of concentration required in trees, giving element name, symbol, and most common elemental form available for a tree. Elemental forms in bold predominate.



<b>ion symbol</b>	<b>ionic diameter</b>	<b>diameter of hydrated ion</b>	<b>times hydrated ion larger than ion</b>
<b>K<sup>+</sup></b>	<b>3.3</b>	<b>3.0</b>	<b>0.9 X</b>
<b>Ca<sup>2+</sup></b>	<b>2.3</b>	<b>6.0</b>	<b>2.6 X</b>
<b>Mg<sup>2+</sup></b>	<b>1.6</b>	<b>8.0</b>	<b>5.0 X</b>
<b>Fe<sup>2+</sup></b>	<b>1.6</b>	<b>6.0</b>	<b>3.75X</b>
<b>Fe<sup>3+</sup></b>	<b>1.3</b>	<b>9.0</b>	<b>6.9 X</b>
<b>Cu<sup>2+</sup></b>	<b>1.6</b>	<b>6.0</b>	<b>3.75X</b>
<b>Mn<sup>2+</sup></b>	<b>1.8</b>	<b>6.0</b>	<b>3.3 X</b>
<b>Zn<sup>2+</sup></b>	<b>1.6</b>	<b>6.0</b>	<b>3.75X</b>
<b>Co<sup>2+</sup></b>	<b>1.5</b>	<b>6.0</b>	<b>4.0 X</b>
<b>Ni<sup>2+</sup></b>	<b>1.6</b>	<b>6.0</b>	<b>3.75X</b>

Figure 40: Select size properties of tree essential element ions. Note diameters in angstroms.  
(derived from Kabata-Pendias, 2011)

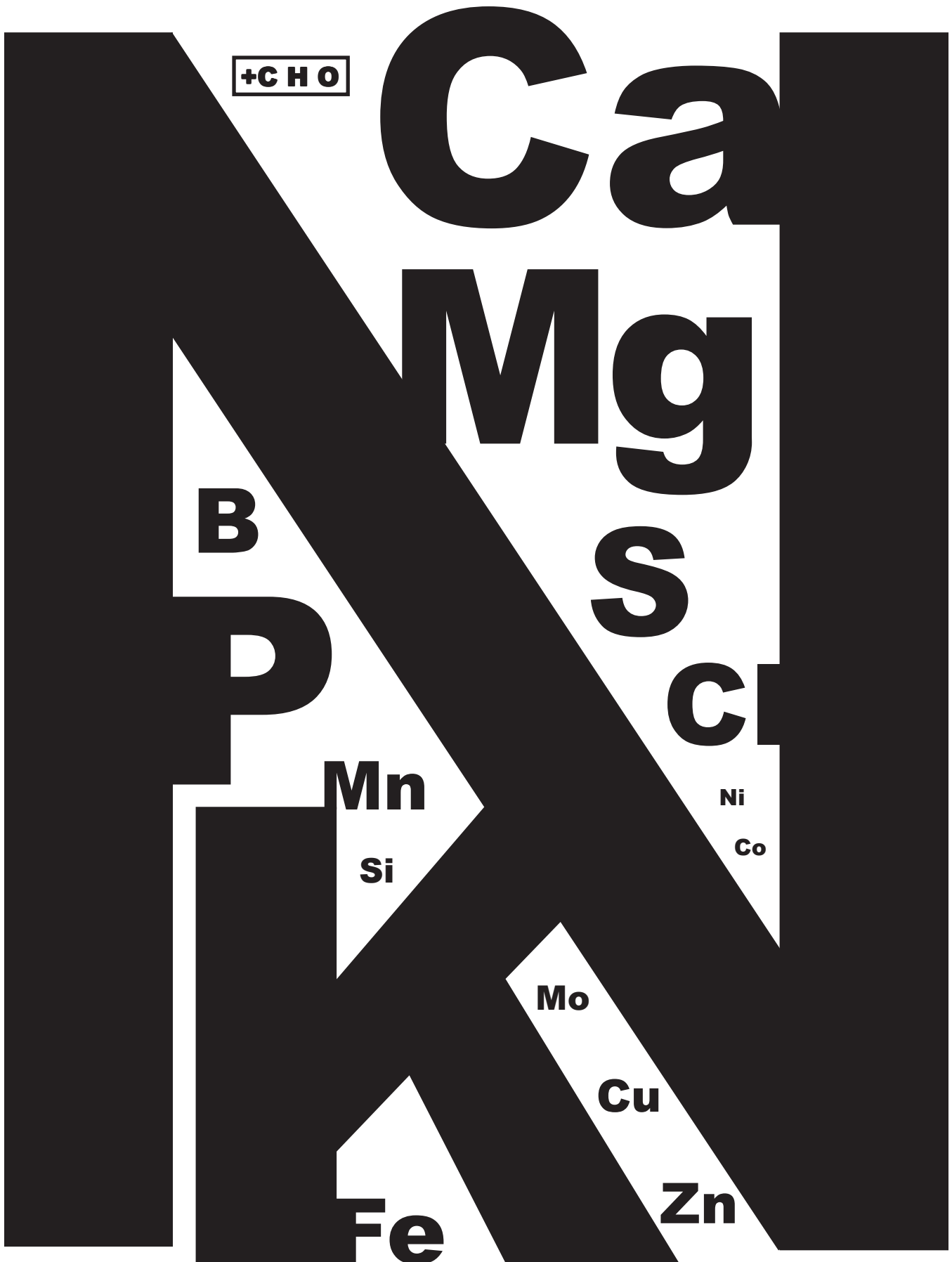


Figure 41: Relative proportion for essential elements in trees.

# Essential Element Descriptions

Essential elements of trees have many attributes. Some element attributes are good for a tree and some are bad for a tree. An element's value to a tree depends upon both its dose (concentration and availability), and the dose of other synergistic or antagonistic elements. This section of the manual will highlight tree essential element attributes, uses, deficiency symptoms, and interactions with other elements and their chemical environments. Remember, few of these elements are ever found in a pure form in our ecological systems. Elements will be reviewed in alphabetical order. Carbon (C), hydrogen (H), and oxygen (O) -- the elements of atmospheric oxygen (O<sub>2</sub>), water (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>) and tree food (carbohydrates = CHO), are left for the end of this section.

## **Boron (B)**

Boron (B) is a hard, brittle, brown solid called a metalloid discovered in 1808. Its name is derived from Persian for a boron containing compound. The rest of its elemental family are all metals. It is never found in pure form. It is used for cleaning products, water softening, antiseptics, heat resistant glass, nuclear reactor rods, and transistors.

Boron is a rare element and the lightest (except for hydrogen) element essential for trees. Boron is one of two essential elements (i.e. silicon is the other) usually present in a tree as a neutral molecule (undissociated form) rather than as an ion. The concentration of boron can vary widely in tissues. Its form in a tree depends upon tissue pH, existing as boric acid (B(OH)<sub>3</sub> / H<sub>3</sub>BO<sub>3</sub>) where pH is less than 7.0, and the borate ion (B(OH)<sub>4</sub><sup>-</sup>) where pH >7.5.

Boron deficiency causes many biological and structural problems in trees. Boron can act as an antibiological agent in trees. When boron is in short supply, pathogen attacks are more effective and move quicker. Both terminal meristems (shoot / root) are seriously impacted by boron deficiency leading to damage and death.

New tissue in boron deficient trees quickly become hard, dry, and brittle. With little boron, leaf blades are stunted and distorted with tip and marginal yellowing, bleaching, and death. New tissue can show atypical periderm cracking and minute eccentric periderm growths (ridges and spots). Because boron is immobile once positioned in trees, new tissues show developing deficiencies first. Slowed root growth is a first symptom of boron deficiency. Boron deficiency impacts many components in trees.

Primary problems with shortages of boron occur in cell walls, membrane functions, and starch, protein, auxin, and nitrate processing. Cell wall structure and middle lamella pectins between cell walls are strengthened and tied together with boron links. Cell membrane health is modified by boron. Nitrate use, general protein production, and associated RNA production and functioning are facilitated by boron. Boron impacts production and storage of starch, modifies growth regulator stability (i.e. auxin), and helps govern lignin production.

Boric acid can be used as a simple, quick, cheap boron fertilizer, but can quickly become toxic, especially to new root tips. Boron containing cleaning materials in grey water systems can damage tree roots. Interestingly, boric acid added to acid soils can partially offset aluminum toxicity.

## **Calcium (Ca)**

Calcium (Ca) is a hard silver-white, reactive metal. Calcium can exist in ten isotopes, six stable, one long-lived (>100,000 years), and three short-lived. It was discovered in 1808 and named after the Latin for "lime." It is not found in its pure form, but is common in a variety of compounds. Calcium

carbonate is limestone and marble. Calcium oxide is lime. Calcium hydroxide is slaked lime. Calcium sulfate is gypsum. Calcium is used in mortar and concrete, iron making, and as a drying agent.

Calcium is an essential element commonly site-enriched for trees, with or without magnesium (i.e. in various liming products). Calcium presents many problems for trees. Calcium is an essential element which is continually and actively exported out of a tree. Roots transport calcium outward using its high concentration gradient inside the tree as the power source. Inside tree cells calcium is held in vacuoles and bound in a special binding protein (i.e. calmodulin), in various cell membranes, and actively transported out of the cell.

Calcium plays an important role in tying primary cell wall constituents together. Calcium cross-links pectin chains similar to boron, and impacts plasmalemma mechanics (i.e. rheology) and transport. Calcium plays a key role in protecting membranes from strong acid pH levels (pH <4.0), and from sodium / salinity problems which disrupts uptake of potassium. Calcium acts as a signal for various environmental cell stress and strain problems including salinity, heat, cold, low oxygen, drought, UV light, toxic aluminum levels, as well as mechanical movement, pathogenic attack, and nodulation by symbionts. Calcium also plays a role in guard cell function in opening stomates.

Unlike other positive (cation) elements like magnesium and potassium, calcium does not activate many enzymes. Calcium plays a significant role in supporting membrane health in cell division, cell expansion, and activity of a growth regulator (auxin). Calcium is part of the materials responsible for sealing living cell to cell connections. A huge amount of calcium is placed into calcium oxalate crystals which comprise as much as 90% of all calcium in a tree. Calcium does not move in a tree once placed and is never remobilized. Acidic rain from natural and human caused events tend to leach calcium away from tree surfaces

Calcium deficiency facilitate and accelerate pest entrance and attack in trees due to weakening of cell walls, especially in roots. Lack of calcium causes shoot and root tips damage and death, cambium development slowed and damaged, compartmentalization responses are negatively impacted, and over new tissue surfaces lesions may occur. Under calcium deficiency in low pH soils, metal toxicities may overshadow calcium shortages. High concentrations of calcium immobilize iron (Fe) in leaves and generate yellowing symptoms.

## **Chlorine (Cl)**

Chlorine (Cl) is a yellow-green poisonous gas. Chlorine can exist in four isotopes, two stable, one long-lived (~300,000 years), and one short-lived. It was discovered in 1774 and named from Greek for “greenish-yellow.” It is used in bleach, plastics, solvents, water purification, acid, insecticides, and refrigerants.

Chlorine is a common ion in many soils and can be a constituent in precipitation (pollution and sea salt sources). Deficiency is rare, but toxicity is common. Chlorine is freely taken up by trees. Within a tree, chlorine can show the greatest variability of toxicity concentrations of any essential element, by as much as 8,000 times. Many fertilizers use a chlorine containing salt to carry essential elements (i.e. KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, and NH<sub>4</sub>Cl). These salts can cause toxicity problems from root desiccation, as well as too high of chlorine concentration. Toxicity symptoms include shoot and root damage and death, and leaf marginal distortion, death, and premature abscission. Chlorine will readily leach from most soils.

Trees require chlorine for a variety of uses. Chlorine is primarily associated with water control and photosynthesis. Chlorine is positioned to move water through tissues (i.e. an osmoticum). Chlorine and potassium (K) are used to open and close guard cells around stomates. Chlorine is part of the initial proton, electron, and oxygen generating step of photosynthesis (LHCII) along with manganese (Mn).

Chlorine helps activate the proton gradient production rotor of ATP on cell membranes. It is found in many organic materials in trees. Chlorine also has limited disease resisting attributes.

Chlorine deficiency is rare in trees. Chlorine deficiency leads to tissue stunting with leaves showing marginal yellowing, wilting, distortion (curling / cupping) and death. Young tree shoots, roots, and leaves are especially vulnerable to chlorine deficiency damage. Roots under low chlorine will present with a stubby, thickened appearance. At the onset of chlorine deficiency, tree leaf tissue color will shift to more blue-green and then bronze.

## **Cobalt (Co)**

Cobalt (Co) is a rare, bright, whitish-blue metal. Cobalt can exist as six isotopes, one stable and the rest short-lived (<5.5 years). It was discovered in 1735 and is named from German for “evil spirit.” It is used as a blue glass colorant, as a steel additive, in high speed cutting tools, for cancer treatments, for magnets, and is part of the animal required B-12 vitamin. Cobalt is magnetic.

Cobalt is essential for tree root function. It is associated with normal tree rhizosphere flora and critical recycling processes in soil. It is required in extremely small concentrations and can quickly become toxic. Cobalt is involved in many interactions with other metals in soil and its availability is tied to soil pH changes. Within a tree it is immobile once placed.

Cobalt accumulates preferentially in tree roots (90% in roots / 10% in shoots). Shoot accumulation is centered in green tissues (leaves, primary cortex, and secondary cortex) where it stabilizes chlorophyll conservation and recycling systems (i.e. slows senescence). Legume trees require cobalt for nodulation and nitrogen fixation systems. Toxicity is first evident as greatly slowed phloem transport processes. Animals require a cobalt containing vitamin (B-12) which is produced by soil bacteria and algae, and taken up into plants. B-12 is not required by, nor produced by, trees.

Cobalt serves a modifying and protective function in trees, stabilizing a growth regulator (auxin) and inhibiting associated high auxin concentration ethylene production. Cobalt is a part of one secondary metabolic pathway in trees and influences CO<sub>2</sub> uptake by tissues. Cobalt is taken up by tree cells only during daytime (not at night) because of the expensive-to-make metal ion carrier required. The form of cobalt made available impacts tree health. Cobalt nitrate has been cited as improving tree drought tolerance. Cobalt chloride was found to increase growth while cobalt acetate additions inhibited growth. As pH falls (becomes more acidic), more cobalt is made available and taken up by trees.

Anaerobic conditions in soil tend to release cobalt. Liming soils (increase pH) and addition of composted organic materials tend to decrease cobalt availability. Soil with high concentrations of manganese (Mn) have less cobalt available for trees due to cobalt being tied up with manganese (Mn). Cobalt and zinc (Zn) interact in interesting ways. Increased zinc (Zn) and cobalt concentrations cause iron (Fe) deficiency. Cobalt toxicity mimics both iron (Fe) and manganese (Mn) deficiency. Cobalt counteracts zinc's (Zn) impact of suppressing potassium (K), calcium (Ca), and magnesium (Mg) uptake.

## **Copper (Cu)**

Copper (Cu) is a soft, reddish-brown metal. Copper can exist in six isotope forms, two stable, and four short-lived. Copper was known to early people and was named from Latin for “Cyprus.” It is easily worked and used for wires, pipes, paints, pesticides, antiseptics, and coins. It is mixed to produce several different materials: brass is copper and zinc; bronze is copper and tin; and monel is copper and nickel.

Copper is one of the essential metals in trees. Copper can quickly become toxic at elevated concentrations. It is used in dozens of enzyme system. Copper is used in electron transport, cell mem-

brane health, and in CO<sub>2</sub> fixation. In tree leaves and secondary cortex, copper is concentrated in an electron transport material which feeds electrons to light harvesting center I (LHCI) called plastocyanin. Copper is also required for the final step in electron transport for respiration, where (with iron (Fe)) oxygen (O) is used to make water. The greatest use for copper in tree cells is part of an enzyme which decomposes damaging oxygen materials (oxygen free radicals). Trees use copper for oxidizing many different materials.

Copper is almost always found in trees as an organically bound compound (phytochelatins) usually associated with sulfur (S). The two forms available in trees is cuprous (Cu<sup>+</sup>) which is colorless, and the more oxidized cupric (Cu<sup>++</sup>) which is brown to blue in color. The cupric form is only found in an organic compound form within a tree. In tree soil, copper is available below a pH of 6.1. As pH increases (more basic), copper become progressively more unavailable. Soils with pH >7.5 tend to be copper deficient. As a general rule, copper solubility in soil decreases 99% for each increase in pH value.

Copper deficiency cause tree shoot and root damage and death, while stimulating release of dormant buds which generates a characteristic bushy or broomed look. Tree leaves may appear small. Leaf blade edges may be rolled and distorted. Leaves will first present with an atypical blue-green color moving to yellow. Leaf blades can also develop dead spots. Twig internodes are shortened. Young periderm can show small areas with corky patches and small lesions, sometimes with gums and resins exuded (exanthema). Copper deficiency mimics potassium (K) deficiency. Copper toxicity in contrast, is first noticeable as stunted root growth, dead roots, and leaf yellowing. Copper toxicity mimics iron (Fe) deficiency chlorosis.

Copper has many interactions with other tree essential elements. As phosphorus (P) and potassium (K) are increased, less copper is available. This effect is most noticeable with increasing phosphorus (P) levels. As copper concentrations increase, the less zinc (Zn) and molybdenum (Mo) are available to trees, but the more manganese (Mn) is available. Copper sulphate (CuSO<sub>4</sub>) alone or in a mixture with various lime products have been used for centuries as fungicides, algicides, and herbicides. Copper sulphate is soluble in water and cheap. Continued use of copper based fungicides can lead to iron (Fe) deficiencies.

## **Iron (Fe)**

Iron (Fe) is a shiny, silver-white, easily corroded metal. Iron can exist as eight isotopes, four stable, one long-lived (~1.5 million years), and three short-lived. Iron was known to early people and its name is from Anglo-Saxon. It is the most common metal in our culture. Iron is never found in its pure form. It is used in steel making. Iron is magnetic.

Iron is a universal component of plant life. Trees use iron in a myriad of tasks. Iron is stored in trees as ferritin, an iron complex protein. Iron is used in a tree in heme and iron-sulfur proteins which utilize the easily reversible energy states of iron. Heme groups play an important part in attracting damaging oxygen radicals, especially in photorespiration and when a tree is under anaerobic conditions. The iron-sulfur (Fe-S) proteins are used throughout a tree in electron transport chains.

Iron-sulfur (Fe-S) and iron-copper (Fe-Cu) combinations are responsible for almost all electron conserving processes in a tree, including ATP production. The photosynthetic system is filled with iron containing electron transport materials like cytochromes and ferredoxin. Iron is also critical to nitrogen (N) and sulfur (S) metabolism processes. Chlorophyll production and maintenance requires iron and is sensitive to deficiency. Iron also is used with copper (Cu) in the final respiration step in trees reducing oxygen to water.

Iron is found in two ionic forms in soil, ferrous ( $\text{Fe}^{++}$ ) and ferric ( $\text{Fe}^{+++}$ ). Iron in aerobic soil exists either as insoluble oxides or as the ferric form ( $\text{Fe}^{+++}$ ) bound in organic compounds. In a tree, iron is taken up by membrane carriers in the ferrous form which is then processed using cell energy into the ferric form. Tree roots exude protons and organic acids which lowers rhizosphere pH and increases iron solubility while facilitating binding of iron into organic structures. This process also occurs with phosphates.

Iron deficiency is similar to manganese (Mn) deficiency. The deficiency symptoms are concentrated in young tissues because iron, once placed, is immobile. In young leaves, yellowing occurs between vascular bundles (veins), eventually leading to the entire leaf yellowing and beginning to prematurely senesce. Soil with high pH (more basic), high calcium concentrations, and / or high calcium carbonate concentrations (lime) accelerate iron immobilization in leaves and associated tissue yellowing and bleaching. High manganese (Mn), copper (Cu), and zinc (Zn) concentrations, especially under acid conditions, can also lead to iron deficiencies.

Soil compaction, over watering / flooding (anaerobic conditions), and high pH lead to iron deficiency. Iron is minimally soluble in a soil between a pH of 7.0 and 9.0. Above pH 6, insoluble iron-phosphate complexes are generated minimizing phosphorus availability. Iron concentrations are very low on calcareous soils especially around pH 8.0. Iron toxicity can occur when too much iron is added to an acid soil causing tree roots to appear brown and dead, and leaves darken and die without abscission. Fertilization with iron should be in the form of an organic compound or iron phosphate.

## **Magnesium (Mg)**

Magnesium (Mg) is a light weight, reactive silver-white metal. Magnesium can exist in five isotopes, three stable and two short lived. It was discovered in 1755 and named for the area of Magnesia in Thessaly. It is abundant in the Earth's crust and in seawater. It is used for various metal alloys, airframes, missiles, fireworks, flares, light bulbs, medicines, and epsom salt (magnesium sulphate). It is critical for trees principally because it is the center of chlorophyll molecules.

A significant part of the Earth's crust is made of magnesium. This is a common essential element used by trees in a host of processes. Magnesium activates more enzymes than any other element. It is at the core of chlorophyll, scattered as a facilitator along carbon acquisition and transformation processes, and key to production in ATP energy systems. Magnesium helps maintain the structure of DNA and RNA. Magnesium also stimulates (with potassium (K)) proton pumps on living membranes. Magnesium is also responsible for assuring effective starch management in leaves. Many physiological processes requiring magnesium are all slowed and damaged by its deficiency, even before visible symptoms are noticed.

Magnesium is highly conserved and mobile in a tree. Energy in a tree can not be captured or used without magnesium. Magnesium deficiency is first noticed in older leaves margins and in leaf blade islands of yellowing and death. Leaves with patches of yellowing, which eventually engulf the entire leaf, is common. A noticeable color change of magnesium shortage occurs in many leaves, with yellowing closely followed by coloration from the protective pigment anthocyanin.

Magnesium deficiency can mimic potassium (K) deficiency and must be carefully diagnosed. Poor drainage, drought, cold temperatures, acidic pH, and excess leaching can all lead to magnesium deficiency. Any increase in potassium (K) or calcium (Ca) availability tends to decrease magnesium. Iron (Fe), zinc (Zn), and manganese (Mn) are all chemically and biologically antagonistic with magnesium, while phosphorus (P) availability can help increase magnesium availability. In acid soils, aluminum (Al) suppresses magnesium uptake in trees.

In the past, manure was the best way to add magnesium in a low cost manner. Now there are many magnesium fertilizers which are soluble and cheap. Dolomitic limestone has been a key enrich-

ment product for trees, adding both calcium (Ca) and magnesium. Unfortunately, care is needed in using dolomite because the magnesium dissolves out first leaving the calcium (Ca) behind to more slowly dissolve. This leads to problems with people thinking there is plenty of magnesium present because they see remains of the dolomite, when actually magnesium has been gone for some time. Most recommendations suggest separate soluble magnesium and calcium (Ca) products be added to tree soils. The ratio of calcium (Ca) to magnesium should be approximately 3Ca / 1 Mg. Magnesium toxicity can show symptoms of calcium (Ca) and potassium (K) deficiency.

In some parts of the country where magnolia family trees grow, epsom salts have been a traditional soil enrichment. This salt is magnesium sulphate. Early in the last century people noticed great improvement in magnolia family tree color when epsom salts were added. Magnolia family trees have a problem taking up adequate magnesium in acid soils. Also, ammonium fertilizers inhibit magnesium uptake during cool parts of the growing season. Nitrate additions facilitate magnesium uptake.

## **Manganese (Mn)**

Manganese (Mn) is a hard, whitish-gray metal not found in its pure form in nature. It can exist as seven isotopes, one stable, five short-lived and one long-lived (~3.7 million years). It was discovered in 1774 and was named from the Latin word for “magnet.” Manganese is similar to iron in it will rust. It is used in steel making, as a glass colorant, and in batteries.

Manganese is a metal used in small amounts, but essential to a number of key processes in trees. Manganese serves as the center block upon which water is split at the start of photosynthesis (LHCII) and oxygen (O) is given off. Manganese helps facilitate photosynthesis. Manganese is also part of a scavenger enzyme which removes damaging oxygen radicals inside cells. Manganese activates several other enzymes.

Manganese stimulates and supports amino acid and lignin synthesis. Pest resistance in trees is facilitated by adequate levels of manganese by increasing lignification, generating more defensive compounds when tissue is challenged, and chemically inhibiting several fungal enzymes. In some uses within a tree, manganese and magnesium (Mg) are interchangeable in limited amounts.

Manganese is an essential element tied in many ways to oxygen management in a tree. Manganese is immobile in a tree and any deficiency will show on new tissues. Deficiency is usually seen on fully expanded new leaves, not on new-forming leaves. Manganese is commonly deficient in soil pH from 7.3 - 8.5, as well as in soils with free calcium-carbonate (CaCO<sub>3</sub>). Generally, as pH increases manganese availability declines sharply. Organic soils and soils with high concentration of composted organic matter tend to tie up manganese.

Manganese deficiency commonly generates uneven mottled yellowing and bleaching between leaf veins mimicking iron (Fe) deficiency, where (iron (Fe) deficiency presents more evenly through out tissues. Leaves and new shoots will show dead patches, marginal and tip bleaching, and discolored streaks and leaf veins may become darker as blades become more yellow in color. Manganese deficiency may also present with stunted tissues. Manganese deficiency symptoms usually occur on the outside of the middle crown areas while magnesium (Mg) deficiency is usually seen at the crown top in new tissues. The time between yellowing and bleaching of leaf tissues and death is usually short. Manganese deficiency is mistaken and misdiagnosed for magnesium (Mg), iron (Fe), or sulfur (S) deficiencies.

Manganese toxicity occurs in anaerobic and acid soils (along with cobalt (Co) and nickel (Ni)). Under these conditions of manganese toxicity, bark lesions, and leaf deformation and speckling can occur. More and more manganese is taken up as pH falls (becomes more acidic).



## **Molybdenum (Mo)**

Molybdenum (Mo) is a rare, hard, silver metal not found in pure form. Molybdenum can exist as eleven isotopes, seven stable, one long-lived (~3,500 years), and three short-lived. It was discovered in 1782 and named from the Greek for “lead” because it was often confused with graphite and lead containing minerals. It is used as a steel additive and in military hardware, petroleum catalysts, and for medical uses.

Molybdenum is by far the heaviest metal essential to trees. It plays a key role in nitrogen processing. Although there are few other functions for molybdenum, it must be present for healthy trees. The production of two tree growth regulators (i.e. auxin & ABA) depend upon molybdenum. Molybdenum, as a heavy metal, must be attached within a biological protein framework to function. A total of five enzyme systems in trees use molybdenum, dominated by nitrogen assimilation and transport.

For tree fertilization systems using nitrate, molybdenum is required for nitrate use. Without molybdenum, nitrate fertilization will tend to present symptoms of nitrogen deficiency symptoms. Molybdenum is needed for the internal nitrate to nitrite conversion step, nitrogen gas conversion to ammonia in nitrogen fixing symbionts, and in uric acid synthesis. Molybdenum is essential for the nitrate reductase enzyme and responsible for nitrogen fixing by microorganisms like tree root nodule symbionts.

Molybdenum is mobile throughout a tree and any deficiency will present across the entire crown. Molybdenum deficiency shows leaf blade yellowing between pale green leaf veins. Tree leaves may develop a mottled appearance similar to iron (Fe) or manganese (Mn) deficiency, and then begin to curl, distort and die. On sites with weathered acid soil, well drained coarse soils, and organic soil, leaves may all show molybdenum deficiencies. Low temperatures and high nitrogen (N) concentrations can induce deficiencies. Nitrogen (N) deficiencies need to be remedied with assurance of molybdenum availability.

Molybdenum inhibits iron (Fe) use by trees. Molybdenum availability is facilitated by phosphorus (P) and inhibited by sulfur (S). Trees take up molybdenum in the form of the molybdate ion ( $\text{MoO}_4^{2-}$ ). This ionic form is closely tied to soil pH. If  $\text{pH} > 5$  then molybdenum is in the form of  $\text{MoO}_4^{2-}$ , if  $\text{pH} < 5$  molybdenum is in the forms of  $\text{HMoO}_4^-$  and  $\text{H}_2\text{MoO}_4$ . For every whole pH unit above pH5, molybdenum solubility increases by roughly 100X. Liming soils will increase molybdenum (if present). Molybdenum additions are usually required on sandy soils, and carefully managed on acid soils as the molybdenum will be tied up (unavailable peak around pH4.0) with iron (Fe) and aluminum (Al). Molybdenum toxicity generates a unique golden yellow new shoot color and misshapened leaves.

Enriching a site with molybdenum is easy as it requires so little molybdenum to affect a change. Molybdenum can be added as composted organic matter in aerobic soils, if the organic matter came from soils with molybdenum. An ammonium molybdate fertilizer source is also available. Addition of phosphorus (P) can release bound molybdenum.

## **Nickel (Ni)**

Nickel (Ni) is a silver metal. Nickel can exist as ten isotopes, five stable, one long-lived (~75,000 years), and four short-lived. Nickel was discovered in 1751 and named from German for “Satan’s copper.” It is used as a green glass colorant and in metal plating, heating elements, stainless steel, many alloys, coins, magnets, and rechargeable batteries. Nickel is magnetic.

Nickel is needed in extremely small amounts by trees. It is found associated with one primary enzyme called urease which facilitates conversion of urea to carbon-dioxide and ammonia. This is a vital nitrogen transformation process in trees. Nickel has also been cited as assisting in disease resistance in trees. Increasing nickel concentrations can quickly become toxic to tree tissues. Lime can be used to reduce nickel toxicity.

Nickel deficiency is difficult to diagnosis because it is required in such small amounts. Nickel deficiency presents with symptoms similar to an iron (Fe) or zinc (Zn) deficiency. Nickel deficiency generates marginal yellowing, distortion, and stunting of leaves, with new shoots becoming brittle with distorted buds and loss of apical dominance and apical control. Nickel deficiency initiates a premature senescence process. Nickel deficiency also greatly limits absorbing root initiation and growth. Tree root damage and cold soils during the bud swelling period of early Spring tend to show nickel deficiency. Nickel deficiency causes an toxic accumulation of urea in tissues, which are damaged and die. This urea toxicity occurs regardless of the type of nitrogen source available.

Nickel availability is dependent upon soil pH. Values of pH >6.7 have poor nickel solubility, while pH values <6.5 provide more solubility. As in cobalt (Co) and manganese (Mn), as pH drops (more acidic) more nickel becomes available. Interactions with other elements are subtle but are important to recognize. As nickel concentrations decline, iron (Fe) availability declines. High concentrations of zinc (Zn), copper (Cu), manganese (Mn), iron (Fe), calcium (Ca), and magnesium (Mg) all induce nickel deficiency. Especially with zinc (Zn), copper (Cu), and manganese (Mn) fertilization, nickel availability can plummet. Anaerobic soil conditions tend to increase nickel (and cobalt (Co)) availability. Nickel can be added where needed by using NiSO<sub>4</sub> or Ni-organic complex enrichments in small amount.

## **Nitrogen (N)**

Nitrogen (N) is a gas, but all other elements in its family are metals or metalloids. It can exist as four isotopes, two stable and two short-lived. It was discovered in 1772. The name is derived from Greek meaning “forming native soda.” Nitrogen gas is relatively inert, colorless, and orderless. It comprises ~78% of the atmosphere. Nitrogen is used in the food industry as preservatives, refrigerants, protective gas covers, and used in fertilizers, explosives, and medical diagnostic systems.

Nitrogen is the premier element in soil which trees exert tremendous energy to procure. It is usually the major component of general fertilizers, and usually represents the element of greatest expense with which to enrich a site. A tree requires greater amounts of nitrogen than any other essential element derived from the soil. Only water is needed in more abundance than nitrogen for tree health. Nitrogen availability limits tree growth in most ecological systems.

Nitrogen is key to modifying how carbon chains function. Nitrogen is a component of all amino acids, nucleic acids, and proteins. Nitrogen has a tremendous oxidation / reduction range going from nitrate (NO<sub>3</sub><sup>-</sup>) with valance of +5 through dinitrogen gas (N<sub>2</sub>) with a valance of 0 to ammonium (NH<sub>4</sub><sup>+</sup>) with a valance of -3. This eight electron difference allows for many uses to be made of nitrogen products.

To capture, reduce, transport, and use nitrogen, many transformations must occur. Trees spend a great amount of energy (15-20% of annual energy capture) to manage and conserve nitrogen. Molybdenum (Mo), iron (Fe), sulfur (S), and cobalt (Co) are all needed to take-up and process nitrogen. When these elements are in low concentrations, nitrogen uptake and processing is constrained. An interesting trade-off must be made with magnesium (Mg). Darkness and excess magnesium (Mg) inhibits the molybdenum (Mo) complex from processing nitrogen, but magnesium (Mg) is required for this processing. A careful balancing of magnesium (Mg) and molybdenum (Mo) in nitrogen processing is required. Nitrogen deficiency impacts almost everything in a tree, especially sulfur (S) transformations and use. Nitrogen enrichment is both common place and complicated. Every complete fertilizer contains nitrogen.

## **Phosphorus (P)**

Phosphorus (P) is a non-metal which is highly reactive in pure form and very poisonous. It can be found in three isotopes, one stable and two short-lived. It was discovered in 1669 and was named from Greek for “light bearer.” Phosphorus is essential for bioenergy systems, animal bones and teeth, and genetic materials. It is used in fertilizers, detergents, and for phosphorescent coatings. The pure form must be stored under water to keep it from reacting with the atmosphere.

Phosphorus is found everywhere in tree physiology. Phosphorus provides structural connections in DNA and RNA. Phosphorus is a key component separating the living inside from the dead outside of a tree, by holding together phospholipids found in all membranes. Phosphorus is an activator for energy transfer (i.e. ATP) and carbon chain manipulations. It activates enzymes and modifies proteins. Phosphorus is temporarily attached to various compounds in order to energize reactions or to position materials for further processing. Phosphorus is a universal energy and metabolism element. Phosphorus is also used as a pH buffer inside cells. It always occurs with a +5 valence whether in phosphate ( $\text{PO}_4^{3-}$ ) or pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ).

Phosphorus deficiency symptoms are so global and intricate in a tree, care must be taken to not miss other element deficiencies being masked at the same time. Phosphorus deficiency leads to darkened or blue-green foliage, leaf dwarfing, heavy anthocyanin discoloration (red / purple pigments), and more tannins (browns) produced in leaves along veins. Phosphorus deficiency tends to present with stunted shoots. It is usually more of a growth problem than a foliage problem at the beginning of phosphorus deficiency. Older tree tissues will show phosphorus deficiency first as new tissue acts as a sink for remobilized phosphorus.

High concentration of phosphorus can lead to zinc (Zn) and copper (Cu) deficiencies. Below a pH of 5.0, phosphorus is deficient under most conditions. Aerobic conditions with adequate moisture is needed for good phosphorus availability. Phosphorus enrichment can be used anytime. There are many phosphorus enrichment materials of various costs for use on tree sites. Phosphorus enrichment is common place and found associated with nitrogen (N) and potassium (K) in various mixtures and formulations.

## **Potassium (K)**

Potassium (K) is a soft, whitish-silver, extremely reactive metal. Potassium can occur as five isotopes, two stable, one extremely long-lived (>1 billion years), and two short-lived. It was discovered in 1807 and its name was derived from “potash.” It is used in fertilizers (potash). The pure metal must be stored in kerosine to prevent it from reacting violently with water or humidity. It is used in oxygen rebreathers, batteries, fertilizers, glass, food preservatives, soap, explosives, and for rock dating.

Potassium is the most abundant cation found in trees. It exists not as a part of structures and compounds, but as a free ion in the symplast where its concentration is maintained at a near constant level. Potassium activates, not builds, organic materials. Many enzymes require a univalent cation for activation, and as such, sodium (Na) can substitute for potassium in a limited way. In brackish water, potassium is taken up in order to keep sodium (Na) out. Potassium is used in trees (like sodium (Na) in animals) to maintain cell electronic equilibrium by balancing anion charges. For example, polymers of materials like DNA, which is a polyanion, requires potassium to maintain a neutral charge.

Potassium primes protein synthesis machinery, provides osmotic force, and is the ionized water bath for chemical reactions of a tree cell. Potassium is pumped into guard cells of the leaf to open stomates. It is used in other cells to maintain pressure against cell walls (turgor pressure). Potassium is used in transport systems and helps balance pH levels across internal membranes to provide for proton banking used in ATP production. Potassium is also used in transporting (co-transport) sucrose and

amino acids across exterior cell membranes. Potassium is responsible for phloem loading of transport sugars.

Potassium deficiency first presents as darkened or blue-green colored leaves. Both photosynthesis and respiration processes decline and collapse. Water conservation processes in leaves are compromised. Over time marginal leaf scorch develops in leaves, usually starting at the tip. Leaves will be stunted and internodes will not expand. Older leaves will show deficiency symptoms first as potassium is remobilized and moved to young tissue. Shoots will be stunted and die back with increasing deficiency. Potassium deficiency presents symptoms similar to phosphorus (P) deficiency.

Potassium enrichment is common place and found associated with nitrogen (N) and phosphorus (P) in various mixtures and formulations. It is important potassium deficiency testing be based upon fresh tree leaf or shoot sap, not on dry weight of tissue. Potassium has been traditionally enriched through addition of herbivore manure and plant ashes to a site.

## **Silicon (Si)**

Silicon (Si) is a metalloid with unique electrical properties. Silicon can exist in five isotopes, three stable, one short-lived, and one long-lived (~100 years). It was discovered in 1824 and named for the Latin name for “flint.” It is the second most abundant element in the Earth’s crust (~26%) and is usually found combined with oxygen. It is found as quartz and flint stones, and used in watches, glass, ceramics, semiconductors, solar cells, and silicone rubbers.

Silicon is an element whose essentiality is greatly debated among mineral nutritionists. It has been established as absolutely essential in some types of algae and in a primitive plant called scouring-rush (*Equisetum*). Silicon is used for a number of tasks in trees and is considered essential by silicon researchers. Many older agronomic, annual and non-woody plant texts and review papers do not consider silicon essential.

Silicon is found in large concentrations in the Earth’s crust and most soils. Silicon is usually found as silicic acid ( $H_4SiO_4$ ) in soils, approaching 500 times the concentration of phosphates. Silicon is found within trees in great amounts. As in other soil elements, silicon is transported through a tree in the water stream. Once incorporated in cell materials, the organo-silicates function with a valence of +5 or +6, not the elemental valence of +4.

Because of its super abundance in nature, silicon deficiency is almost nonexistent. Lack of deficiency does not change its essential nature in trees. Silicon is responsible for mitigating stress and stimulating defensive compounds (i.e. phytoalexins) in trees. Silicon strengthens and stiffens cells walls in trees. Silicon enrichment under deficient conditions stimulates higher chlorophyll concentrations in leaves. Silicon substitutes for phosphates in DNA / RNA production systems providing chemical and structural stability.

Silicon strengthens leaves to resist and minimize pest attacks. Potassium silicate accumulates in epidermal tissue outer walls just under the leaf cuticle. Silicon appears to be most needed in supporting absorbing root functions and growth. Silicon is critical on organic, tropical, heavily leached and acidic soils. Silicon has also been cited in managing metal toxicity under acidic conditions, especially aluminum (Al). Because silicate and phosphate compete for soil location sites, silicon enrichment or increased availability pushes phosphates into tree-available forms.

Although enrichment of sites with silicon is usually rarely required, the low cost calcium silicate or the more expensive potassium silicate can be used.

## **Sulfur (S)**

Sulfur (S) is a brittle solid, reactive non-metal which is yellow in color. Sulfur can exist in five isotopes four stable and one short-lived. It was known to early people and its name is derived from Sanskrit. The Latin name for sulfur is defined as brimstone. It is used in building materials, food preservatives, medicines, fertilizers, matches, batteries, bleach, detergents, paints, gunpowder, and rubber manufacturing.

Sulfur is used in similar ways as nitrogen (N), but not to its extent and diversity. Sulfur requirements average less than 1/20th of nitrogen (N) requirements in trees. Sulfur is required in the electron transport chains of photosynthesis and respiration within iron-sulfur (Fe-S) protein complexes. Sulfur is part of two structural amino acids and several coenzymes. Other sulfur containing amino acids are considered stress amino acids and generated under a variety of environmental stress conditions.

In trees, sulfur uptake and transformations require tremendous energy input and careful management. Up to 5-10% of tree energy has been cited as involved with sulfur management. Trees incorporate sulfur using magnesium (Mg), nitrogen (N) and iron (Fe). Sulfur is used in trees because of its great range of chemical activity (oxidation / reduction). For example, sulfate ( $\text{SO}_4^{2-}$ ) has a valance of +6, solid sulfur (S) has a valance of 0, and hydrogen sulfide ( $\text{H}_2\text{S}$ ) has a valance of -2.

Sulfur deficiency first impacts nitrogen (N) uptake and incorporation. As such, sulfur deficiency presents nitrogen (N) deficiency symptoms. Symptoms begin in young leaves moving to mature leaves because once placed, sulfur is difficult to move within a tree, unlike nitrogen (N). Symptoms include leaf yellowing and shoot stunting, thinning, and structural weakness.

Many fertilizers use sulfur not for its essentiality or reversal of deficiency, but for ease of transport and low cost connections to other elements. Sulfur is also added to sites to control / change pH levels, impacting other elements. Sulfur and sulfur compounds are commonly used for element enrichment processes in soils.

## **Zinc (Zn)**

Zinc (Zn) is a hard, brittle, bluish-silver metal resistant to corrosion. Zinc can exist in ten isotopes, five stable, the rest all short-lived. It was known in the 1200s in India, and later identified and named from German for “tin.” It is used for galvanizing steel and in batteries, coins, castings, paints, sunscreen, photocopiers, and cathode ray tubes.

Zinc is a divalent (+2) metal cation, but unlike most of the other metals, does not undergo valence changes (i.e. no oxidation / reduction cycles). There are many zinc using or zinc activated enzymes in trees. Zinc functions to activate proteins sometimes as the active site and sometime as a structural or conformational component. Many times zinc is seen cross-linking sulfur (S) in proteins.

Zinc is required in trees for the proper transcription of DNA and gene expression. It is a key component in photosynthetic enzymes. Zinc is required for growth regulator (auxin) synthesis and for combining amino acids into proteins. Under anaerobic conditions, zinc helps detoxify alcohol accumulations. In soils, zinc at low to neutral pH is found in the form  $\text{Zn}^{2+}$  and at high pH is found in the form of  $\text{ZnOH}^+$ . High pH (>8.2) tends to generate insoluble zinc ( $\text{ZnCO}_3$ ) and produce zinc deficiencies in trees.

Zinc deficiency in trees is first seen as leaves darkening and taking on a blue-green color which fades into a general yellowing. Leaves become stunted with a mottled appearance between veins, and eventually become distorted and die. Tree shoots become stunted with internodes not expanding and then becoming distorted and die. Roots tend to exude gums and resins, and stop growth. Zinc deficiency is common in highly weathered and calcium (Ca) rich soils with pH >8.2 where zinc becomes

insoluble. In organic soils, or soils with a large amount of composted organic matter, zinc tends to become bound up and unavailable.

As zinc becomes more deficient, more phosphorus (P) is taken up by trees. Zinc competes with nickel (Ni) for transport and activation sites, generating zinc deficiencies when nickel (Ni) concentrations are too great. High concentrations of zinc suppresses availability of potassium (K), calcium (Ca), and magnesium (Mg). Under anaerobic conditions, or through enrichment, cobalt (Co) minimizes this effect.

Zinc is easily added to enrich tree sites with many effective and low cost products. Traditionally, zinc nitrate ( $Zn(NO_3)_2$ ) as a 1% foliar application has been used for small trees and shrubs. In some cases and under some conditions, this foliar spray has caused leaf damage. Using  $ZnSO_4$  as a 0.18% solution with hydrated lime has been cited as minimizing zinc damage to leaves as a foliar spray. Zinc has not been found to be effective as a trunk injection or implant. Mycorrhizae in trees tend to mitigate and protect trees from zinc toxicity impacts.

The Others!

The three remaining elements not described above are carbon (C), hydrogen (H), and oxygen (O). They are intimately associated with all life. No deficiency can exist of these elements in trees because the very fabric of tree life is woven of these three elements. They are gathered from the environment as diatomic gases, as part of other compounds, and most notable from carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ). Each of these three elements in their pure form are briefly described below.

**Carbon (C)** is a non-metal which easily links to itself and other elements. Carbon was known to early people with its name from Latin for charcoal or coal. It can exist in five isotopes, two stable, one long-lived (~5,300 years), and two short-lived. Carbon is found in nature in five physical forms: diamond, graphite, fullerenes, “white” carbon, and coal. Life is dependent upon the chemical qualities of carbon. Any study of living systems revolve around organic or carbon chemistry. It is used for energy, steel making, carbonation, dry ice, charcoal, abrasives, and archeological dating.

**Hydrogen (H)** is the simplest element, commonly with one proton and one electron. Hydrogen is an odorless, colorless, and highly flammable gas discovered in 1776. Hydrogen is named from the Greek for “water forming.” It is by far the most common element in the universe. Hydrogen can exist as three isotopes. There is little of this element in a pure gas form in the atmosphere because it is so light it has been eroded away and lost to space. On Earth, hydrogen is concentrated in water. It is an elemental constituent of fertilizers, foods, chemical feedstocks, and weapons.

**Oxygen (O)** is a colorless, odorless gas which comprises ~ 21% of the atmosphere. Oxygen can exist in four isotopes, three stable and one short-lived. It was discovered in 1774. The name oxygen is derived from Greek meaning “acid forming.” It combines with many other elements (oxides) and comprises ~46% of the Earth’s crust. Oxygen is the dominant atom in water. It is essential for life because of its oxidative (i.e. electron stealing) ability.

# Conclusions

Essential elements are named such because they are indispensable for tree life. The unique physical chemistry and biochemistry values of tree essential elements lie with their structure, size, and reactivity.

The recipe of tree life is dependent upon the proportions of essential elements. Basic atoms of essential elements have little meaning -- it is their biological context and framework surrounding these elements which make them essential.