SOIL-PLANT NUTRIENT CYCLING AND ENVIRONMENTAL QUALITY

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"In recent years the 'human rights' issue has generated much interest and debate around the world. It is a utopian issue and a noble goal to work toward. Nevertheless, in the real world, the attainment of human rights in the fullest sense can not be achieved so long as hundreds of millions of poverty stricken people lack the basic necessities for life. The right to dissent does not mean much to a person with an empty stomach, a shirtless back, a roofless dwelling, the frustrations and fear of unemployment and poverty, the lack of education and opportunity, and the pain, misery and loneliness of sickness without medical care. It is my belief that all who are born into the world have the moral right to the basic ingredients for a decent, human life."

Norman E. Borlaug

1970 Nobel Peace Prize

"Learning science and thinking about science or reading a paper is not about learning what a person did. You have to do that, but to really absorb it, you have to turn it around and cast it in a form as if you invented it yourself. You have to look and be able to see things that other people looked at and didn't see before. How do you do that? There's two ways. Either you make a new instrument, and it gives you better eyes, like Galileo's telescope. And that's a great way to do it, make such a nice instrument that you don't have to be so smart, you just look and there it is. Or you try to internalize it in such a way that it really becomes intuitive. Working on the right problem is only part of what it takes to succeed. Perseverance is another essential ingredient."

Steven Chu

1997 Nobel Prize, Physics

intuition: immediate apprehension or cognition; without evident rational thought and inference; quick and ready insight

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1. ORGANIC MATTER

Nutrient Supplying Power of Soil

In the past 150 years, CO_2 levels in the atmosphere have increased from 260 to 365 ppm (Follett and McConkey, 2000) and it is expected to rise 1.5 to 2.0 ppm per year (Wittwer, 1985). This increase is believed to have increased the average temperature of the earth by 0.5 °C and thus various reports of global warming as a result of increased evolution of CO_2 into earth's atmosphere (Perry, 1983). It is possible to decrease the release of CO_2 to the atmosphere by choosing an alternative energy source. However, total control of the release of CO_2 is not easy because there are so many different sources, including the production of cement, gasoline-driven automobiles, burning of fuels for home heating, cooking, etc. (Wallace et al., 1990). There are, however, several benefits associated with increased atmospheric CO_2 including increased water use efficiency, nitrogen use efficiency and production in many crops.

If the expected fossil fuel CO_2 released for many years could be stored as soil organic matter, vastly enhanced productive soil would result. This option requires increased biomass to produce the needed soil organic matter, but this could be achievable due to increased CO_2 supplies in the atmosphere (Wallace et al., 1990). Obstacles to increasing the level of soil organic matter are; 1) needed organic matter supplies, 2) needed nitrogen to give around a 10:1 carbon:nitrogen ratio necessary for stable soil organic matter, and 3) efficiency in microbial activity that can result in more stable soil organic matter, instead of burn out resulting in return of CO_2 to the atmosphere (Wallace et al., 1990).

It is seldom understood that organic matter contents in soils can be increased via various management practices. Increased use of no-till management practices can increase soil organic matter. After ten years of no-tillage with corn, soil organic carbon in the surface 30 cm was increased by 0.25% (Blevins et al. 1983). Probably the least understood is increased N rates in continuous crop production on resultant soil organic matter levels. Various authors have documented that N rates in excess of that required for maximum yields result in increased biomass production (decreased harvest index values e.g., unit grain produced per unit dry matter). This results in increased amounts of carbon from corn stalks, wheat stems, etc., that are incorporated back into soil organic matter pools. Although this effect is well documented, the deleterious effects of increased fertilizer N rates on potential NO_3 leaching and/or NO_3 surface runoff should be considered where appropriate.

Use of green manures and animal wastes have obvious impacts on soil organic matter when used on a frequent basis.

The native fertility of forest and grassland soils in North America has declined significantly as soil organic matter was mined by crop removal without subsequent addition of plant and animal manures (Doran and Smith, 1987). For literally thousands of years, organic matter levels were allowed to increase in these native prairie soils since no cultivation was ever employed. As soil organic matter levels declined, so too has soil productivity while surface soil erosion losses have increased. Because of this, net mineralization of soil organic nitrogen fell below that needed for sustained grain crop production (Doran and Smith, 1987). Work by Campbell, 1976 demonstrates that to maintain yields with continuous cultivation, supplemental N inputs from fertilizers, animal manures or legumes are required (Figure 1.1).

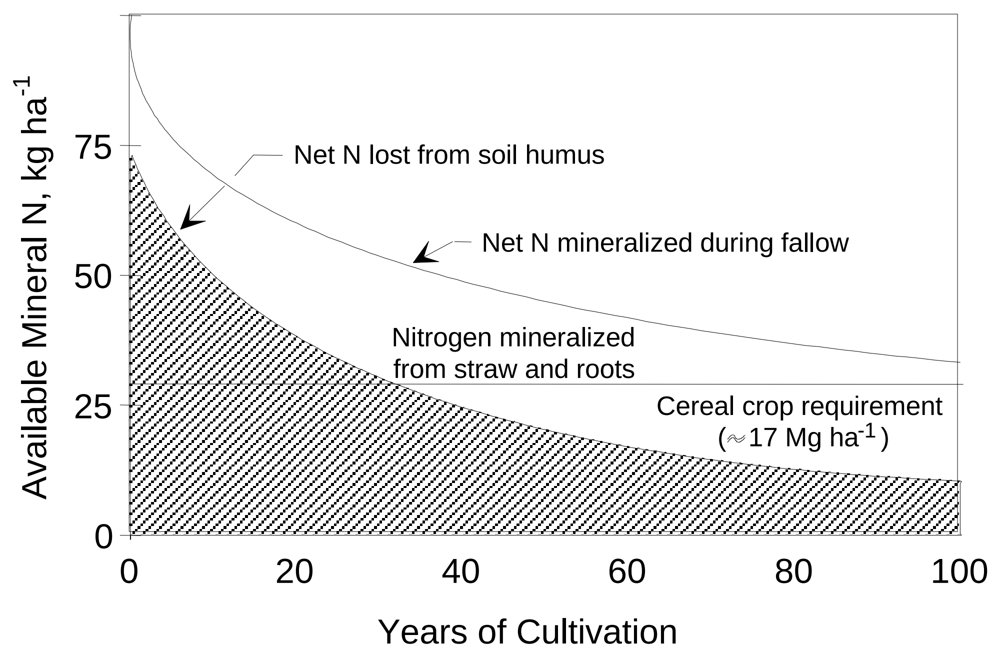


Figure 1.1. Influence of cultivation time on relative mineralization from soil humus and wheat residue. (From Campbell et al. (1976)).

When the reddish prairie soils of Oklahoma were first cultivated in the late 1800s, there was approximately 4.0% soil organic matter in the surface 1 foot of soil. Within that 4.0% organic matter, there were over 8000 lb of N/acre. Following more than 100 years of continuous cultivation, soil organic matter has now declined to less than 1%. Within that 1% organic matter, only 2000 lb of N/acre remains.

N removal in the Check (no fertilization) plot of the Magruder Plots

20 bu/acre * 60 lb/bu * 100 years = 120000lbs
120000 lbs * 2%N in the grain = 2400 lbs N/acre over 100 years
8000 lbs N in the soil (1892)
2000 lbs N in the soil (1992)
2400 lbs N removed in the grain
=3600 lbs N unaccounted

The effects that management systems will have on soil organic matter and the resultant nutrient supplying power of the organic pools are well known. Various management variables and their effect on soil organic matter are listed;

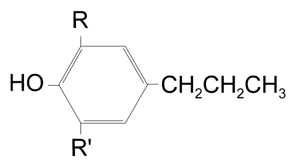
Organic Matter Management	Effect
1) tillage	+/-
conventional	-
zero	+
2) soil drainage	+/-
3) crop residue placement	+/-
4) burning	-
5) use of green manures	+
6) animal wastes and composts	+
7) nutrient management	+/-
excess N	+

Composition of Organic Matter

The living component which includes soil microorganisms and fauna make up a relatively small portion of total soil organic matter (1-8%). It functions however as an important catalyst for transformations of N and other nutrients (Doran and Smith, 1987). The majority of soil organic matter is contained in the nonliving component that includes plant, animal and microbial debris and soil humus.

Common components of soil organic matter and their relative rates of decay are listed in Table 1.1. Cellulose generally accounts for the largest proportion of fresh organic material. It generally decays rather rapidly, however, the presence of N is needed in order for this to take place. Lignin components decompose much more slowly and thus, any nutrients bound in lignin forms will not become available for plant growth. Although lignin is insoluble in hot water and neutral organic solvents, it can be solubilized in alkali solutions. Because of this, we seldom find calcareous soils with extremely high organic matter. All of the polysaccharides decompose rapidly in soils and thus serve as an immediate source of C for microorganisms. Decomposition of these respective components is illustrated in Figure 1.2.

Table 1.1. Components of soil organic matter, rate of decomposition and composition of each fraction.

Form	Formula	Decomposition	Composition
Cellulose	**$(C_6H_{10}O_5)n$**	**rapid ***	**15-50%**
Hemicellulose			**5-35%**
glucose	**$C_6H_{12}O_6$**	**moderate-slow**	
galactose			
mannose			
xylose	**$C_5H_{10}O_5$**	**moderate-slow**	
Lignin(phenyl-propane)		**slow**	**15-35%**
Crude Protein	**$RCHNH_2COOH$****	**rapid**	**1-10%**
Polysaccharides			
Chitin	**$(C_6H_9O_4 \cdot NHCOCH_3)n$**	**rapid**	
Starch	**glucose chain**	**rapid**	
Pectins	**galacturonic acid**	**rapid**	
Inulin	**fructose units**		

*** - decomposition more rapid in the presence of N**
**** - amino acid glycine (one of many building blocks for proteins)**

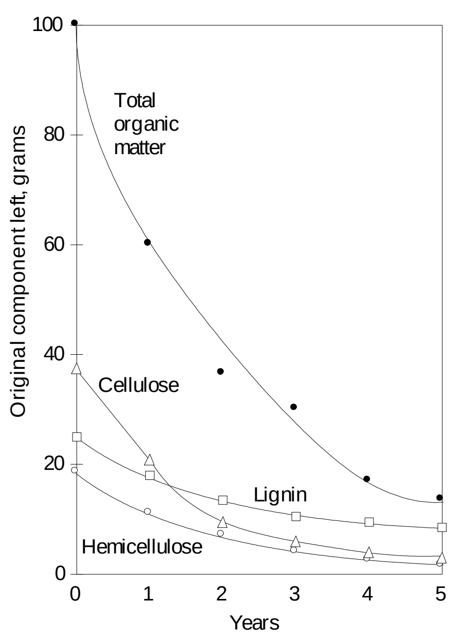


Figure 1.2. Decomposition of Miscanthus sinensis leaf litter.

Table 1.2. Composition of mature cornstalks (*Zea mays* L.) initially and after 205 days of incubation with a mixed soil microflora, in the presence and absence of added nutrients (Tenney and Waksman, 1929)

Constituents or fraction	Initial composition %	Composition after 205 days (%) No nutrients added	Nutrients added
Ether and alcohol soluble	6	1	<1
Cold water soluble	11	3	4
Hot water soluble	4	4	5
Hemicelluloses	18	15	11
Cellulose	30	13	6
Lignins	11	23	24
Crude protein	2	9	11
Ash	7	19	26

The composition of mature cornstalks before and after 205 days of incubation with a mixed soil in the presence and absence of added nutrients is listed in Table 1.2. As decomposition proceeds, the water soluble fraction (sugars, starch, organic acids, pectins and tannins and array of nitrogen compounds) is readily utilized by the microflora (Parr and Papendick, 1978). Ether and alcohol-soluble fractions (fats, waxes, resins, oils), hemicelluloses and cellulose decrease with time as they are utilized as carbon and energy sources. Lignin, tends to persist and accumulate in the decaying biomass because of its resistance to microbial decomposition. Decomposition rates of crop residues are often proportional to their lignin content and some researchers have suggested that the lignin content may be a more reliable parameter for predicting residue decomposition rates than the C:N ratio (Alexander, 1977). Vigil and Kissel (1991) included the lignin-to-N ratio and total soil N concentration (in g/kg) as independent variables to predict potential N mineralization in soil. They also noted that the break point between net N mineralization and net immobilization was calculated to be at a C/N ratio of 40.

A simple illustration of the carbon cycle is found in Figure 1.3. The carbon cycle revolves around CO_2, its fixation and regeneration. Chlorophyll-containing plants utilize the gas as their sole carbon source and the carbonaceous matter synthesized serves to supply the animal world with preformed organic carbon. Upon the death of the plant or animal, microbial metabolism assumes the dominant role in the cyclic sequence (Alexander, 1977). Without the microbial pool, more carbon would be fixed than is released, CO_2 concentrations in the atmosphere would decrease and photosynthesis rates would decrease.

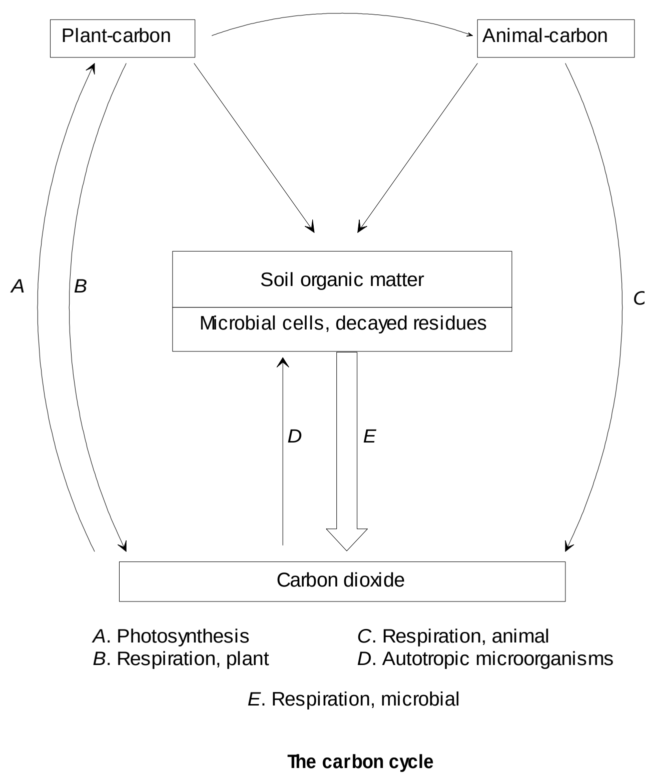


Figure 1.3. Simple illustration of the carbon cycle (from Alexander, 1977). "Higher plants use light to convert water (H_2O) and carbon dioxide (CO_2) to glucose ($C_6H_{12}O_6$) and oxygen (O_2)."

C:N Ratios as Related to Organic Matter Decomposition

In general, the following C:N ratios are considered to be a general rule of thumb in terms of what is expected for immobilization and mineralization.

C:N Ratio	Effect
30:1	immobilization
<20:1	mineralization
20-30:1	immobilization = mineralization

Unfortunately, C:N ratios say nothing about the availability of carbon or nitrogen to microorganisms. The reason for this is because we are not aware of what makes up the carbon (C) component. In tropical soils, significantly higher proportions of lignin will be present in the organic matter. Even though the percent N within the organic matter may be the same, it would be present in highly stable forms that were resistant to decomposition. Therefore, mineralization rates in organic matter that contain high proportions of lignin will be much smaller. The C:N ratios discussed were generally developed from data obtained in temperate climates. Therefore their applicability to tropical soils is at best minimal.

Decomposition of Organic Matter (Mineralization)

1. percent organic matter
2. organic matter composition
3. cultivation (crop, tillage, burning)
4. climate (moisture, temperature)
5. soil pH
6. N management (fertilization)
7. soil aeration

During the initial stages of decomposition of fresh organic material there is a rapid increase in the number of heterotrophic organisms accompanied by the evolution of large amounts of carbon dioxide. If the C:N ratio of the fresh material is wide, there will be a net N immobilization. As decay proceeds, the C:N ratio narrows and the energy supply of carbon diminishes.

The addition of materials that contain more than 1.5 to 1.7% N would ordinarily need no supplemental fertilizer N or soil N to meet the demands of the microorganisms during decomposition (Parr and Papendick, 1978). Note that the 'demands of the microorganisms' is what is discussed first, with no regard as to what plant N needs might be. The addition of large amounts of oxidizable carbon from residues with less than 1.5% N creates a microbiological demand for N which can immobilize residue N and available inorganic soil N for extended periods. The addition of supplemental inorganic fertilizer N to low N residues can accelerate their rate of decomposition (Parr and Papendick, 1978).

In the thousands of years prior to the time cultivation was initiated, C and N had built up in native prairie soils. However, the C:N ratio was wide, reflecting conditions for immobilization of N. The combined influence of tillage and the application of additional organic materials (easily decomposable wheat straw and/or corn stalks) is illustrated in Figure 1.4. Cultivation alone unleashed a radical decomposition of the 4% organic matter in Oklahoma soils. When easily decomposable organic materials are added back to a cultivated soil, CO_2 evolution increases and NO_3 is initially immobilized. However, within one yearly cycle in a temperate climate, the net increase in NO_3 is reflected in Figure 1.4 via mineralization of the freshly added straw/stalks and native organic matter pools. With time, the percent N in added organic material increases while the C:N ratio decreases (Figure 1.5). However, it is important to note that in order for this to happen, some form of carbon must be lost from the system. In this case CO_2 is being evolved via the microbial decomposition of organic matter.

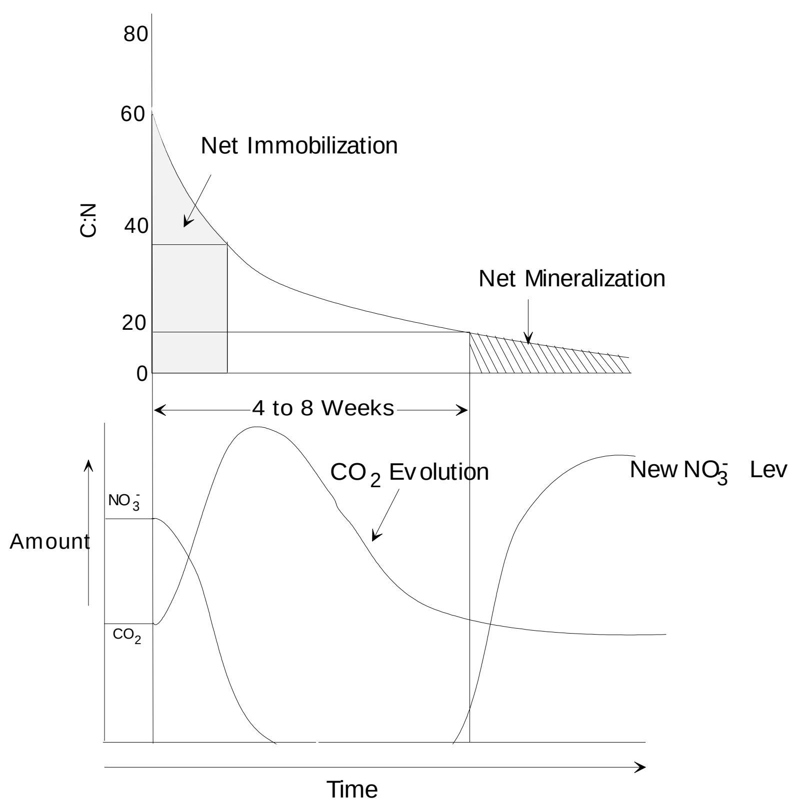


Figure 1.4. Effect of cultivation and addition of straw materials on immobilization and mineralization of N and associated evolution of CO_2

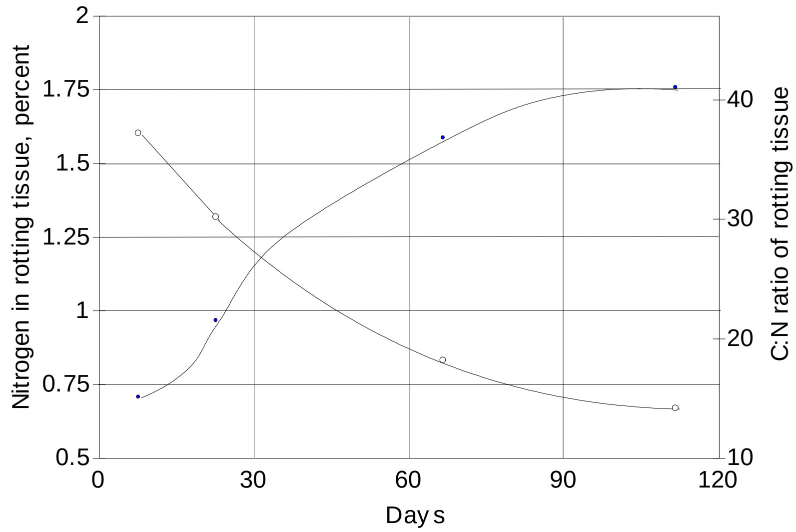


Figure 1.5. Changes in the nitrogen content of decomposing barley straw (From Alexander, 1977).

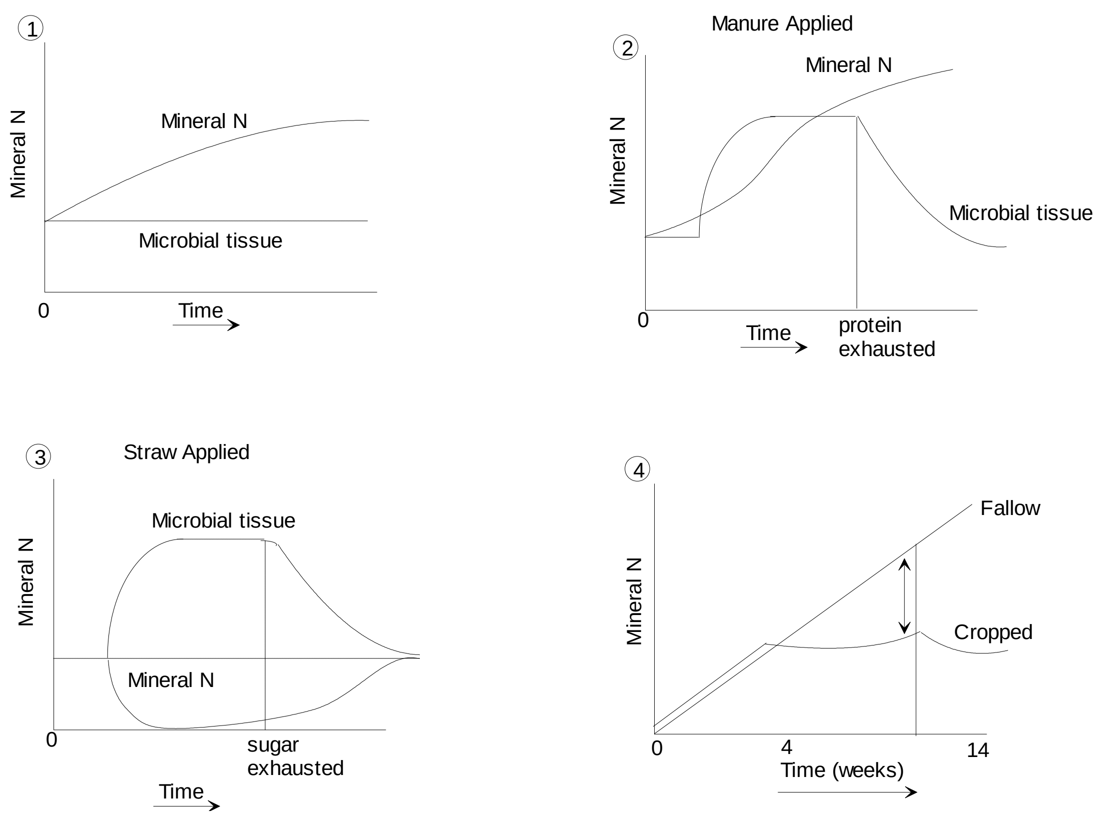


Figure 1.6. Changes in soil mineral N as a function of time, and addition of manure and straw.

Table 1.2. Example calculations of total N in organic matter fractions in soils and expected amounts of N mineralized on a yearly basis.

	Oklahoma		Tropical Soil	
	min	max	min	max
Organic Matter, %	1	2	4	12
1 ha (0-15cm), kg	2241653	2241653	2241653	2241653 (P_b = 1.47)
Organic, matter, kg	22416	44833	89666	268998
% N in OM (5%)	0.05	0.05	0.05	0.05
kg N in OM (Total)	1120.8	2241.6	4483.3	13449.9
% N mineralized/yr (3%)	0.03	0.03	0.03	0.03
TOTAL (kg N/ha/yr)	33.6	67.2	134.4 ?	403.5 ?

D_B= Mass of dry soil/volume of solids and voids

2000000 pounds/afs
ft^3*0.02832 = m^3
0.4535 lb/kg
1 ha = 2.471ac
1 ha = 10000m^2
1 ac = 4047m^2

2000000 lb = 907184.74 kg = 907.184 Mg
43560 ft^2 * 0.5 ft = 21780 ft^3 = 616.80m^3

907.184Mg/616.80m^3 = D_B 1.4707

10000m^2 * 0.15m = 1500 m^3
2241653 kg /1000 = 2241.6 Mg
2241.6/1500 = D_B 1.49 (g/cm^3 = Mg/m^3)

What will happen if
- **a) bulk density is changed?**
- **b) % N in organic matter?**
- **c) % N mineralized per year?**

Organic Matter = 0.35 + 1.80 * (organic carbon) Ranney (1969)

Microorganisms

The most important function of the microbial flora is usually considered to be the breakdown of organic materials, a process by which the limited supply of CO_2 available for photosynthesis is replenished (Alexander, 1977).

Five major groups of microorganisms in the soil are:

1. Bacteria
2. Actinomycetes
3. Fungi
4. Algae
5. Protozoa

Soil Bacteria: 10^8 to 10^{10} / g of soil

Heterotroph: (chemoorganotrophic) require preformed organic nutrients to serve as sources of energy and carbon.

1. Fungi
2. Protozoa
3. Most Bacteria

Autotroph: (lithotrophic) obtain their energy from sunlight or by the oxidation of inorganic compounds and their carbon by the assimilation of CO_2.

Photoautotroph: energy derived from sunlight

1. Algae (blue-green, cyanobacteria)
2. Higher Plants
3. Some Bacteria

Chemoautotroph: energy for growth obtained by the oxidation of inorganic materials.

1. Few Bacterial species (agronomic importance)
   a. nitrobacter, nitrosomonas and thiobacillus

2. ESSENTIAL ELEMENTS

Arnon's Criteria of Essentiality

1. Element required to complete life cycle.
2. Deficiency can only be corrected by the ion in question.
3. Element needs to be directly involved in the nutrition of the plant and not indirectly via the need of another organism.

Any mineral element that functions in plant metabolism, whether or not its action is specific (Tisdale et al., 1985).

C, H, O, N, P, and S (constituent of proteins)
Ca, Mg, K, Fe, Mn, Mo, Cu, B, Zn, Cl, Na, Co, V, Si (essential to one or more plants)

'CHOPKNS CaFe MgB Mn Cl CuZn Mo'

Mobile Nutrients

A. Plant
   1. deficiency symptoms appear in the lower older leaves
B. Soil
   1. can be taken up from a large volume of soil

Immobile Nutrients

A. Plant
   1. deficiency symptoms appear in the upper younger leaves
B. Soil
   1. taken up from a small volume of soil

Deficiency Symptom	Element	Mobility Soil	Mobility Plant	Form taken up by Plants
overall chlorosis seen first on lower leaves	N Nitrogen	Yes	Yes	NO_3^-,NO_2^-,NH_4^+
purple leaf margins	P Phosphorus	No	Yes	$HPO_4^=$,$H_2PO_4^-$,H_3PO_4
chlorotic leaf margins	K Potassium	No	Yes	K^+
uniform chlorosis, stunting (younger leaves)	S Sulfur	Yes	Yes(no) N*S interaction	$SO_4^=$,SO_2^*
stunting - no root elongation	Ca Calcium	No	No	Ca^{++}
interveinal chlorosis, veins remain green	Fe Iron	No (ls)	No	Fe^{+++},Fe^{++}
interveinal chlorosis	Mg Magnesium	No (ls)	Yes/No	Mg^{++}
reduced terminal growth = chlorotic tips	B Boron (NM)	Yes	No	$H_3BO_3^\circ$
interveinal chlorosis	Mn Manganese	No	No	Mn^{++}, Mn^{+++}
wilting, chlorosis, reduced root growth	Cl Chlorine	Yes	Yes	Cl^-
young leaves, yellow & stunted	Cu Copper	No (ls)	No	Cu^{++}
interveinal chlorosis in young leaves	Zn Zinc	No (ls)	No	Zn^{++}
interveinal chlorosis, stunting	Mo Molybdenum	Yes/No(ls)	No	$MoO_4^=$
dark green color	Na Sodium	No(ls)	Yes	Na^+
	C Carbon			CO_2
	H Hydrogen			H_2O
	O Oxygen			H_2O

* absorbed through plant leaves
(NM) Non Metal
(ls) Low Solubility

Mo availability increases with soil pH, other micronutrients show the opposite of this.
Immobile nutrients in plant; symptoms of deficiency show up in the younger leaves.
Stage of growth when deficiency symptom is apparent = later stage

3. THE NITROGEN CYCLE

NITROGEN:

- Key building block of the protein molecule upon which all life is based
- Indispensable component of the protoplasm of plants animals and microorganisms
- One of the few soil nutrients lost by volatilization and leaching, thus requiring continued conservation and maintenance
- Most frequently deficient nutrient in crop production

Nitrogen Ion/Molecule Oxidation States

Nitrogen ions and molecules that are of interest in soil fertility and plant nutrition cover a range of N apparent oxidation states from -3 to +5. It is most convenient to illustrate these oxidation states using common combinations of N with H and O, because H can be assumed in the +1 oxidation state (H^{+1}) and O in the -2 oxidation state ($O^{=}$). The apparent N oxidation state, and the electron configurations involved may be depicted as follows.

Hydrogen:

The electron configuration in the ground state is 1s1 (the first electron shell has only one electron in it), as found in H_2 gas. Since the s shell can hold only two electrons, the atom would be most stable by either gaining another electron or losing the existing one. Gaining an electron by sharing occurs in H_2, where each H atom gains an electron from the other resulting in a pair of electrons being shared. The electron configuration about the atom, where: represent a pair of electrons, may be shown as

H:H and the bond may be shown as H-H

Hydrogen most commonly exists in ionic form and in combination with other elements where it has lost its single electron. Thus it is present as the H^+ ion or brings a + charge to the molecule formed by combining with other elements.

Oxygen:

The ground state of O, having a total of eight electrons is 1s2, 2s2, 2p4. Both s orbitals are filled, each with two electrons. The 2p outer or valence orbital capable of holding six electrons, has only four electrons, leaving opportunity to gain two. The common gain of two electrons from some other element results in a valence of -2 for O ($O^{=}$). The gain of two electrons also occurs in O_2 gas, where two pairs of electrons are shared as

O::O and the double bond may be shown as O=O

Nitrogen:

The ground state of N is 1s2, 2s2, 2p3. It is very similar to that for oxygen, except there is one less electron in the valence 2p orbital. Hence, the 2p orbital contains three electrons but, has room to accept three electrons to fill the shell. Under normal conditions, electron loss to form N^{+}, N^{2+} or N^{3+} or electron gain to form N^{-}, N^{2-}, or N^{3-} should not be expected. Instead, N will normally fill its 2p orbital by sharing electrons with other elements to which it is chemically (covalent) bound. Nitrogen can fill the 2p orbital by forming three covalent bonds with itself as in the very stable gas N_2.

The Nitrogen cycle is not well understood, largely because of how it is communicated. Similar to the way we communicate the differences between normal, saline, sodic and saline-sodic soils, we should do the same for response variables in the Nitrogen cycle. In addition to temperature and pH included below, we could add reduction/oxidation, tillage (zero vs. conventional), C:N ratios, fertilizer source and a number of other variables. These mechanistic models would ultimately lead to many 'if-then' statements/decisions that could be used within a management strategy.

>50F	denitrification	volatilization
<50F	leaching	leaching

7.0

Soil pH

Assuming that we could speed up the nitrogen cycle what would you change?

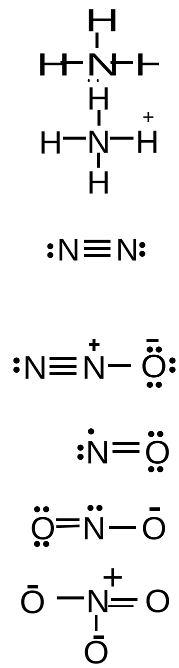
1. Aerated environment (need for O_2)
2. Supply of ammonium
3. Moisture
4. Temperature (30-35C or 86-95F) <10C or 50F
5. Soil pH
6. Addition of low C:N ratio materials (low lignin)

Is oxygen required for nitrification?
Does nitrification proceed during the growing cycle? (low C:N ratio)

N Oxidation States:

oxidized: loses electrons, takes on a positive charge
reduced: gains electrons, takes on a negative charge

Ion/molecule	Name	Oxidation State
NH_3	ammonia	-3
NH_4^+	ammonium	-3
N_2	diatomic N	0
N_2O	nitrous oxide	+1
NO	nitric oxide	+2
NO_2^-	nitrite	+3
NO_3^-	nitrate	+5
H_2S	hydrogen sulfide	-2
$SO_4^=$	sulfate	+6



N: 5 electrons in the outer shell

- loses 5 electrons (+5 oxidation state NO_3)
- gains 3 electrons (-3 oxidation state NH_3)

O: 6 electrons in the outer shell

- is always being reduced (gains 2 electrons to fill the outer shell)

H: 1 electron in the outer shell

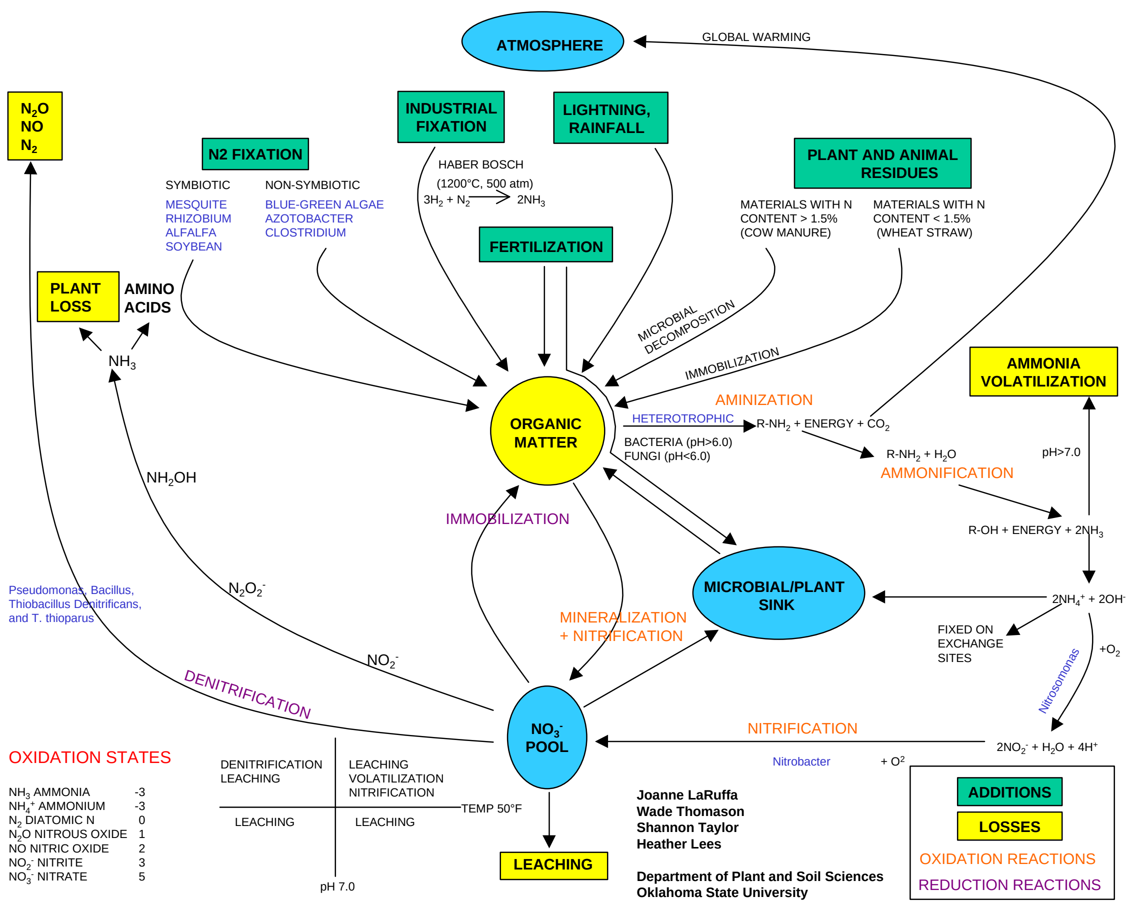
N is losing electrons to O because O is more electronegative
N gains electrons from H because H wants to give up electrons

N recommendations

1. Yield goal (2lb N/bu)
   a. Applies fertilization risk on the farmer
   b. Removes our inability to predict 'environment' (rainfall)
2. Soil test
   a. For every 1 ppm NO_3, N recommendation reduced by 2lbN/ac

Nitrite accumulation?

1. high pH
2. high NH_4 levels (NH_4 inhibits nitrobacter)

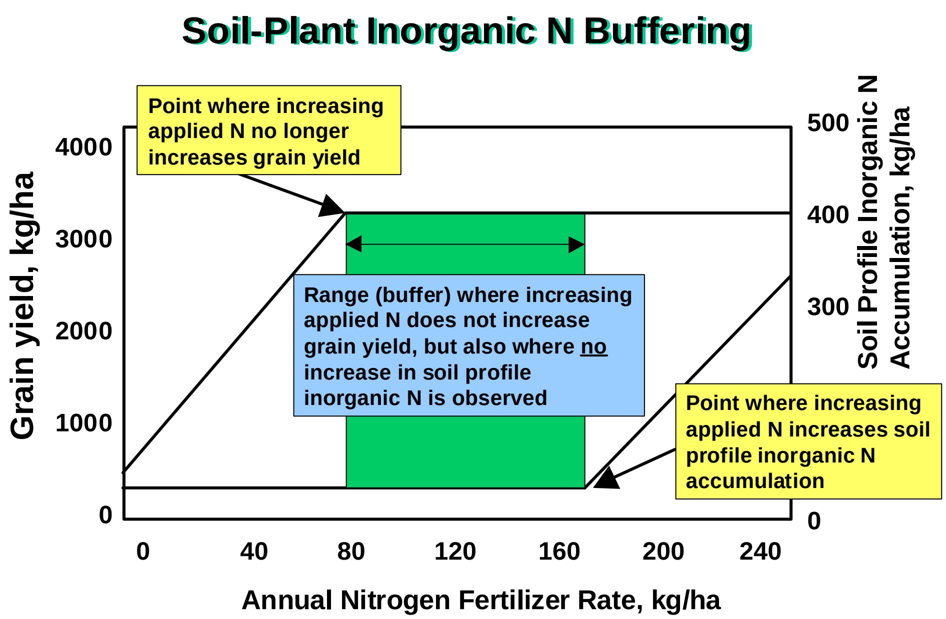


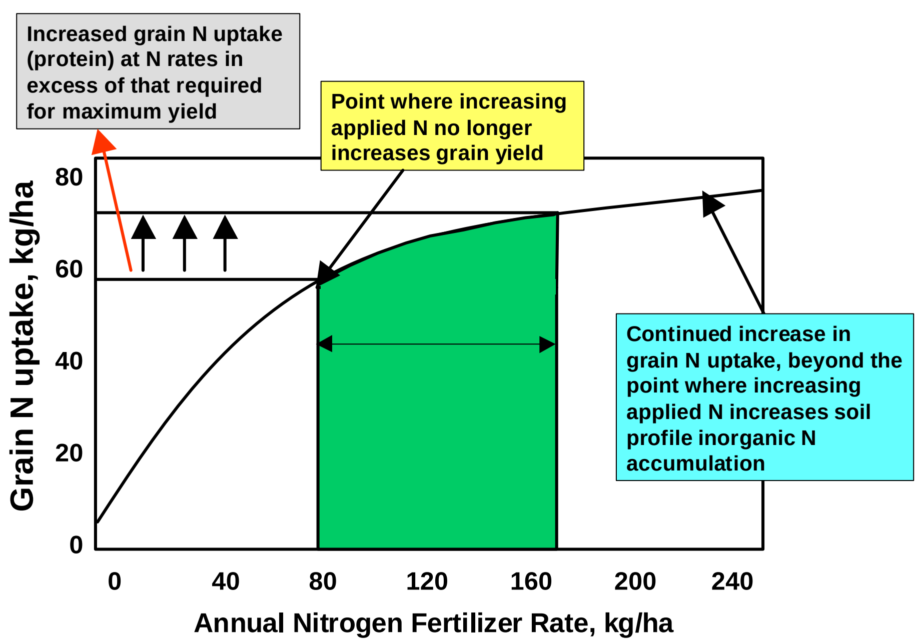
NITROGEN CYCLE

Inorganic Nitrogen Buffering

Inorganic nitrogen buffering is defined as the ability of the soil-plant system to control the amount of inorganic N accumulation in the rooting profile when N fertilization rates exceed that required for maximum yield.

If N rates required to detect soil profile NO_3 accumulation always exceeded that required for maximum yields, what biological mechanisms are present that cause excess N applied to be lost via other pathways prior to leaching?





Nitrogen Buffering Mechanisms

1. Increased Applied N results in increased plant N loss (NH_3)
2. Higher rates of applied N - increased volatilization losses
3. Higher rates of applied N - increased denitrification
4. Higher rates of applied N - increased organic C, -- increased N in organic pools
5. Increased applied N - increased grain protein
6. Increased applied N - increased forage N
7. Increased applied N - increased straw N

Ammonia Volatilization

· Urease activity
· Temperature
· CEC (less when high)
· H buffering capacity of the soil
· Soil Water Content
· Air Exchange
· N Source and Rate
· Application method
· Crop Residues

$NH_4^+ \leftrightarrow NH_3 + H^+$

If pH and temperature can be kept low, little potential exists for NH_3 volatilization. At pH 7.5, less than 7% of the ammoniacal N is actually in the form of NH_3 over the range of temperatures likely for field conditions.

Chemical Equilibria

A+B $\leftrightarrow$ AB
Kf = AB/A x B
AB $\leftrightarrow$ A+B
Kd = A x B/AB
Kf = 1/Kd (relationship between formation and dissociation constants)

Formation constant (Log K°) relating two species is numerically equal to the pH at which the reacting species have equal activities (dilute solutions).

pKa and Log K° are sometimes synonymous

Henderson-Hasselbalch
pH = pKa + log [(base)/(acid)]

when (base) = (acid), pH = pKa

Urea

- Urea is the most important solid fertilizer in the world today.
- In the early 1960's, ammonium sulfate was the primary N product in world trade (Bock and Kissel, 1988).
- The majority of all urea production in the U.S. takes place in Louisiana, Alaska and Oklahoma.
- Since 1968, direct application of anhydrous ammonia has ranged from 37 to 40% of total N use (Bock and Kissel, 1988).
- Urea: high analysis, safety, economy of production, transport and distribution make it a leader in world N trade.
- In 1978, developed countries accounted for 44% of the world N market (Bock and Kissel, 1988).
- By 1987, developed countries accounted for less than 33%.

Share of world N consumption by product group

	1970	1986
Ammonium sulfate	8	5
Ammonium nitrate	27	15
Urea	**9**	**37**
Ammonium phosphates	1	5
Other N products (NH_3)	36	29
Other complex N products	16	8

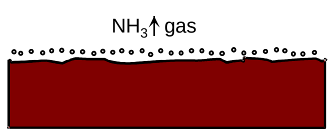
Urea Hydrolysis

increase pH (less H^+ ions in soil solution)

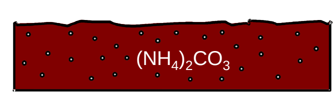
$CO(NH_2)_2 + H^+ + 2H_2O$ --------> $2NH_4^+ + HCO_3^-$
pH 6.5 to 8
$HCO_3^- + H^+$ ---> $CO_2 + H_2O$ (added H lost from soil solution)

$CO(NH_2)_2 + 2H^+ + 2H_2O$ --------> $2NH_4^+ + H_2CO_3$ (carbonic acid)
pH <6.3

1. Urea Fertilizer Broadcast



2. Urea Fertilizer Incorporated



$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3$
urea, water, ammonium carbonate

1. $(NH_4)_2CO_3 + H_2O \rightleftharpoons 2NH_3\uparrow + 2H_2O + CO_2\uparrow$
ammonium carbonate, water, ammonia, water, carbon dioxide

2. $(NH_4)_2CO_3 + Ca\text{-}X \rightarrow 2NH_4OH + CaCO_3$
ammonium carbonate, soil calcium, ammonium hydroxide, calcium carbonate

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
ammonium hydroxide, ammonium, hydroxide

Potential for gaseous loss from applied urea, both broadcast and incorporated.

During hydrolysis, soil pH can increase to >7 because the reaction requires H^+ from the soil system.

(How many moles of H^+ are consumed for each mole of urea hydrolyzed?) 2

In alkaline soils less H^+ is initially needed to drive urea hydrolysis on a soil already having low H^+.

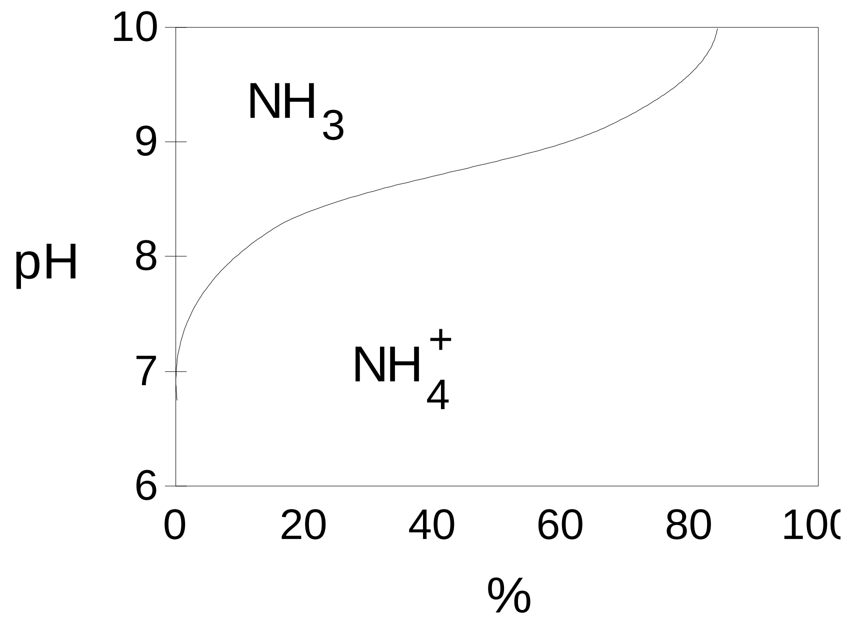
In an alkaline soil, removing more H^+(from a soil solution already low in H^+), can increase pH even higher

$NH_4^+ + OH^-$ ---> NH_4OH ---->$NH_3 + H_2O$

pH = pKa + log [(base)/(acid)]

At a pH of 9.3 (pKa 9.3) 50% NH_4 and 50% NH_3

pH	Base (NH_3)	Acid (NH_4)
7.3	1	99
8.3	10	90
9.3	50	50
10.3	90	10
11.3	99	1



Equilibrium relationship for ammoniacal N and resultant amount of NH_3 and NH_4 as affected by pH for a dilute solution.

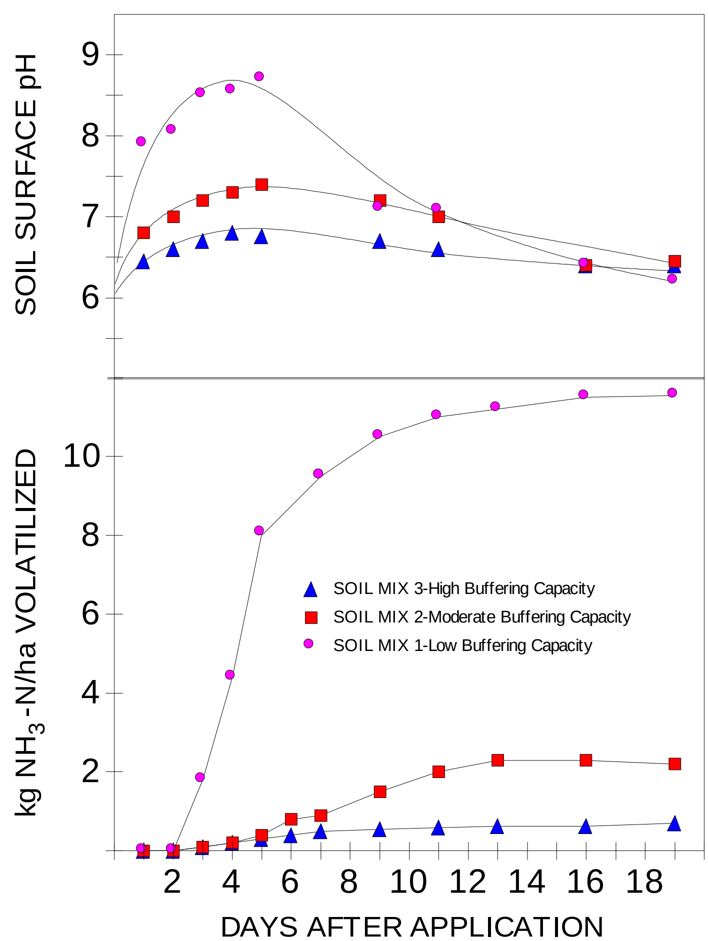
As the pH increases from urea hydrolysis, negative charges become available for NH_4^+ adsorption because of the release of H^+ (Koelliker and Kissel)

Decrease NH_3 loss with increasing CEC (Fenn and Kissel, 1976) assuming increase pH = increase CEC, what is happening?

In acid soils, the exchange of NH_4^+ is for H^+ on the exchange complex (release of H here, resists change in pH, e.g. going up)

In alkaline soils with high CEC, NH_4 exchanges for Ca, precipitation of $CaCO_3$ ($CO_3^=$ from HCO_3^- above) and one H^+ released which helps resist the increase in pH

However, pH was already high.



Soil surface pH and cumulative NH_3 loss as influenced by pH buffering capacity (from Ferguson et al., 1984).

Ernst and Massey (1960) found increased NH_3 volatilization when liming a silt loam soil. The effective CEC would have been increased by liming but the rise in soil pH decreased the soils ability to supply H^+

Rapid urea hydrolysis: greater potential for NH_3 loss. Why?
management: dry soil surface, incorporate, localized placement- slows urea hydrolysis

H ion buffering capacity of the soil:

Ferguson et al., 1984
(soils total acidity, comprised of exchangeable acidity + nonexchangeable titratable acidity)

A large component of a soils total acidity is that associated with the layer silicate sesquioxide complex (Al and Fe hydrous oxides). These sesquioxides carry a net positive charge and can hydrolyze to form H^+ which resist an increase in pH upon an addition of a base.

H^+ ion supply comes from:

1. OM
2. hydrolysis of water
3. Al and Fe hydrous oxides
4. high clay content

A soil with an increased H^+ buffering capacity will also show less NH_3 loss when urea is applied without incorporation.

1. hydroxy Al-polymers added (carrying a net positive charge) to increase H^+ buffering capacity.
2. strong acid cation exchange resins added (buffering capacity changed without affecting CEC, e.g. resin was saturated with H^+).

resin: amorphous organic substances (plant secretions), soluble in organic solvents but not in water (used in plastics, inks)

Consider the following

1. H^+ is required for urea hydrolysis.
2. Ability of a soil to supply H^+ is related to amount of NH_3 loss.
3. H^+ is produced via nitrification (after urea is applied): acidity generated is not beneficial.
4. What could we apply with the urea to reduce NH_3 loss?

an acid; strong electrolyte; dissociates to produce H^+;increased H^+ buffering; decrease pH

reduce NH_3 loss by maintaining a low pH in the vicinity of the fertilizer granule (e.g. H_3PO_4)

Factors Affecting Soil Acidity

Acid: substance that tends to give up protons (H^+) to some other substance
Base: accepts protons
Anion: negatively charged ion
Cation: positively charged ion

Base cation: ? (this has been taught in the past but is not correct)

Electrolyte: nonmetallic electric conductor in which current is carried by the movement of ions

H_2SO_4 (strong electrolyte)
CH_3COOH (weak electrolyte)

$$HA \xrightarrow{H_2O} H^+ + A^-$$

potential acidity → active acidity

1. Nitrogen Fertilization

   A. ammoniacal sources of N

2. Decomposition of organic matter

   OM ------> $R\text{-}NH_2 + CO_2$
   $CO_2 + H_2O$ --------> H_2CO_3 (carbonic acid)
   H_2CO_3 ------> $H^+ + HCO_3^-$ (bicarbonate)

   humus contains reactive carboxylic, phenolic groups that behave as weak acids which dissociate and release H^+

3. Leaching of exchangeable bases/Removal
   Ca, Mg, K and Na (out of the effective root zone)
   -problem in sandy soils with low CEC

a. Replaced first by H and subsequently by Al (Al is one of the most abundant elements in soils. 7.1% by weight of earth's crust)

b. Al displaced from clay minerals, hydrolyzed to hydroxy aluminum complexes

c. Hydrolysis of monomeric forms liberate H^+

d. $Al(H_2O)_6^{+3} + H_2O$ -----> $Al(OH)(H_2O)^{++} + H_2O^+$

monomeric: a chemical compound that can undergo polymerization

polymerization: a chemical reaction in which two or more small molecules combine to form larger molecules that contain repeating structural units of the original molecules

4. Aluminosilicate clays
   Presence of exchangeable Al
   $Al^{+3} + H_2O$ -----> $AlOH^{=} + H^+$

5. Acid Rain

Acidification from N Fertilizers (R.L. Westerman)

1. Assume that the absorbing complex of the soil can be represented by CaX
2. Ca represents various exchangeable bases with which the insoluble anions X are combined in an exchangeable form and that X can only combine with one Ca
3. H_2X refers to dibasic acid (e.g., H_2SO_4)

$(NH_4)_2SO_4$ -----> NH_4^+ to the exchange complex, $SO_4^{=}$ combines with the base on the exchange complex replaced by NH_4^+

Thought: Volatilization losses of N as NH_3 preclude the development of H^+ ions produced via nitrification and would theoretically reduce the total potential development of acidity.

Losses of N via denitrification leave an alkaline residue (OH^-).

Table X. Reaction of N fertilizers when applied to soil.

---

1. Ammonium sulfate
   - **a.** $(NH_4)_2SO_4 + CaX \text{ ---->} \; CaSO_4 + (NH_4)_2X$
   - **b.** $(NH_4)_2X + 4O_2 \xrightarrow{\text{nitrification}} 2HNO_3 + H_2X + 2H_2O$
   - **c.** $2HNO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + H_2X$

     Resultant acidity = $4H^+$ /mole of $(NH_4)_2SO_4$

2. Ammonium nitrate
   - **a.** $2NH_4NO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + (NH_4)_2X$
   - **b.** $(NH_4)_2X + 4O_2 \xrightarrow{\text{nitrification}} 2HNO_3 + H_2X + 2H_2O$
   - **c.** $2HNO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + H_2X$

     Resultant acidity = 2H+ /mole of NH_4NO_3

3. Urea
   - **a.** $CO(NH_2)_2 + 2H_2O \text{ ---->} \; (NH_4)_2CO_3$
   - **b.** $(NH_4)_2CO_3 + CaX \text{ ---->} \; (NH_4)_2X + CaCO_3$
   - **c.** $(NH_4)_2X + 4O_2 \xrightarrow{\text{nitrification}} 2HNO_3 + H_2X + 2H_2O$
   - **d.** $2HNO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + H_2X$
   - **e.** $H_2X + CaCO_3 \xrightarrow{\text{neutralization}} CaX + H_2O + CO_2$

     Resultant acidity = $2H^+$ /mole of $CO(NH_2)_2$

4. Anhydrous Ammonia
   - **a.** $2NH_3 + 2H_2O \text{ ---->} \; 2NH_4OH$
   - **b.** $2NH_4OH + CaX \text{ ---->} \; Ca(OH)_2 + (NH_4)_2X$
   - **c.** $(NH_4)_2X + 4O_2 \xrightarrow{\text{nitrification}} 2HNO_3 + H_2X + 2H_2O$
   - **d.** $2HNO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + H_2X$
   - **e.** $H_2X + Ca(OH)_2 \xrightarrow{\text{neutralization}} CaX + 2H_2O$

     Resultant acidity = 1H+/mole of NH_3

5. Aqua Ammonia
   - **a.** $2NH_4ON + CaX \text{ ---->} \; Ca(OH)_2 + (NH_4)_2X$
   - **b.** $(NH_4)_2X + 4O_2 \xrightarrow{\text{nitrification}} 2HNO_3 + H_2X + 2H_2O$
   - **c.** $2HNO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + H_2X$
   - **d.** $H_2X + Ca(OH)_2 \xrightarrow{\text{neutralization}} CaX + 2H_2O$

     Resultant acidity = 1H+/mole of NH_4OH

6. Ammonium Phosphate
   - **a.** $2NH_4H_2PO_4 + CaX \text{ ---->} \; Ca(H_2PO_4)_2 + (NH_4)_2X$
   - **b.** $(NH_4)_2X + 4O_2 \xrightarrow{\text{nitrification}} 2HNO_3 + H_2X + 2H_2O$
   - **c.** $2HNO_3 + CaX \text{ ---->} \; Ca(NO_3)_2 + H_2X$

     Resultant acidity = 2H+/mole of $NH_4H_2PO_4$

---

4. NITROGEN USE EFFICIENCY

In grain production systems, N use efficiency seldom exceeds 50 percent. Variables which influence N use efficiency include

a. Variety
b. N source
c. N application method
d. Time of N application
e. Tillage
f. N rate (generally decreases with increasing N applied)
g. Production system

   1. Forage
   2. Grain

Olson and Swallow, 1984 (27-33% of the applied N fertilizer was removed by the grain following 5 years)

h. Plant N loss
i. Soil type (organic matter)

Calculating N Use Efficiency using **<u>The Difference Method</u>**

Applied N kg/ha	Grain Yield kg/ha	N content %	N uptake kg/ha	Fertilizer Recovery %
0	1000	2.0	20	-
50	1300	2.1	27.3	(27.3-20)/50=14.6
100	2000	2.2	44	(44-20)/100=24
150	2000	2.3	46	(46-20)/150=17

Estimated N use efficiency for grain production systems ranges between 20 and 50%. The example above does not include straw, therefore, recovery levels are lower. However, further analysis of forage production systems (Altom et al., 1996) demonstrates that N use efficiency can be as high as 60-70%. This is largely because the plant is harvested prior to flowering thus minimizing the potential for plant N loss. Plant N loss is known to be greater when the plant is at flowering and approaching maturity. It is important to observe that estimated N use efficiencies in forage production systems do not decrease with increasing N applied as is normally found in grain production systems. This is suggestive of 'buffering' whereby increased N is lost at higher rates of applied N in grain production systems, but which cannot take place in forage production systems.

Work by Moll et al. (1982) suggested the presence of two primary components of N use efficiency: (1) the efficiency of absorption or uptake (Nt/Ns), and (2) the efficiency with which the N absorbed is utilized to produce grain (Gw/Nt) where Nt is the total N in the plant at maturity (grain + stover), Ns is the nitrogen supply or rate of fertilizer N and Gw is the grain weight, all expressed in the same units. Other parameters defined in their work and modifications (in italics) are reported in Table 4.2.

Recent understanding of plant N loss has required consideration of additional parameters not discussed in Moll et al. (1982). Harper et al. (1987) documented that N was lost as volatile NH_3 from wheat plants after fertilizer application and during flowering. Maximum N accumulation has been found to occur at or near flowering in wheat and corn and not at harvest. In order to estimate plant N loss without the use of labeled N forms, the stage of growth where maximum N accumulation is known to occur needs to be identified. The amount of N remaining in the grain + straw or stover, is subtracted from the amount at maximum N accumulation to estimate potential plant N loss (difference method). However, even the use of difference methods for estimating plant N loss are flawed since continued uptake is known to take place beyond flowering or the point of maximum N accumulation.

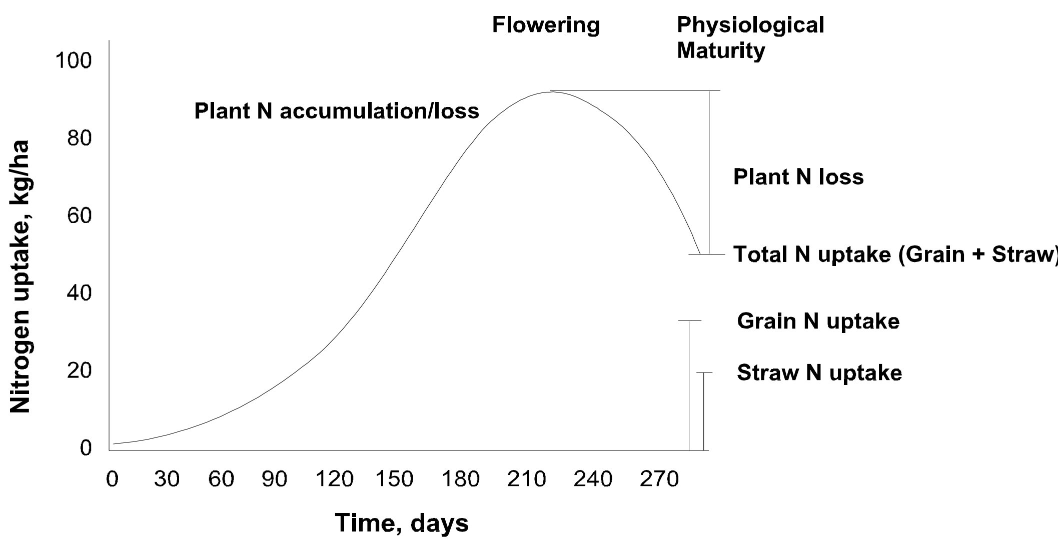


Figure 4.1 Total N uptake in winter wheat with time and estimated loss following flowering.

Francis et al. (1993) recently documented that plant N losses could account for as much as 73% of the unaccounted-for N in ^{15}N balance calculations. They further noted that gaseous plant N losses could be greater when N supply was increased. Similar to work by Kanampiu et al. (1997) with winter wheat, Francis et al. (1993) found that maximum N accumulation in corn occurred soon after flowering (R3 stage of growth). In addition, Francis et al. (1993) highlighted the importance of plant N loss on the development and interpretations of strategies to improve N fertilizer use efficiencies.

Consistent with work by Kanampiu et al. (1997), and Daigger et al. (1976), Figure 4.1 illustrates winter wheat N accumulation over time. Estimates of plant N loss are reported in Table 4.1. Harper et al. (1987) reported that 21% of the applied N fertilizer was lost as volatile NH_3 in wheat, of which 11.4% was from both the soil and plants soon after fertilization and 9.8% from the leaves of wheat between anthesis and physiological maturity. Francis et al. (1993) summarized that failure to include direct plant N losses when calculating an N budget leads to overestimation of N loss from the soil by denitrification, leaching and ammonia volatilization.

$$NO_3^- + 2e \xrightarrow[\text{(nitrate reductase)}]{} NO_2^- + 6e \xrightarrow[\text{(nitrite reductase)}]{} NH_4^+$$

Reduction of NO_3^- to NO_2^- is the rate-limiting step in the transformation of N into amino forms.

Does the plant wake up in the morning and turn on the TV to check the weather forecast, to see if it should assimilate NO_3 and attempt to form amino acids?

Could we look at the forecast and attempt to communicate with the plant, letting it know that weather conditions will be good (or bad), thus proceeding with increased NO_3 uptake?

Major pathways for assimilation of NH_3

1. Incorporation into glutamic acid to form glutamine, a reaction catalyzed by glutamine synthetase (Olson and Kurtz, 1982)
2. Reaction of NH_3 and CO_2 to form carbamyl phosphate, which in turn is converted to the amino acid arginine.
3. Biosynthesis of amides by combination of NH_3 with an amino acid. In this way aspartic acid is converted to the amide, asparagine.

Table 4.1. Means over N rate and variety for protein, NUE components and estimated plant N loss, Perkins, OK 1995 (from Kanampiu et al., 1997)

	Protein %	N-use efficiency (Gw/Ns)	Uptake efficiency (Nt/ Ns)	N-utilization efficiency (Gw/Nt)	Fraction of N translocated to grain(Ng/Nt)	Grain yield/ grain N (Gw/Ng)	N loss (kg ha^{-1}) (Nf-(Ng+Nst)
N rate, kg ha^{-1}				means			
0	14.8	0	0	23.2	0.60	38.8	16.4
45	15.9	23.3	1.0	22.9	0.63	36.5	25.0
90	17.4	11.0	0.6	20.2	0.61	33.2	25.8
180	17.6	7.0	0.4	20.5	0.62	33.5	31.4
SED	0.40	1.1	0.05	1.12	0.03	0.89	6.74
Variety:							
Chisholm	16.3	11.8	0.5	22.4	0.6	35.3	21.8a
Karl	17.5	13.1	0.6	23.0	0.7	33.0	26.6a
2180	17.4	18.1	0.8	22.7	0.7	33.4	27.9a
TAM W-101	15.5	11.7	0.6	21.4	0.6	37.4	24.7a
Longhorn	15.0	14.7	0.8	19.5	0.5	38.5	22.3a
SED	0.45	1.5	0.07	1.27	0.04	1.18	7.33

The ability of the soil-plant system to efficiently utilize N for food production (grain or forage) can be considered in four aspects: (1) efficiency of the plant to assimilate applied N, (2a and 2b) once assimilated, the ability of the plant to retain and incorporate N into the grain, (3) efficiency of the soil to supply/retain applied N for plant assimilation over long periods of time and (4) composite system efficiency.

Uptake efficiency should be estimated using Nf/Ns (Eup) instead of Nt/Ns (Eha) as proposed by Moll et al. (1982). More N is assimilated at earlier stages of growth, therefore, uptake efficiency should be estimated at the stage of maximum N accumulation and not at maturity when less N can be accounted for. The component Nt/Ns as proposed by Moll et al. would be better defined as harvest uptake efficiency or physiological maturity uptake efficiency. We define uptake efficiency as the stage where maximum N is taken up by the plant divided by the N supplied.

(1) Uptake efficiency Eup=Nf/Ns

Unlike the description by Moll et al. (1982), uptake efficiency should be partitioned into two separate components since plant N loss (from flowering to maturity) can be significant (Daigger et al., 1976; Harper et al., 1987; Francis et al., 1993). The fraction of N translocated to the grain should be estimated as Ng/Nf and not Ng/Nt as proposed by Moll et al. (1982) since more N was accumulated in the plant at an earlier stage of growth (Kanampiu et al., 1997). Plants losing significant quantities of N as NH_3 would have very high fractions of N translocated to the grain when calculated using Nt instead of Nf. In terms of plant breeding efforts, this could be a highly misleading statistic. A second component, the translocation index is proposed that would reflect the ability of a plant genotype or management practice to incorporate N accumulated at flowering into the grain.

(2a) fraction of N translocated to the grain Et=Ng/Nf
(2b) translocation index Eti=Ng/Nf * (1/Nl)

The ability of the soil-plant system to utilize outside sources of N for food production (grain or forage) depends on the efficiency of storage in the soil. The efficiency of the soil to supply N to plants is strongly influenced by immobilization and mineralization with changing climate and environment.

Over a growing season, storage efficiency will be equal to the difference between fertilizer N added (Ns) minus maximum plant uptake (Nf) plus the difference between total soil N at the beginning and end of the season, all divided by fertilizer N added.

Esg = [(Ns-Nf)-(St1-St2)]/Ns

(3) soil (management system) supply efficiency Es=Ns/(Sv+Sd+Sl) where Sv, Sd and Sl are estimates of soil volatilization, denitrification and leaching losses from the soil, respectively.

Lastly, a composite estimate of efficiency for the entire system (soil and plant) can be estimated as follows

(4) composite system efficiency   Ec=Eup*Es=Nf/(Sv+Sd+Sl)

It is important to note that these efficiency parameters can be determined without having to determine total N in the soil. Avoiding total soil N analyses is noteworthy since the precision of present analytical procedures (Kjeldahl or dry combustion) approach ± 0.01%. This translates into approximately ± 220 kg N/ha (depending on soil bulk density) which is often greater than the rate of N applied, thus restricting the ability to detect N treatment differences.

Will increased NUE lead to increased NO_3 leaching?

Data from Kanampiu et al. (1995)

NUE Sinks:	Increased NUE	No Change
	------------- kg / ha	--------------
Total N Applied	180	180
Plant N uptake (at flowering)	68	71
Final Grain N uptake	42	40
Plant N loss	26	31
Denitrification	10	15
Immobilization	80	80
Balance	22	14
Leaching	?	?

Table 4.2. Components of nitrogen use efficiency as reported by Moll et al. (1982) and modifications (in bold italics) for grain crops.

Component	Abbreviation	Unit
Grain weight	Gw	kg ha^{-1}
Nitrogen supply (rate of fertilizer N)	Ns	kg ha^{-1}
Total N in the plant at maturity (grain + stover)	Nt	kg ha^{-1}
N accumulation after silking	Na	kg ha^{-1}
N accumulated in grain at harvest	Ng	kg ha^{-1}
Stage of growth where N accumulated in the plant is at a maximum, at or near flowering	***Nf***	***kg ha^{-1}***
Total N accumulated in the straw at harvest	***Nst***	***kg ha^{-1}***
Estimate of gaseous loss of N from the plant	***Nl =Nf-(Ng+Nst)***	***kg ha^{-1}***
Flowering uptake efficiency	***Eup=Nf/Ns***	
Harvest uptake efficiency **(Uptake efficiency)**	***Eha=Nt/Ns***	
Translocation index (accumulated N at flowering translocated to the grain)	***Eti =Ng/Nf * (1/Nl)***	
Soil supply efficiency	***Es=Ns/(Sv+Sd+Sl)***	
Composite system efficiency	***Ec=Eup*Es=Nf/(Sv+Sd+Sl)***	
Utilization efficiency	Gw/Nt	
Efficiency of use	Gw/Ns	
Grain produced per unit of grain N	Gw/Ng	
Fraction of total N translocated to grain	Et=Ng/Nt	
Fraction of total N accumulated after silking	Na/Nt	
Ratio of N translocated to grain to N accumulated after silking	Ng/Na	

N DISCUSSION

Magruder Plots
1892: 4.0 % organic matter = 0.35+ 1.8 OC
OC = 2.03%
TN = 0.16%
Pb = 1.623 (0-12")

lb N/ac = D_B * ppm N * 2.7194
= 1.623 * 1600 * 2.7194
=7061

1997
OC = 0.62%
TN = 0.0694%
lb N/ac = 1.623*694*2.7194
=3063

Difference: 7061 - 3063 = 3998 lbs N

Grain N removal
14.6 bu/ac * 60 lb/bu = 876 lbs
876 lbs * 105 years = 91980 lbs grain
91980 lbs * 0.022086 %N = 2031 lbs N

Plant N loss
10.7 lb/ac/yr (Kanampiu et al., 1995)
105 * 10.7 = 1130 lbs N

Denitrification
2.85 lb/ac/yr (Aulakh et al. 1984)
105 * 2.85 = 300 lbs N

Balance 537 lbs N

Year 1 denitrification, ammonification
Denitrification, ug/g = 50.0 * OC + 6.2 (Burford and Bremner, 1975)
= 50.0 * 2.03 + 6.2
= 107.7 ug/g
= 107.7 * 1.623 * 2.7194
= 475.34 lb/ac (0-12")

New Balance 61.66 lb N/ac
(0.58 lb N/ac/yr unaccounted)

Not included in this balance sheet is the amount of N that would be deposited via rainfall, and the amount lost via ammonification, both of which would be important.

Denitrification losses the first year were likely much higher since increased NO_3-N would have been present as a result of mineralized N from a very large total N pool. Burford and Bremner (1975) applied the equivalent of 800 lb NO_3-N/ac and found that denitrification losses were extremely high. Although their work has little relevance to annual denitrification losses expected under field conditions, it does provide some insight into what might have happened in the first year when soils were first tilled.

Miscellaneous

When adequate inorganic N was present, the incorporation of straw in conventional till or the application of straw on the surface of zero till approximately doubled the accumulative gaseous N losses (increased supply of energy to denitrifying organisms) (Aulakh et al., 1984).

From 71 to 77% of the surface applied fertilizer N remaining in the profiles was in the 0 to 0.1 m soil layers (Olson and Swallow, 1984).

Late N application can be efficiently taken up by plants, and does not decrease soil N uptake. To achieve acceptable grain protein levels for bread wheat in this irrigated cropping system, N should be supplied late in the season to improve N uptake during grain fill (Wuest and Cassman, 1992)

5. USE OF STABLE AND RADIOACTIVE ISOTOPES

Historical

Einstein: Relativity theory (1905), quantum theory
Roentgen: discovered x-rays
Becquerel: first recognition of radioactivity
Rutherford: transmutations "changing one element to another"
Bremsstrahlung: identified secondary x-rays
Curie - Joliot: first induced artificial radioactivity (1934)

Isotopes are atoms of the same element that differ in mass. They have the same number of protons and electrons but have a different mass which is due to the number of neutrons.

1. All radio isotopes have a particular kind of radiation emission
2. Energy and mass are equivalent (Einstein)
3. All radio nuclides have a characteristic energy of radiation
4. All radio nuclides possess a characteristic rate of decay

1 mole of X has 6.025×10^{23} atoms
one gram of ^{14}N has (14 g/mole)
$\underline{6.025 \times 10^{23} \text{ atoms/mole}}$ * 1 mole/14g = 4.3×10^{22} atoms/g

Avogadros # = # of molecules in one gram molecular weight of any substance.

Dealing with reactions in the outer ring that compromise and produce chemical reactions.

	atomic mass units (amu)	charge
proton	1.007594	+
electron	0.000549	-
neutron	1.008986	none

${}^{m}_{z}E$ ${}^{1}_{1}H$ ${}^{4}_{2}He$

E- element
m - mass
z - atomic number (# of protons in the nucleus)

All hydrogen atoms have one proton

${}^{1}_{1}$**H**	${}^{2}_{1}$**H**	${}^{3}_{1}$**H**
stable	stable deuterium	radioactive tritium
mass = 1	mass=2	mass=3
no neutron	1 neutron	2 neutrons
1 proton	1 proton	1 proton
1 electron	1 electron	1 electron

${}^{12}_{6}$**C**	${}^{13}_{6}$**C**	${}^{14}_{6}$**C**
stable	stable	radioactive
mass=12	mass=13	mass=14
6 neutrons	7 neutrons	8 neutrons
6 protons	6 protons	6 protons
6 electrons	6 electrons	6 electrons

<u>Chemical versus Nuclear Reactions:</u>

1. $2Na^{+} + H_2O$ ----> $2NaOH + 2H^{+}$
3-5 eV in this reaction

2. ${}^{4}_{2}He$ + ${}^{9}_{4}Be$ ----> ${}^{12}_{6}C$ + ${}^{1}_{0}n$
10 million eV in this reaction

In a nuclear reaction, we have to balance both mass and proton number.

Transmutation: changing one element into another

${}^{35}_{17}Cl$ + ${}^{1}_{0}n$ ------> ${}^{32}_{15}P$ + ${}^{4}_{2}He$

${}^{32}_{16}S$ + ${}^{1}_{0}n$ ------> ${}^{32}_{15}P$ + ${}^{1}_{1}p$

Chemical reactions involve changes in the outer electronic structure of the atom whereas nuclear reactions involve changes in the nucleus

Radiation Units/Definitions:

erg: work done by a force of one dyne acting through a distance of 1 cm.
= 1.0 dyne/cm of 1.0 g - cm^2/sec^2

dyne: force that would give a free mass of one gram, an acceleration of one centimeter per second per second

Curie: amount of any radioactive material in which 3.7×10^{10} atoms disintegrate (decay or loss of radioactivity) per second.

1 B_q (becquerel) 1 dps
1 uC = 3.7×10^4 dps
1 mC = 3.7×10^7 dps = 2.22×10^9 dpm
1 C = 3.7×10^{10} dps = 2.22×10^{12} dpm

Rad = 100 ergs/g absorbing material (quantity of radiation equivalent to 100 ergs/g of exposed tissue).

1 Rad = 1/100 Roentgen

eV = electron volt (amount of energy required to raise one electron through a potential of one volt)
1 eV = 1.6×10^{-12} erg
1 MeV = 1.6×10^{-6} erg
specific ionization: # of ion pairs produced/unit distance penetrated.

Chernobyl: 100 million Curies released

${}^{137}_{55}Cs$ (30 year half life) and ${}^{90}_{38}Sr$ (28 year half life) were the major radioactive isotopes of concern in that accident

Production Methods:

1. Particle accelerators
2. Nuclear reactors
3. Atomic explosions

Mass Energy Equivalents:
$E = MC^2$

1 amu = 1.66×10^{-24} g
= reciprocal of Avogadro's #

E = energy (ergs)
M = mass (grams)
C = velocity of light (cm/sec)
= 186000 miles/sec
= 3×10^{10} cm/sec

How much energy does 1 amu have?

$E = (1.66 \times 10^{-24}$ g$) (3 \times 10^{10}$ cm/sec$)^2$
$=1.49 \times 10^{-3}$ ergs
$= (1.49 \times 10^{-3}$ ergs$)/(1.6 \times 10^{-6}$ erg/Mev$) = 931$ MeV

Calculate the amount of energy in 1 gram of ^{235}U?
1g/235g/mole x 6.025 x 10^{23} atoms/mole x 0.215amu/atom x 931MeV/amu

= 5.12×10^{23} MeV
= 2.3×10^{14} kilowatt hours (12 years of electricity for 1 household)
1 kilowatt hour = 2.226×10^{9} MeV
only 1/5 or 0.215 of ^{235}U is converted to energy (split)

Fusion: Making hydrogen atoms combine resulting in released energy
-no remnant radioactivity
-no atmospheric contamination

$^{2}_{1}H$ +	$^{3}_{1}H$	---> $^{4}_{2}He$	+ $^{1}_{0}n$
deuterium	tritium	(alpha)	

2½ gallons of tritium would provide the U.S. with energy for 1 year if fusion were feasible.

Fission: "Splitting atoms"
-results in the production of radioactive materials

$^{235}_{92}U + ^{1}_{0}n$ ---> $^{97}_{36}Kr$ + $^{138}_{56}Ba + ^{1}_{0}n$ + energy
$^{235}_{92}U + ^{1}_{0}n$ ---> $^{90}_{38}Sr$ + $^{144}_{54}Xe + 2\,^{1}_{0}n$ + energy

$^{138}_{56}Ba$ is a fission fragment
Strictly chance of actually knowing what we will have as products from the bombardment of $^{235}_{92}U$ with neutrons.

$^{235}_{92}U$ "controlled reaction that is a chain reaction" using uranium rods

^{238}U accounts for 99.3 percent of the uranium found on earth
$^{235}_{92}U$ is used for fission, because it splits easier.

neutrons emitted in fission can produce a chain reaction

Nuclear fission taps about 1/1000 of the total possible energy of the atom.

Sources of Radiation

A. Particulate

1. Alpha (nucleus of the He atom, mass = 4 and charge = +2)
Charge +2, mass 4 ($^{4}_{2}He$) high specific ionization, limited penetration, come only from high z (# of protons) atoms.

$^{226}_{88}Ra$ --> $^{222}_{86}Rn$ + $^{4}_{2}He$ + energy
$^{238}_{92}U$ --> $^{234}_{90}Th$ + alpha + 4.19 MeV

Radionuclides which emit alpha are changed into another nuclide with a mass of 4 units less and 2 fewer protons

Three sheets of paper are sufficient to stop alpha radiation.
- when an alpha particle loses energy it attracts electrons and becomes a neutral helium atom.
- not used in plant biology and soil studies.

2. Beta "negatron" (high neutron:proton ratio, originates from the nucleus like alpha)

- neutron in the nucleus changes to a proton, increasing the atomic # by one.

$^{32}_{15}P$ ---> $^{32}_{16}S$ + B^{-} + e^{-} + v(+1.71 Mev)

3. Beta "positron" (low neutron:proton ratio, comes from the nucleus which has too many protons)

- proton in the nucleus changes to a neutron, decreasing the atomic number by one.

$^{30}_{15}P$ ---> $^{30}_{14}Si$ + B^{+} + e^{+} + v(+3.3 Mev)

4. Neutrino

B. Photons (a quantum of radiant energy)

1. Gamma, does not have a mass (electromagnetic radiation with the speed of light)

- is not a mode of radioisotope decay but rather associated with particulate emission.
- can penetrate inches of lead

$^{60}_{27}Co$ ---> $^{60}_{28}Ni$ + B^- +gamma + gamma
0.31MeV 1.17 MeV 1.33 MeV

Radio isotope decay schemes result in transmutation of elements that leave the nucleus in a suspended state of animation. Stability is reached by emitting one or more gamma photons.

2. X-ray emitting by electron capture (too many protons and not enough neutrons)

- emitted when cathode rays of high velocity fall directly on a metallic target (anticathode) in a vacuum tube.
- highly penetrating electromagnetic radiation (photons) with a short wave-length.
- identical to gamma rays if their energies are equal
- electron from K ring is pulled into the nucleus
- chain reaction of K ring pulling electron into K from L and so on.
- emission as an x-ray is external to the nucleus (come from the outer shell of the atom)

3. Cosmic radiation (radiation from outer space)

- mixture of particulate radiation (neutrons) and electromagnetic radiation.

Source of Radiation

	specific ionization	penetration	charge	nucleus	
alpha	high	low	+2	inside	^{226}Ra, ^{238}U, ^{242}Pu*
beta (negatron)	medium	med	+1	inside	
beta (positron)@	medium	med	-1	inside	^{90}Sr, ^{32}P
gamma	low	high	none	inside	^{60}Co
X-ray		high		outside	^{59}Ni

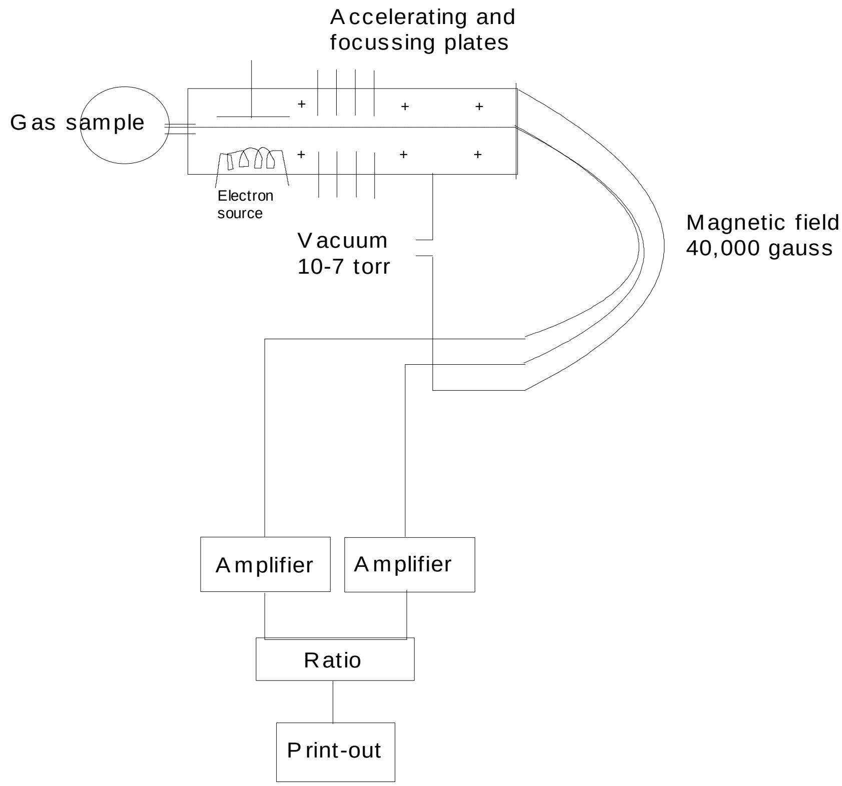
* - naturally occurring
@ - characteristic of the majority of radioisotopes used in biological tracer work

Measurement:

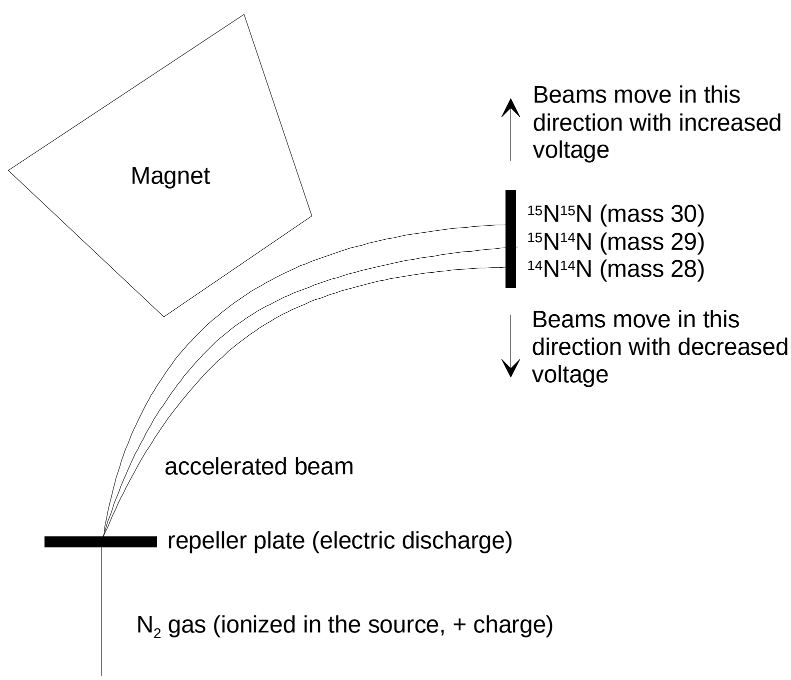
A. ionization takes place in an enclosed sensitive medium between two oppositely charged electrodes (ionization chambers, Geiger-Muller)
B. systems that do not depend on ion collection but make use of the property that gamma-ray photons (also alpha and beta) have for exciting fluorescence in certain substances (scintillation)
C. ionizing radiations affect the silver halide in photographic emulsions which show a blackening of the areas exposed to radiation (autoradiography)

Geiger-Muller Counter: (positron) will not measure gamma.
G-M tube filled with Ar or He. Ionizing radiation passing through the gas in the tube causes electrons to be removed from the atoms of gas; form ion-pairs (pairs of electrons and positive ions). Under the influence of an applied field, some of the electrons move towards the anode and some of the positive ions towards the cathode. Charges collect on the electrodes and initiate pulses; a continuous stream of these pulses constitute a weak electric current.

Mass Spectrometer:
Positive ions are produced from molecules or atoms by subjecting them to an electric discharge or some other source of high energy. The positive ions are accelerated by means of an electric field and then passed through a slit into a magnetic field. The slit serves to select a beam of ions. The charged particles follow a curved path in the magnetic field which is determined by the charge to mass ratio of the ion. When two ions with the same charge travel through the tube, the one with the greater mass will tend to follow the wider circle.



Block diagram of a double collector mass spectrometer (Vose, 1980)



The voltage in the source can be changed prior to reaching the repeller to work with heavier or lighter isotopes (carbon).

Newer instruments are set up to change the current on the magnet for different elements instead of accelerating voltage (applied to everything in the source)

Scintillation: (alpha, positron, negatron, gamma)

When certain materials (zinc sulfide) are exposed to gamma photons or particulate radiation they emit scintillation's or flashes of light. The scintillation's are produced by a complex process involving the production of an excited (higher energy) state of the atoms of the material. When the orbital electrons of these atoms become deexcited, the excess energy is then given off in an infinitely small time as a flash of light (scintillation).

Autoradiography:

Radiation Levels:
Limits: 1/10 Rad/week

X-ray (dentist)	1-5 rads
0-25 rads	no injury
25-50 rads	possible blood change, shortened life span
50-100 rads	blood changes
100-200	definite injury (possibly disabled)
200-400	definite disability, possible death
400-600	50% chance of dying
>600	assured fatal

Radiation Treatment:

1. Nucleic acid injections: enhance blood manufacturing capabilities of the body (blood cells affected most)
2. Bee sting venom (has R-SH radical)
3. Mercaptan

There are four stable or heavy isotopes of potential interest to researchers in soil and plant studies (^{18}O, ^{2}H, ^{13}C and ^{15}N)

Nitrogen ^{15}N

(N_2 gas bombarded by electrons) N_2 gas

(cryogenic distillation of nitric oxide) (microdiffusion techniques)

1. non radioactive
2. no time limits on experiment (versus half-life problems associated with radioactive materials)
3. less sensitive than for measuring radioactive elements where we can accurately determine 1 atom disintegrating
4. mass spec needs 10^{12} atoms before it can be measured
5. mass spectrometry is more complicated.
6. high enrichment needed in agricultural work
7. high cost associated with purchasing this isotope $250/g
8. need 3/10 enrichment for 1 year experiments.
9. discrimination of plants for ^{14}N versus ^{15}N
10. more sensitive than total N procedures

Nitrogen: radioactive isotopes of N have extremely short half-lives to be of significant use in agriculture (^{13}N $t_{½}$ =603 seconds)

N_2	% present in atmosphere
^{14}N ^{14}N	99.634
^{15}N ^{14}N	0.366

Ratio needs to be established before starting the experiment: (e.g., background levels)

100g	$^{15}NH_4{}^{15}NO_3$	5% enriched	$200
100g	$^{15}NH_4{}^{15}NO_3$	10% enriched	$400

Instead of the specific activity of a sample used in the case of radioisotopes, the term % abundance is used for stable isotopes. The % ^{15}N abundance is the ratio of ^{15}N to ^{15}N + ^{14}N atoms

Because the natural environment has an ^{15}N abundance of 0.3663%, the amount of ^{15}N in a sample is expressed as %<u>^{15}N atom excess</u> over the natural abundance of 0.3663. (subtracting 0.3663 from the determination of ^{15}N abundance to obtain <u>^{15}N atom excess</u>).

mass spec: detection to 0.002 atom excess:
Essentially measuring the intensity of ion currents (R)

$$R = {}^{14}N\,{}^{14}N/{}^{15}N\,{}^{14}N$$

% ^{15}N abundance = 100/2R + 1

By measuring the height of the ^{14}N ^{14}N and ^{15}N ^{14}N peaks (corrected for a background reading), the R values are determined and the % ^{15}N abundance calculated.

Sample Preparation:
N in plant and soil samples must first be converted into N_2 gas.
1. Kjeldahl digestion - distillation into acid - total N determined by titration - aliquot taken for transformation into N_2 gas (Rittenberg Method)

$2NH_4Cl + 3NaBrO^* + 2NaOH \dashrightarrow N_2 + 5H_2O + 3NaBr + 2NaCl$
*alkaline sodium hypobromite
(Vose, p 156)

2. Dumas method (sample heated with CuO at high temperatures (> 600°C) in a stream of purified CO_2 and the gases liberated are led over hot Cu to reduce nitrogen oxides to N_2 and then over CuO to convert CO to CO_2. The N_2-CO_2 mixture thus obtained is collected in a nitrometer containing concentrated alkali which absorbs the CO_2 and the volume of N_2 gas is measured.

ERRORS/DILUTION:
1. N in grain, N in tissue
2. N in organic fractions (immobilized)
3. Inorganic soil N
4. Plant N loss
5. N leaching

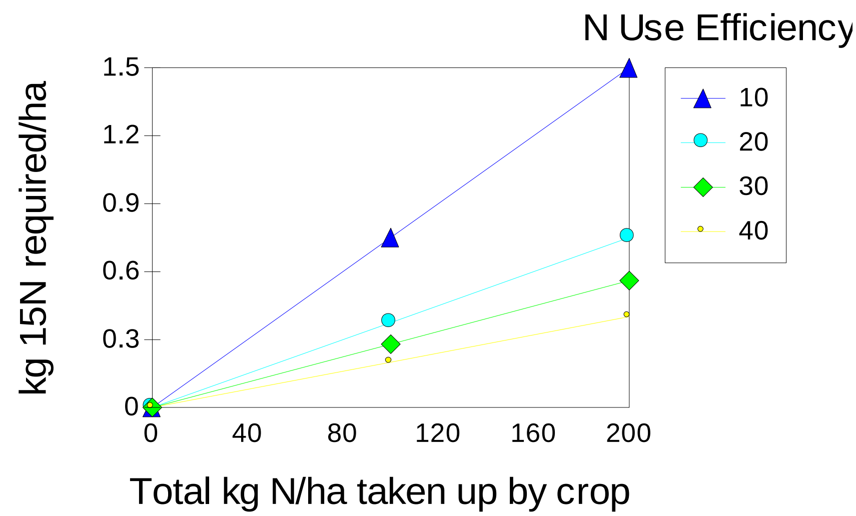
For analysis by mass spectrometer, the analytical error including sub-sampling is approximately 0.01% ^{15}N atom excess for a single sample. Improved instrumentation has taken this to 0.002% ^{15}N atom excess.

Therefore samples should contain at least 0.20 % ^{15}N atom excess. (5% error)

1% atom excess ^{15}N is adequate for fertilizer experiments where the crop takes up a substantial portion of the applied fertilizer.

30-50% atom excess is required for soils experiments where turnover processes are high and where various fates of N exist (plant N loss, leaching, plant uptake, grain uptake, etc.). For this reason, ^{15}N studies are usually small due to the price.

If 80 kg N/ha are to be applied in an experiment where the total N uptake is likely to be 100 kg N/ha and the expected utilization of N fertilizer were 30 %, then 0.33 kg/ha of ^{15}N is required (Vose, p. 165, using Figure X from Fried et al.).



Therefore, the enrichment required for a rate of application could be as low as 0.41% ^{15}N atom excess (0.33/80 * 100)

Enriched ^{15}N:

materials with a greater than natural concentration of ^{15}N

% plant N derived from fertilizer = $\dfrac{\%^{15}N \text{ excess in sample}}{\%\ ^{15}N \text{ excess in fertilizer}}$

Depleted ^{15}N:

materials with a lower than natural concentration of ^{15}N (0.003 - 0.01 atom % ^{15}N) or (< 0.01 atom % ^{15}N)

- use of isotopic ^{14}N
- studies involving residual soil nitrogen are not practical with depleted materials due to the high dilution factor.

% plant N derived from the fertilizer =

(Nu - Nt)/(Nu - (Nf/n))

Nu =atom % ^{15}N in unfertilized plants
Nt = atom % ^{15}N in fertilized plants
Nf = atom % ^{15}N in the fertilizer (for example 0.006%)
n = the plant discrimination factor between ^{14}N and ^{15}N.
If it is assumed that there is no discrimination between 14N and ^{15}N, then n = 1.

Fertilizer N Recovery (Varvel and Peterson, 1991)
1. Difference method

$$PFR = \frac{(NF)-(NC)}{R}$$

NF = total N uptake in corn from N fertilized plots
NC = total N uptake in corn from unfertilized plots
R = rate of fertilizer N applied
PFR = percent fertilizer recovery

2. Isotopic method (Depleted material)

$$PFR = \frac{(NF) \times (C-B)/D}{R}$$

NF = total N uptake in corn from N fertilized plots
B = atom % ^{15}N of plant tissue from N fertilized plots
C = atom % ^{15}N of plant tissue from unfertilized plots (0.366%)
D = depleted atom % ^{15}N in applied N fertilizer
R = rate of applied ^{15}N-labeled fertilizer

3. Isotopic method (Enriched material, Sanchez et al., 1987)
F = As-Ar/Af-Ar

F= fraction of total N uptake derived from ^{15}N enriched fertilizer
As = atom % ^{15}N measured in the harvested plant sample
Af = atom % ^{15}N in the enriched fertilizer
Ar = atom % ^{15}N of the reference harvested plant material from non ^{15}N enriched fertilizer treatments

Ef = F x total N uptake
Ef = uptake of ^{15}N enriched fertilizer

Shearer and Legg (1975) found that $d^{15}N$ of wheat plants decreased as the N application rate increased.

$$d^{15}N = \frac{\text{atom \% } ^{15}N \text{ (sample)} - \text{atom \% } ^{15}N \text{ (standard)}}{\text{atom \% } ^{15}N \text{ (standard)}} \times 1000$$

15N composition of the total N of grain and leaf samples of corn (*Zea mays* L.) decreased systematically as N fertilizer rates increased (Kohl et al., 1973). This result was considered to be consistent with increasing contributions of fertilizer N to plants as the rate of applied N increased.

Hauck and Bremner, 1976

percent nitrogen recovered (plant or soil) =

$$= \frac{100P\,(c-b)}{f(a-b)}$$

P = total N in the plant part or soil in kg ha^{-1}
f = rate of ^{15}N fertilizer applied
a = atom percent ^{15}N in the labeled fertilizer
b = atom percent ^{15}N in the plant part or soil receiving no ^{15}N
c = atom percent ^{15}N in the plant part or soil that did receive ^{15}N

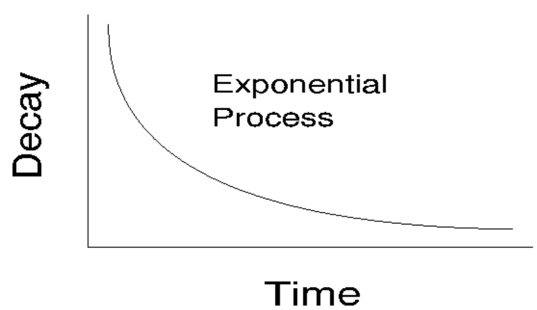
unlabeled N uptake = (total N uptake in grain and straw) - [N rate(% recovery of ^{15}N in grain and straw)]

Agronomic Applications

Applications:
half-life: time required for half of the radioactive atoms to undergo decay (loss of half of its radioactivity)

^{32}P ($t_{½}$ = 14.3 days)
^{14}C ($t_{½}$ = 5568 yrs)

λ: Decay constant (fraction of the number of atoms of a radioisotope which decay per unit time)



A: Activity (decay intensity which is proportional to the number of radioactive atoms present)
N: number of radioactive atoms present at time t and λ is the decay constant
$\lambda = 0.693/t_{½}$
$N = N_o e^{-\lambda t}$
$A = \lambda N$

N for 1 g of pure ^{32}P = $6.025 \times 10^{23}/32$ atoms/g
= 1.88×10^{22} atoms/g

Isotope Effects:
All tracer studies assume that the tracer behaves chemically and physically as does the element to be studied (tracee).

Discrimination of the plant /soil microflora
Isotopic Exchange (^{42}K , cytoplasm, exclusion K_2SO_4, KCl)

Phosphorus ^{32}P

1. mobile in the plant
2. found to concentrate in the grain
3. mobility of P in the plant allows for increased concentration in younger tissue and fruiting bodies.
4. strong beta emitter resulting in acceptable characteristics for autoradiograph techniques.

Agronomic uses:

1. P use efficiency
2. Method of placement
3. P fixation

In general, ^{32}P is no longer useful after approximately 7 half lives or 100.1 days.

EXAMPLES:

1. What will the activity of 5 mC ^{32}P in 5 ml be in 36 days?
$N = No\ e^{-\lambda t}$
$A = Ao\ e^{-\lambda t}$
$\lambda = 0.693/t_{½}$ = 0.693/14.3 = 0.04846
t = 36 days
$-\lambda t = 1.744$
$e^{-\lambda t} = 0.1748$

A = 5 mC/5ml * 0.1748
= 0.1748 mC/ml

2. You intend to set up a field experiment for evaluating the P delivery capacity of a given soil.

a. P rate= 18.12 kg/ha (18120 g/ha)
b. Crop will utilize 10 % of that applied.
c. Need a count of 1000 cpm at the end of the experiment.
d. Instrument has a 20% counting efficiency for ^{32}P.
e. A 10 gram sample will be used from a total plot weight of 3628 kg/ha.
   10/3628000 = 0.000002756

What should the specific activity of the fertilizer be in mC/g P if 110 days will lapse between planting and sample assay?

1000 cpm = $Ao\ e^{-\lambda t}$
1000 cpm = $Ao * e^{-(0.693/14.3)(110)}$

$1000\ cpm = Ao\ e^{-5.33}$

$Ao = 1000/0.0048403 = 2.06596 \times 10^5$ cpm
2.0659×10^5 cpm ÷ 60 sec/min = 3.443×10^3 dps
3.443×10^3 dps ÷ 0.10 (crop utilization efficiency) = 3.443×10^4 dps
3.443×10^4 dps ÷ 0.20 (counting efficiency) = 1.7216×10^5 dps
1.7216×10^5 dps ÷ 0.000002756 (dilution) = 6.2468×10^{10} dps
6.2468×10^{10} dps ÷ 3.7×10^7 dps/mC (constant) = 1.688×10^3 mC
1.688×10^3 mC ÷ 18120 g = 9.317×10^{-2} mC/g P

3. How much ^{32}P would you put into a system to assure 500 cpm after 2 months using an instrument with a 10% counting efficiency and 10% P utilization efficiency?

$A = Ao\ e^{-\lambda t}$
$500\ cpm = Ao * e^{-(0.693/14.3)(60)}$
$Ao = 500/0.0546 = 9.157 * 10^3$ cpm
$9.157 * 10^3$ cpm ÷ 0.10 (crop utilization efficiency) = $9.157 * 10^4$ cpm
$9.157 * 10^4$ cpm ÷ 0.10 (counting efficiency) = $9.157 * 10^5$ cpm
$9.157 * 10^5$ cpm ÷ 2.22×10^9 cpm/mC (constant) = 4.13×10^{-4} mC

1 mC ^{32}P weighs 3.5×10^{-9} g
4.13 x 10-4 mC x 3.5 x 10-9 g/mC = 1.44 x 10-12 g 32P

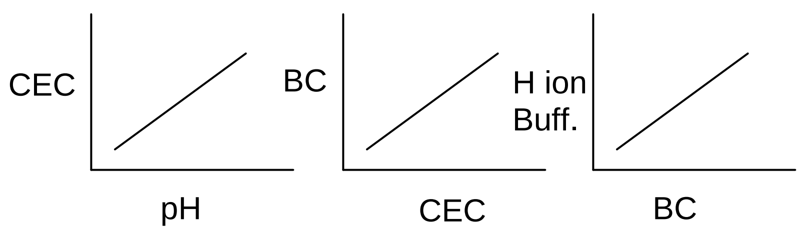
6. EXCHANGE

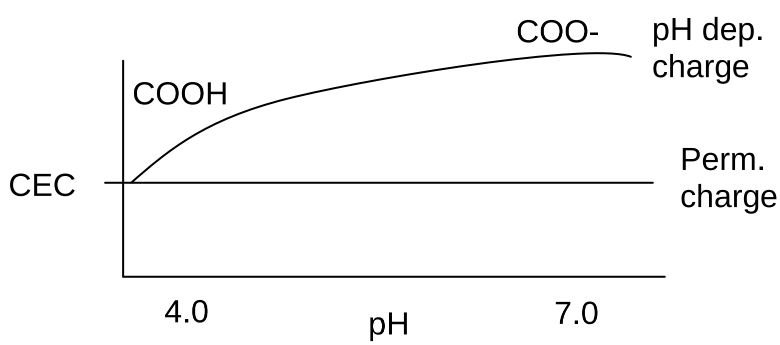
Absorption: interception of radiant energy or sound waves
Adsorption: adhesion in an extremely thin layer of molecules to the surfaces of solid bodies or liquids with which they are in contact.

Soils containing large amounts of mineral clay and organic matter are said to be highly buffered and require large amounts of added lime to increase the pH.

Sandy soils with small amounts of clay and organic matter are poorly buffered and require only small amounts of lime to change soil pH, (Tisdale, Nelson, Beaton and Havlin, p.94)

Buffering capacity (BC): represents the ability of the soil to re-supply an ion to the soil solution.





You should never use a buffered solution (fixed pH) for CEC. If a 1 N NH_4OAc solution were used to displace the cations on the exchange complex of a soil with a pH of 5.0, CEC would be overestimated as pH dependent charge sites would be included (specifically organic matter) that would not have been present at the soils natural pH.

Ions must exist in soils as solid compounds or adsorbed to cation/anion exchange sites.

Can be described by the ratio of the concentrations of absorbed (Δ Q) and solution (Δ I) ions; BC = Δ Q/Δ I

The BC in soil increases with increasing CEC, organic matter and other solid constituents in the soil.

For most minerals the strength of cation adsorption or lyotropic series is:
$Al^{+++}>Ca^{++}>Mg^{++}>K^{+}=NH_4^{+}>Na^{+}$

ions with a higher valence are held more tightly than monovalent cations (exception, H^{+})
$Al^{+++}>H^{+}>Ca^{++}>Mg^{++}>K^{+}=NH_4^{+}>Na^{+}$

The degree of replaceability of an ion decreases as its dehydrated radius increases. Cations are attracted toward, and anions are repelled from, negatively charged soil colloids. These interactions follow Coulomb's law where;

$F=qq'/Dr^2$

F is the force of attraction or repulsion
q and q^1 are the electrical charges (esu, equal to 2.09 x 10^9 individual electronic charges)
r is the distance of charge separation (cm)
D is the dielectric constant (=78 for water at 25°C)

The strength of ion retention or repulsion increases with increasing ion charge, with increasing colloid charge and with decreasing distance between the colloid surface and either the source of charge or the soluble ion.

Interaction between ions increases with concentration and with the square of the ion charge. The parameter embracing the concentration and charge effects is the ionic strength (I) of the solution.

$I = ½ \text{ sum } Mi\ Zi^2$

where M is the molarity, Z is the charge of each ion i.
Ionic strength measures the effective ion concentration by taking into account the pronounced effect of ion charge on solution properties. A solution has only one ionic strength but each of its constituent ions may have a different activity coefficient.

Exchangeable bases: Ca^{++} Mg^{++} K^{+} and Na^{+}

Exchangeable acidity:
1. H ions obtained from the hydrolysis of exchangeable, trivalent Al
2. Hydrolysis of partially hydrolyzed and nonexchangeable Al
3. Weakly acidic groups, mostly on organic matter
4. Exchangeable H

In the early days of soil science there was no agreement on the pH of the soil at which exchangeable acidity was to be determined. Bradfield, 1923 noted that the usual substance used to increase the pH of acid soils is $CaCO_3$ and that the maximum pH obtainable with $CaCO_3$ is pH 8.3. Therefore base saturation is defined as the quantity of base adsorbed by a soil in the presence of $CaCO_3$ equilibrated with air having a CO_2 content of 0.03% (Thomas, 1982).

Cation Exchange Capacity (CEC):

1. Sum total of exchangeable cations on the exchange complex expressed in meq/100g (Ca^{++}, Mg^{++}, K^+, Na^+, H^+, Al^{+++})
2. Quantity of readily exchangeable cations neutralizing negative charge in the soil
3. Exchange of one cation for another in a solution phase
4. Soils capacity to adsorb cations from an aqueous solution of the same pH, ionic strength, dielectric constant and composition as that encountered in the field.

Extract sample with neutral 1 N ammonium acetate. (NH_4OAc)

- exchange complex becomes saturated with NH_4
- extract same soil with 1N KCl (different salt solution), K^+ replaces NH_4
- quantity of ammonium ions in the leachate is a measure of CEC

example:
-filtrate has 0.054 g of NH_4
(20 g of soil extracted)
1 meq of NH_4 = (14+4)/1000
= 0.018g/meq or 18g/eq
0.054/0.018 = 3 meq
3 meq/20g = 15meq/100g

increase clay, increase CEC
increase OM, increase CEC
increase 2:1 clays, increase CEC

1:1 clays:	1-10 meq/100g
2:1 clays:	80-150 meq/100g

Effective CEC

Extraction with an unbuffered salt which would give a measure of the CEC at the soils normal pH.

Use of neutral N ammonium acetate (7.0) will result in a high CEC on acid soils because of the adsorption of NH_4 to the pH dependent charge sites.

Why?
1.At high pH, H^+ are weakly held and may be exchanged; pH dependent charge
2.Deprotonation (dissociation of H from OH groups at the broken edges of clay particles which is the prime source of negative charge in 1:1 clay minerals) occurs only at high pH (7.0 and up)

Kamprath: unbuffered salt solution, 1.0 N KCl will extract only the cations held at active exchange sites at the particular pH of the soil. The exchangeable acidity is due to Al and H.

CEC Problems

1. Presence of $CaCO_3$ and/or $CaSO_4$ (dissolution) and the presence of salt in arid type soils. Dissolution of $CaCO_3$ and/or $CaSO_4$ will cause Ca to exchange for Mg, K and Na instead of NH_4 replacing all of these. When 1 N KCl is then added to displace the NH_4 (from NH_4OAc) less NH_4 is detected in the filtrate than what should have been present.
2. Variable charge soils (high content of more difficult exchangeable aluminum-hydroxy "cations"). Exchangeable Al and its hydroxy forms are not readily exchanged with monovalent cation saturation solutions. This error results in an underestimation of CEC.

CEC Methods

1.Polemio & Rhoades (1977) arid soils containing carbonates, gypsum and zeolites.
   a. Saturation of exchange sites with Na (pH 8.2) 0.4N NaOAc + 0.1N NaCl
   b. Extraction with 0.5N $MgNO_3$

c. Na determined (soluble Na from saturation step deducted from total Na to obtain exchangeable Na)
d. Method will determine CEC as a result of permanent charge but not for variable charged soils (pH)

2. Gillman (1979) acid soils
   a. Saturation of exchange sites with $BaCl_2$ (solution of a concentration approximately equivalent in ionic strength to the soil solution)
   b. Extraction with $MgSO_4$ to replace Ba with Mg ($MgSO_4$ concentration is adjusted to achieve an ionic strength comparable with that of the soil solution)
   c. Ba determined

The use of unbuffered solutions throughout ensures that natural soil pH is not significantly altered.

The underlying factor which has caused various researchers to develop alternative methods for determining CEC was how to deal with pH dependent charges (pH of the saturating solution and replacement solution). This is important considering the pH is a logarithmic function of H+ where 10 times as much H occurs in solution at pH 5 as pH 6.

Base Saturation

Reflects the extent of leaching and weathering of the soil.
It is the percentage of total CEC occupied by cations, Ca^{++}, Mg^{++}, Na^+ and K^+, where each is determined separately from the NH_4OAc extract (Atomic Absorption - interception of radiant energy)

Amount present in soil
Ca 0.03g
Mg 0.008g
Na 0.021g
K 0.014g

Meq of each cation (amount present/g per meq)
Ca = 0.03/0.02 = 1.5
Mg = 0.008/0.012 = 0.66
Na = 0.021/0.023 = 0.91
K = 0.014/0.039 = 0.36
=3.43meq/20g
=17.15 meq/100g

CEC = 20 meq/100g
BS = 17.15/20 = 85.85%

BS = CEC - (H^+ + Al^{+++}) / CEC * remember this is exchangeable H^+ and Al^{+++}
pH and BS are positively correlated
Why would pH and BS be positively correlated if pH and CEC were not?

Anion Exchange (Kamprath)

Adsorption of anions to + charged sites in hydrous oxide minerals where the hydrous oxides are amphoteric (have - and + charge depending on pH and therefore have AEC and CEC).

Order of adsorption strength $H_2PO_4^-$ > $SO_4^=$ >NO_3^- = Cl^-

pH < 7.0

More in weathered soils (1:1) containing hydrous oxides of Fe and Al (exposed OH groups on the edges of clay minerals)

Soils which have pH dependent charges.
Anion exchange of 43meq/100g at an acidic equilibrium pH of 4.7.
Can a soil have a net positive charge? (unlikely)

Is $H_2PO_4^-$ adsorption on soils anion exchange? yes
only physically adsorbed initially but soon precipitate as Ca-P in alkaline soils and Fe or Al-P in acid soils.

Can P applications induce S deficiencies in acid soils?

Acid soil: S levels low --> P exchange for S on exchange complex (anion exchange) and $SO_4^=$ can be leached.

90% of all water soluble bases will be leached as sulfate (Pearson et al, 1962)

Kamprath et al. (1956)
1. Increased P concentration in solution reduced the amounts of $SO_4^=$ adsorbed by the soil.
2. Amount of sulfate adsorbed decreased as the pH of the soil suspension increased (4 to 6).

Aylmore et al. (1967)

1. Sulfate adsorption on clays possessing positive edge charges + oxides of Fe and Al (highly resistant to leaching and less available for plant growth)
2. Sulfate adsorbed on kaolinite clay is weakly held and easily released

Fox et al. (1964)

$Ca(H_2PO_4)_2$ best extracting solution for S

AEC negatively correlated with Base Saturation

7. PHOSPHORUS FERTILIZERS

Rock Phosphate

$Ca_{10}(PO_4)_6(OH)_2$
Hydroxyapatite
$Ca_{10}(PO_4)_6F_2$ or Cl_2 or OH_2
Fluorapatite
27-41% P_2O_5

Calcium Orthophosphates

P fertilizers:

1. water soluble
2. citrate soluble (dissolves more P than water)

OSP ordinary superphosphate (0-20-0)

- rock phosphate + sulfuric acid
- mixture of monocalcium phosphate and gypsum
- 16-22% P_2O_5 (90 % water soluble)
- 8-10% S as $CaSO_4$

TSP triple or concentrated superphosphate (0-46-0)

- rock phosphate + phosphoric acid
- essentially all monocalcium phosphate
- 44 to 52% P_2O_5 (98% water soluble)
- < 3% S
- major phosphate mineral is monocalcium phosphate monohydrate (MCP)

DAP Diammonium phosphate (18-46-0)

- Reacting wet process H_3PO_4 with NH_3
- 46-53% P_2O_5

MCP monocalcium phosphate monohydrate $Ca(H_2PO_4)_2$ $2H_2O$ (highly water soluble)
DCPD dicalcium phosphate dihydrate $CaHPO_4$* $2H_2O$ - brushite
DCP dicalcium phosphate $CaHPO_4$, 53% P_2O_5 - monetite

congruent dissolution of $Ca(H_2PO_4)_2$ $2H_2O$ into Ca^{++} and H_2PO_4 ions occurs at a pH of 4.68

Examples:

1. P deficient
2. S deficient
3. pH 5.5
4. anion exchange 20 meq/100g

- Apply triple superphosphate with gypsum
- Supersaturate the band with respect to Ca and precipitate P as DCP and or DCPD which will be slowly available with time.

Lindsay (1979)

- including NH_4^+, K^+, Ca^{++} and Mg^{++} enables these cations to be included in the initial reaction products.
- MCP contains sufficient Ca to precipitate half of P as DCPD or DCP.
- In acid soils, Fe and Al generally precipitate the additional P.
- Avoid anion exchange interaction (P displacing S from the complex)

Low Soil pH (<5.5) P precipitates as Al and Fe phosphates

a. variscite ($ALPO_4 * 2H_2O$)
b. strengite ($FePO_4 * 2H_2O$)

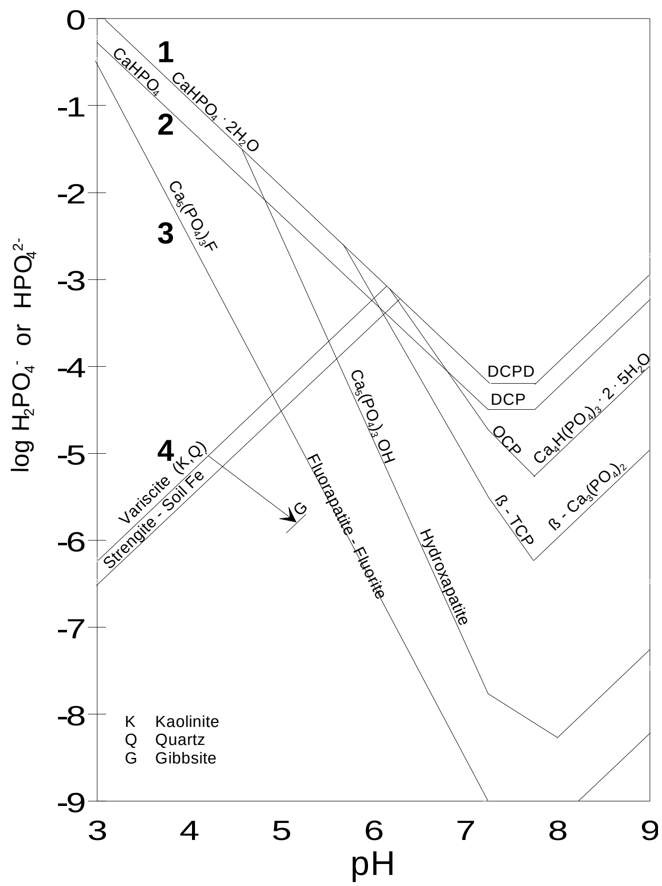
Moderate to High pH, P precipitates as Ca phosphates (several)

a. dicalcium phosphate ($CaHPO_4$)
b. dicalcium phosphate dihydrate ($CaHPO_4 * 2H_2O$)
c. hydroxyapatite $Ca_5(PO_4)_3OH$
d. fluorapatite $Ca_5(PO_4)_3F$ (rock phosphate)

Precipitation - Dissolution of phosphate minerals is pH dependent:
Precipitation/Dissolution can be determined by using P solubility diagrams.

1. Soil solution ($H_2PO_4^-$) and pH above the line (precipitation)
2. Soil solution ($H_2PO_4^-$ and pH below the line (dissolution)

pH 4.5	Event	Precipitate Formed
1. add fertilizer	soluble P added	-
2. 1 - 2	soluble P decreases	DCP
3. 2-3	DCP dissolves	FA
4. 3-4	FA dissolves	Variscite



Example of precipitation/dissolution (1-4)

Can P fertilizers be used as a source of Lime? if enough is applied, yes, but this will not be economical

8. THEORETICAL APPLICATIONS IN SOIL FERTILITY

1. Liebig's law of the minimum
2. Bray's Nutrient Mobility Concept
3. Sufficiency (SLAN)
4. Mitscherlich
5. Bray modified Mitscherlich
6. Base Cation Saturation Ratio

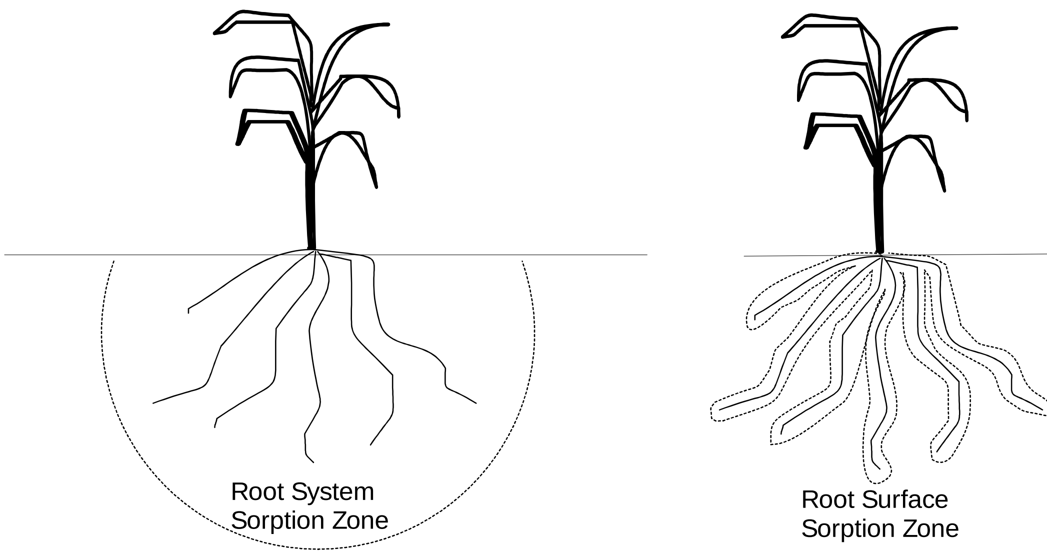
Liebig's law of the minimum (Justus von Liebig 1803-1873)

He stated that the nutrient present in least relative amount is the limiting nutrient.

soil contained enough N to produce 50 bu/ac
soil contained enough K to produce 70 bu/ac
soil contained enough P to produce 60 bu/ac
N would be the limiting nutrient.

Crop used up all of the deficient nutrient in the soil making the yield directly proportional to the amount of the deficient nutrient present and the crop content of the nutrient.

Bray Nutrient Mobility Concept



Sufficiency: SLAN (Sufficiency Levels of Available Nutrients)

a. Range of nutrient (insufficient to sufficient)
b. Amount extracted from the soil is inversely proportional to yield increases from added nutrients.
c. Calibrations exist for the changing levels of available nutrients with fertilizer additions and yield response.
d. Concept assumes little if any effect of the level of availability of one ion on that of another.
e. Recognizes that an addition of the most limiting element may cause more efficient utilization of a less limiting element.

Mathematical expression of the law of diminishing returns where increases in yield of a crop per unit of available nutrient decreases as the level of available nutrient approaches sufficiency.

The concept is based on Mitscherlich's equation:

$dy/dx = (A-y)c$

Yield increases (dy) per unit of available nutrient (dx) decrease as the current yield (y) approaches a maximum yield (A) with c being a proportionality constant.

The derivative was developed for studying tangent lines and rate of change. The first derivative is the slope of the tangent line at x_o
$d/dx\ x^n = nx^{n-1}$

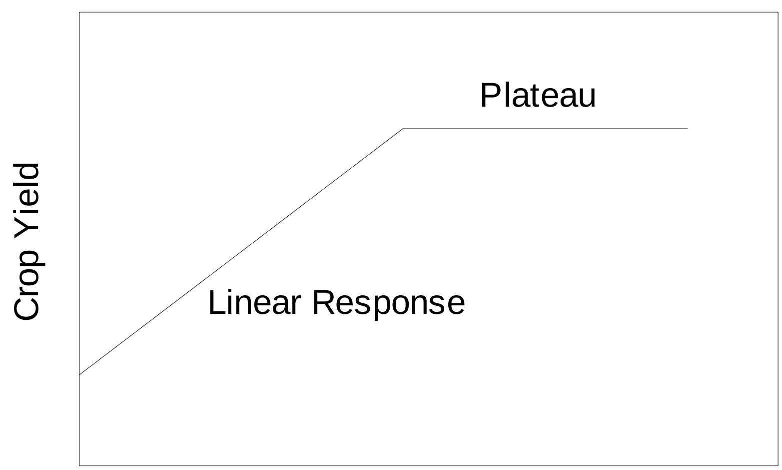
Quadratic: $Y = bo + b_1x - b_2x^2$

$0 = b_1-2b_2x$
$2b_2x = b1$
$x=b_1/-2b_2$

Plant Response to Soil Fertility as Described by the Percent Sufficiency and the Mobility Concept

Simply stated, plants respond to the total amount present of mobile nutrients and to the concentration present of immobile nutrients in soils. Stated this way, yield is directly related (proportional) to the total amount of nutrient present in the soil. However, yield response to immobile nutrients is not related to the total amount of the "available form" present in the soil, but instead is a function of the concentration of available form at, or very near, the root surface. Ideally, the response of crops to mobile nutrients should be linear because mobile nutrients (like water) are not decreased in availability by reaction with the soil. The linear response to mobile nutrients continues with each added increment of the nutrient until the yield potential for that growing environment has been reached, after which it is zero (see figure below)

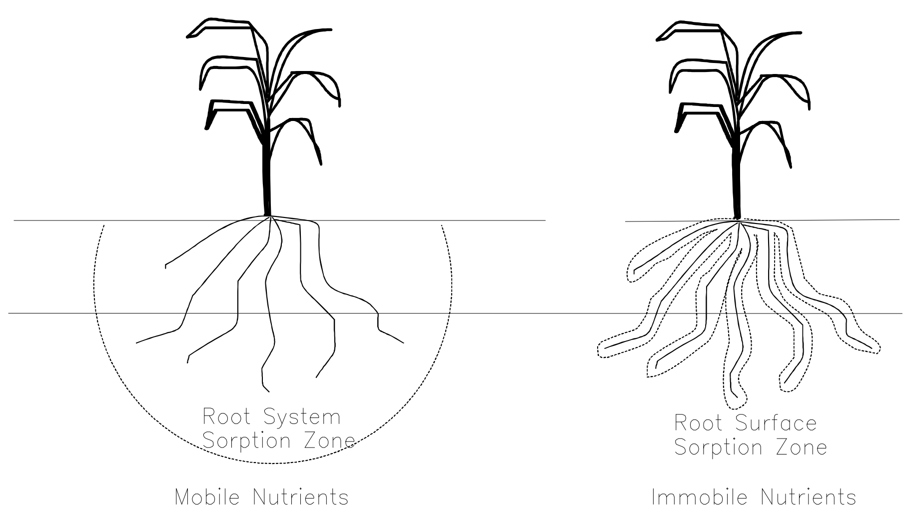
Response to Mobile Nutrients



Available Mobile Nutrient

The ideal situation is not found in soils, only in hydroponics and when the physical phase of the growth media is not reactive, such as with glass beads. However, because the reaction of some nutrients with soil is sometimes minimal (e.g. nitrate-N in cultivated soils with minor potential for immobilization and mineralization of N), they are considered relatively mobile and response tends to follow the ideal. Hence, “rules of thumb” have been developed to guide the use of mobile nutrients like nitrogen, such as “it takes 2 lbs N/bushel of wheat”. The 2 lbs is calculated from the protein or N content (on average) of a bushel of wheat, with the added assumption that measured soil nitrate-N and added fertilizer N will be only 70% utilized. Bray’s mobility concept implies that if available N, for example, is limited to some level below maximum yield potential then a yield plateau will occur at that point. For example, if there is enough total amount of available mobile nutrient to produce the yield potential (20 bu.) and then midway through the season better than average weather conditions result in increasing the yield potential (to 30 bu.), the mobility concept implies the yield will be limited to 20 bu. because the total supply of nutrient will be used up to produce 20 bu. and additional yield can only be obtained if more of the nutrient is added (this is the reason for top dressing wheat midway through the season).

For immobile nutrients, like phosphorus, plants can only extract the nutrient from soil close to the root surface, very little of the nutrient is moved to the root by water in the transpiration stream because soil solution concentrations are minute (< 0.05 ppm for phosphate compared to as high as 100 ppm for nitrate-N). As a plant grows and roots extend out into the soil, roots come in contact with “new” soil from which they can extract phosphate. The amount extracted is limited by the concentration at (or very near) the root-soil interface. If the concentration of phosphate available to the plant at the root -soil interface is inadequate to meet the needs of the plant, then the plant will be deficient in P throughout its development. The deficiency will always be present, and plant growth and crop yield will be limited by the degree to which the immobile nutrient is deficient. Another, perhaps more common way of expressing this nutrient limitation is to state that yield will be



Sufficiency cannot be used for mobile nutrients, because the test is an indication of the total amount available within the profile

Sufficiency can be used here, because as the expand within the profile, the same amount will available as immobile nutrients are taken up vi contact exchange obtained according to the sufficiency of the nutrient supply. When this is expressed as a percentage of the yield possibility then the term percent sufficiency may be applied. Whenever the percent sufficiency is less than 100, plant performance is less than the yield possibility provided by the growing environment. Consequently, it does not matter whether the yield possibility is 20 bu. or 30 bu., if the percent sufficiency is 80, then actual yield obtained (theoretically) will only be 80% of that yield possibility.

The soil test for mobile nutrients is an indicator of the total amount available. If this amount is enough to produce 20 bu/ac, more N would have to be added to the total pool to produce 40 bu/ac. With P, an index is developed that is independent of the environment. If the crop year was good, roots would expand into more volume of soil that had the same level of nutrient supply. Sufficiency is independent of the environment since increased root growth will expand into areas where contact exchange uptake is the same (total amount present in the soil is not greatly affected).

	Mobile	**Immobile**
Concept	yield goal	sufficiency
Environment	dependent	independent
Sorption Zone	root system	root surface
Influence of crop uptake on total available	large	small
Soil test is an indicator of the total available	yes	no
Soil solution concentrations	0-100 ug/g	<0.05 ug/g
Function of	conc. in the root syst.	conc. at the root surf.
Topdress appl.	Yes	No

Example:

Wheat

(4081 kg/ha = 60 bu/ac)

2.5%N in the grain

=102.03 kg N

(4081 kg/ha = 60 bu/ac)

0.36%P in the grain

=14.69 kg P

Soil

0.1% N*10000=1000 ug/g * 1.47 * 1.524 = **2240 kg N/ha** 0-15 cm

NO_3-N: 10 ug/g * 1.47 * 1.524 = **22.40 kg NO_3-N/ha** 0-15 cm

NO_3-N soil test is the actual N available at time X

NO_3-N soil test is valid for one point in time (1 crop or year)

Some states predict N mineralization

0.1% P*10000=1000 ug/g * 1.47 * 1.524 = **2240 kg P/ha** 0-15 cm

P soil test is an index (sufficiency) of availability
P soil test is valid for up to 5 years or more**
10 ug/g P, Mehlich III is not equal to 22.40 kg P/ha
We cannot predict P mineralization

<u>(102.03/2240)*100 = 4.5%</u>
<u>(14.69/2240)*100 = 0.65%</u>

<u>Steps for Using the Sufficiency Concept:</u>

1. Selection or determination of the sufficiency level
   a. estimated from results of studies with a crop on similar soils.
2. Computation of fertilizer required for sufficiency
   a. amount of soluble P required to raise the available P from the initial level to the sufficiency level.
3. Method of supplying the fertilizers (and/or lime)
   a. soil build-up plus crop needs (BUILD-UP) long-term.
   b. crop needs (MAINTENANCE) short-term.

<u>Mitscherlich-Baule percent sufficiency concept:</u>
When more than one nutrient was deficient, the final percent sufficiency is the product of the individual sufficiencies.

Maximum yield when N,P and K are <u>present</u> in sufficient quantities	5000 kg/ha
Yield when N and P are present in sufficient quantities	4000 kg/ha
	4000/5000 = 80% of MAXIMUM
Yield when N and K are <u>present</u> in sufficient quantities	3000 kg/ha
	3000/5000 = 60% of MAXIMUM
What will be the predicted yield when only N is <u>present</u> in sufficient quantities	2400 kg/ha
	5000(0.6 * 0.8)

"present" function of both soil levels and amount applied.

If this percent sufficiency concept is correct, then Liebig's concept of the limiting nutrient is wrong.

Sufficiency Calculations

Present in adequate amounts	Field X	Field Y * Yield kg/ha	Field Z *
NP	**6400**	**<u>9600</u> 12000*.8**	**8000**
NPK	**8000**	**12000**	**<u>10000</u> 8000/.8**
NK	**7200**	**<u>10800</u> 12000*.9**	**<u>9000</u> 10000*.9**
PK	**7000**	**<u>7000</u>**	**<u>7000</u>**
N	**5760 8000*.8*.9**	**8640 12000*.8*.9**	**7200 10000*.8*.9**
% sufficiency K	**NP/NPK = 6400/8000**		**= 0.8**
% sufficiency P	**NK/NPK = 7200/8000**		**= 0.9**

*** - assume that the % sufficiency levels for P and K are the same in field Y and field Z**

Leibig's law of the minimum: correct for mobile nutrients
Mitscherlich: correct for immobile nutrients.

Mitscherlich was incorrect in his use of c values for N 0.122. P=0.60 and K = 0.40.

When the value of c is small a large quantity is needed and visa versa.

Mitscherlich (applicability of this growth function to soil test correlation studies)

The original work by Mitscherlich showed that the **response of plants to nutrients** in the soil can be expressed by a curvilinear function and a logarithmic equation, and further concluded that the regression coefficient c in the equation was constant for each nutrient regardless of any change in environment, plant type, soil and other factors (Balba and Bray, 1956).

$\log (A-y) = \log A - cx$

A = yield possibility when all nutrients are present in adequate amounts but not in excess
y = yield obtained at a given level of x (dy = dx) and when y is always less than A(99%)
c = proportionality constant

NOTE: some texts use c and others c_1, however, it does not matter which one is used, so long as they are defined. Similarly, b and x are used interchangeably

$$\frac{dy}{dx} = c(A-y) \text{ and } \frac{dy}{(A-y)} = dxc$$

log(A-y) = log A - cx

* A and y can be expressed as actual yield or % of the maximum yield

STEP 1.

Experimental locations with different soil test P (b) levels

	NPK	NK	Sufficiency	x	calc.	c
Loc 1	30	20	0.66	12	1.53=2-12c	0.039
Loc 2	40	15	0.375	4	1.79=2-4c	0.051
Loc 3	30	16	0.53	9	1.67=2-9c	0.036
					avg.	0.042

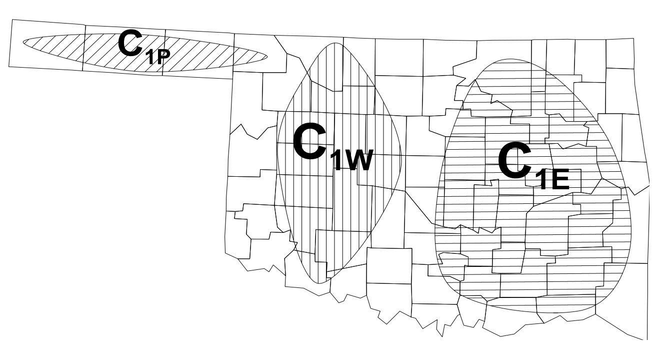
A=100
y = 66
x = 12

log(100-66) = log 100-12c
1.53 = 2 - 12c
12c =0.47
c = 0.039

STEP 2.

Apply value of c where applicable. If the soil pH or soil test K changes over an area, then c has to be altered accordingly.

Now that an average c factor has been determined, we can relate the soil test level of b with yield sufficiency for this element. (CAN determine % SUFFICIENCY)



STEP 3. (Bray Modified Mitscherlich)

Expand Mitscherlich to calculate the amount of fertilizer needed to raise the percent yield from any given starting level to any other desired upper level for which fertilization is desired

$\text{Log}(A-y) = \log A - cb - c_1x$

c_1 = efficiency factor for the method of applying the fertilizer (determined from fertilizer studies). This factor will change accordingly for immobile nutrients (band versus broadcast)

x = quantity of fertilizer that needs to be applied.

STEP 4.

Fertilizer studies c_1 (broadcast P) = 0.0070
c_1 (banded P) = 0.0025

c and c_1 vary with

1. crop
2. planting density/pattern
3. nutrient applied (source)
4. method of application
5. management
6. soil

Yield Possibility

1. soil
2. climate, moisture
3. yield potential (hybrid)
4. planting density and pattern

Soil Nutrient Requirement (level determined)

1. when sampled
2. stage of growth
3. crop
4. form of nutrient applied
5. analytical method

Fertilizer Requirement (x)

1. b
2. fertilizer used
3. crop
4. placement

Bray Modified Mitscherlich

$\text{Log (A-y)} = \text{Log A} - cb - c_1x$

A = maximum yield
y = yield obtained at some level of b
b = soil test index
c = efficiency factor (constant) for b
x = amount of fertilizer added to the soil
c_1 = efficiency factor for x (method of placement)

Example: Soil test value for P = 20
N, K and all other nutrients adequate

kg P/ha	Yield, kg/ha	% Sufficiency
0	2000	40
25	3000	60
50	4500	90
75	5000	100

log (100-40) = log 100 - c(20)
1.778 = 2.00 - c(20)
-0.2218 = -c(20)
c = 0.01109

solve for c

log (5000 - 3000) = log 5000 - 0.01109(20) - c_1(25)
3.301 = 3.477 - c_1(25)
c_1 = 0.00704

log (5000 - 4500) = log 5000 - 0.01109(20) - c_1(50)
2.6989 = 3.477 - c_1(50)
c_1 = 0.0155

average of c_1 = (0.00704 + 0.0155)/2
= 0.011303

STEP 5:
Apply concept (solve for x, determine the amount of fertilizer to be applied)

$\text{Log (A-y)} = \log A - cb - c_1x$

* The dangers of using % yield: It is difficult to determine amounts of fertilizer to add (e.g., 2.0 Mg/ha yield and 4.0 Mg/ha yield).
Assumes that reliable soil test data is available for good soil test correlation.

Fried and Dean (1951)

Assuming that plants take up nutrients from two different sources in direct proportion to the amount available, the A-value was developed as the expression

$$A = B(1-y)/y$$

where; A = amount available nutrient in the soil
B = amount of fertilizer nutrient (standard) applied
y = proportion of nutrient in the plant derived from the standard

"In a true sense, the plant is the only agent that can determine the amount available."

For a specific soil, crop and growing conditions, the A-value is constant, and has been found to be independent of rate of fertilizer application, size of test pot and growth rate.

The A value was primarily developed to determine the availability of P in soil (P supplying power of a given soil).

With the band placement, the A values increased with increasing P rates. This suggests that the availability to plants when P was banded does not remain constant with increasing rates.

Fried and Dean (1951) noted that because it can be assumed that the method of placement does not change the soil phosphorus, the lower A values obtained with the band placement can be attributed to a higher availability of the standard (nutrient applied).

Base Cation Saturation Ratio

<u>For optimum growth of crops, both a best ratio of basic cations and a best total base saturation exist in a soil.</u>

Bear et al. (1945) New Jersey
Percent saturation of cations selected as being "ideal". Work originally conducted on alfalfa. Historically, it is interesting to note that this work was being done at the same time Bray developed the mobility concept.

Ca	65%
Mg	10% (minimum required for alfalfa)
K	5%
H	20%

Ca:Mg > 6.5:1
Ca:K > 13:1
Mg:K > 2:1

Bear et al. (1945) suggested that
1. 10% Mg saturation was minimal for alfalfa
2. Soluble Mg sources were essential for correcting Mg deficiencies in sandy soils
3. Liming above 80% base saturation (20% H) brought about deficiencies of Mn and other micronutrients.

Graham (1959) established ranges or % saturation of the CEC for the 'ideal' soil
Ca: 65-85
Mg: 6-12
K: 2-5
H: ?

- When this proportion exists, you can obtain maximum yield.
- Works only in sandy soils.

Arizona, pH 8, 100% calcium saturated.

<u>Principles Involved:</u>
1. Bonding of cations to exchange sites differs greatly from one type of cation to another and it differs greatly for the same type of cation at different saturations.
2. Exchangeable cations are not proportional to soluble amounts (plant available)
3. Excess of one type of cation may depress the activity and plant uptake of another
4. Adsorbed ion (x) can have marked effects on the ion in question
5. Capacity (total exchangeable) and intensity (activity) of an adsorbed cation influence the total availability of a cation to the plant
6. Saturation of pH-dependent charges increases the activity and plant availability of divalent basic cations

Steps in USING BCSR:
1. Soil analyzed for exchangeable bases
2. Lime required to raise the soil pH to X
3. CEC is determined by totaling basic cations + acidity (exchangeable H and Al), each expressed as meq/100g or cmol/kg
4. Each basic cation expressed as a % of the total CEC
5. Cations must be added to the extent that the existing saturations of basic cations = ranges chosen (e.g., some must decrease and others must increase)

- Works well on low to moderate CEC soils and coarse textured soils, highly weathered soils of low pH that require major adjustments in fertility.
- Useful where it is important to maintain a fairly high level of Mg in the soil to alleviate grass tetany in ruminants.

Grass tetany (low concentrations of Mg and Ca in cool-season grasses in late fall and early spring).

Grass tetany will occur when forage contains $K/(Ca+Mg) > 2.2$ (physiological nutrient imbalance which leads to muscle spasms and deficient parathyroid secretion)

9. SOIL TESTING / CRITICAL LEVEL DETERMINATION

1. Assess the relative adequacy of available nutrients (or lime requirements)
2. To provide guidance on amounts of fertilizers (or lime) required to obtain optimum growth conditions for plants (McLean, 1977).
3. Diagnosis of nutrient limitations before a crop is planted so that corrective measures can be taken.

***Must be fast, reliable and reproducible**

PROBLEMS:

Philosophical differences exist on interpreting the tests which result in radically different fertilizer recommendations

1. Base Cation Saturation Ratio
2. Nutrient Maintenance

Disregarding the soil test level, a quantity of nutrient should be added to replace the amount expected to be removed by the crop. All required nutrients- not feasible.

3. Nutrient Sufficiency

No yield response to nutrients above a certain soil test level.

a. response assured	very low
b. response likely	low
c. response possible	medium
d. response unlikely	high

Depth of Sampling

1. 0-6, 0-8, 0-12, inclusion of subsoil (micronutrients)

Critical Levels

1. Cate Nelson
2. Mitscherlich
3. Quadratic
4. Square Root
5. Linear-plateau

Economic and Agronomic Impacts of Varied Philosophies of Soil Testing (Olson et al., 1982)

Field experiments (1973-1980)
4 locations
Irrigated Corn (Zea mays L.)
5 soil testing laboratories

No differences in yield
No agronomic basis for 'balance' or 'maintenance' concepts
K, S, Zn, Mn, Cu, B, Mg, Fe

Cate and Nelson (1965)

% yield versus soil test level

Two Groups:

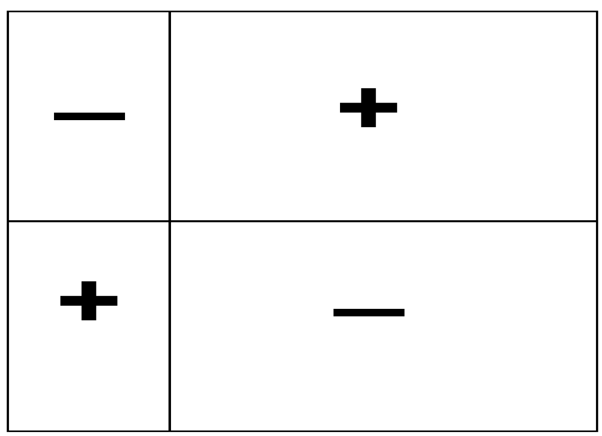
1. probability of response to added fertilizer is small
2. probability of response to added fertilizer is large

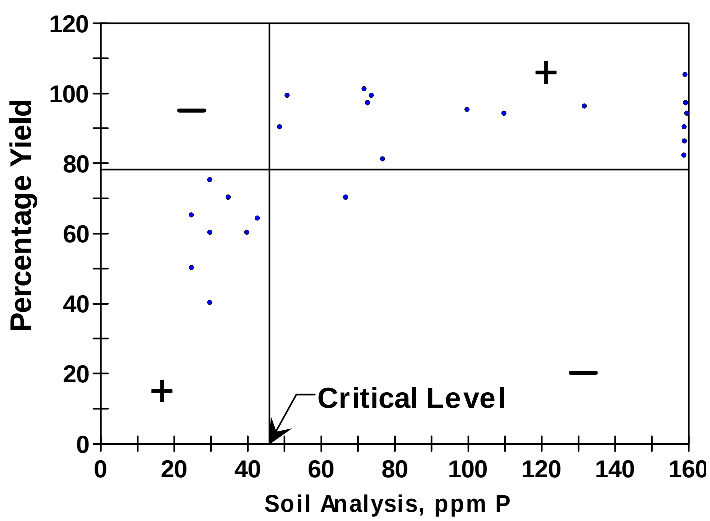
A. Percent yield values obtained for a wide range in locations (fertilizer rate studies)
   - Percent yield = yield at 0 level of a nutrient / yield where all factors are adequate

B. Soil test values obtained (Check Plot)
   - Will generate a single % yield and one soil test value for each location

C. Scatter diagram, % yield (Y axis) versus soil test level (x axis)
   - Range in Y = 0 to 100%

D. Overlay
   - overlay moved to the point where data in the +/+ quadrants are at a maximum
   - point where vertical line crosses the x = critical soil test level





depends on the extraction method used and crop being grown.

Maximizes the computed chi-square value representing the test of the null hypothesis that the # of observations in each of the four cells (quadrants is equal).

2. Mitscherlich
3. Quadratic
4. Square Root
5. Linear Plateau: obtaining the smallest pooled residuals over two linear regressions.

	Equation	MR	MER (dy/dx = PR)
2. Mitscherlich	**Log(A-Y) = Log A - C1(x+b)**		**x=log((2.3*A*c)/PR)/c-b**
3. Quadratic	**y = b0 + b1(x) - b2(x^2)**	**x=0.5 b1/b2**	**x=(PR-b1)/(2*b2)**
4. Square Root	**y = bo + b1(x) + b2(sqrt(x))**	**x=0.25$(b2/b1)^2$**	**x=$(b2/\ \ 2*(PR-b1))^2$**
5. Linear Plateau	**y = bo + b1(x) when x < joint** **y = bo + b1(joint) when x > joint**		

Use of Price Ratios

PR = (price per unit fertilizer) / (price per unit yield)

Optimum rate of fertilizer capable of generating the maximum economic yield is dependent upon the price of fertilizer, the value of the crop and magnitude of fixed production costs. The value of a crop defined as a function of yield and rate of fertilizer can be expressed as:

V = Y * Py = F(x) * Py

where yield (Y) for each fertilizer rate is multiplied by the crop price (Py) per unit of yield. A line describing fertilizer costs per unit area cultivated can be expressed as a function of fixed costs (F) and fertilizer price (Px) times the amount of fertilizer (X)

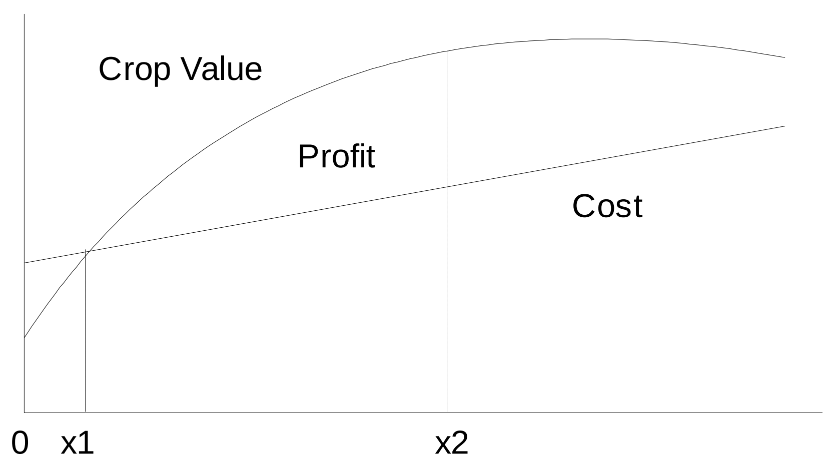
T = F + Px * X

where total cost (T) is a linear function of fertilizer amount, the slope of the line is given by the price of fertilizer and the intercept by the amount of fixed costs involved (F).

A plot of the value and cost functions illustrates the areas where use of fertilizer is profitable. Net profit can only be generated by use of a fertilizer amount equal or greater than 0-x1. Fertilizer should not be used if the value curve is lower throughout than the total cost curve for fertilizer plus fixed costs (F). With fixed costs involved, the amount of fertilizer that can be used profitably is greater than zero or an amount equal to or greater than 0-x1. For fertilizer input greater than 0-x1, crop value exceeds costs and net profit is generated. Profit from fertilizer application can be increased until input reaches the value of 0-x2. This is the level which maximizes profit. At 0-x2 the difference between value and cost is at a maximum.

For each production function the amount of fertilizer which maximizes profit can be found by obtaining the first derivative and setting it equal to the price ratio (PR).

PR = Price per unit of fertilizer / Price per unit of yield
(from Barreto and Westerman, 1985)



Soil Testing for Different Nutrients

Total Nitrogen in Soils:
Surface soils: 0.05 to 0.10%
precision 0.01% = +/- 200 lb/ac

Why would we run total N on soils if the precision is so low?

- long term experiments (differences greater than 200 lb N/ac)
- C:N relationships at the same level of precision

A. Kjeldahl 1883 (organic + inorganic N)
1. digestion to convert organic N to NH_4
2. determination of NH_4 in the digest

(N pool consists of NO_3^-, NH_4^+, NO_2^-, organic N)

devardas: reducing agent, that is a finely powdered mixture of metals that act as a source of donor electrons to reduce NO_3^- and NO_2^- to ammonium

devardas

N pool + K_2SO_4, $CuSO_4$, Se, H_2SO_4 -----> $(NH_4)_2SO_4$
Digest

$(NH_4)_2SO_4$ + NaOH ----> NH_3 + $NaSO_4$ (catch in boric acid)
titrate

K_2SO_4 is used to raise the temperature of the digest (increases speed and completeness of the conversion of organic N to NH_4)

Se, Cu are used as catalysts to promote the oxidation of the organic matter

NO_3 and NO_2 are not included in the total N analysis from dry combustion, but it does not matter since there will be less than 20 lb N /ac as NO_3 and the total N procedure detects to only +/- 200 lbs N/ac

e.g.

0.01	+/- 200 lbs/ac	20 lbs N/ac as NO_3 is lost between 0.01 and 0.02 %total N
0.02	+/- 400 lbs/ac	because its small value exceeded the detection limits.

On a KCl extract: (have both NH_4 and NO_3 in the extract)

1. distill over once (to collect NH_4)
2. add devardas alloy (distill over again to collect NO_3 and NO_2)

devardas alloy: acts as a source of donor electrons to reduce NO_2 and NO_3 to NH_4

problems: N-N and N-O compounds

Dry Combustion (Dumas 1831)

Sample heated with CuO at high temperature (above 600 °C) in a stream of purified CO_2 and the gasses lost are passed over hot Cu to reduce nitrogen to N_2 and then over CuO to convert CO to CO_2. The N_2-CO_2 mixture is collected in a nitrometer containing concentrated alkali which absorbs the CO_2 and the volume of N_2 gas is measured.

$2NH_4Cl + 4CuO \text{ -----> } N_2 + 4H_2O + 2CuCl + 2\,Cu\ (CO_2)$

problems: heterocyclic compounds (pyridine) are difficult to burn

<u>NA-1500</u>

Sample weighed in a tin (Sn) container

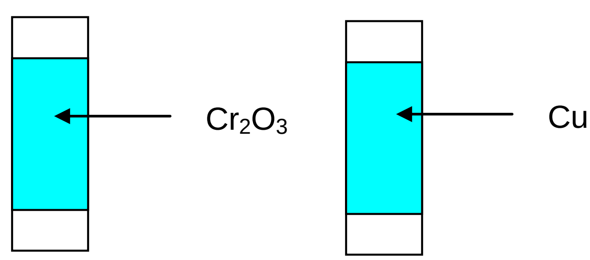
Combustion reactor enriched with pure oxygen (sample oxidation) 1020 °C in combustion tube

Reaches 1700 °C during flash combustion (complete oxidation)

Flash combustion converts all organic and inorganic substances into elemental gases (stable compounds combusted

Combustion products carried by He pass through an oxidation catalyst of Chromium oxide

Combustion Reactor **Reduction Reactor**



$CO + 1/2O_2 = CO_2$ (Cr_2O_3 is accepting electrons)

Cr_2O_3 ensures complete combustion (oxidation) of all organic materials

$NO_x \longrightarrow N_2$ (Cu is donating electrons)

Combustion products (CO, N, NO) and water pass through a reduction reactor (metallic Cu).

Excess O_2 is removed in the reduction reactor (Cu at 650 C).

N oxides from the combustion tube are reduced to elemental N_2 .

Taking CO, N, NOx and converting them to CO_2, N_2.

Gases are separated in a chromatographic column and detected using a thermal conductivity detector (TCD) which gives an output signal proportional to the concentration of the CO_2 and N_2 present.

Rittenberg Method (N_2 gas from sample)

$2NH_4Cl + 3NaBrO + 2NaOH \dashrightarrow N_2 + 5H_2O + 3NaBr + 2NaCl$
sodium hypobromite

Inorganic Nitrogen

NO_3-N
Inorganic N may represent only a small fraction < 2% of the total N in soils (Bremner, 1965)

Nitrate testing does not work in Illinois. Why?
high OM
high mineralization potential
consideration of NH_4
R-NH_2 groups from N cycle

- rapid changes (biological transformations) affect inorganic N analysis

NO_3-N and NO_2-N
1. Phenoldisulfonic acid or chromotrophic acid
   - interference of organic matter, Cl and Fe have affected these colorimetric procedures
2. Selective ion electrodes
   - interference of Cl
   - $(NH_4)_2SO_4$, $AgSO_4$ extracting solution: Ag used to precipitate Cl
3. Cadmium reduction
   - 2 M KCl extract (colorimetric procedure) - samples are stable for several months if stored at low temperatures

- not subject to interference, extremely sensitive making dilution possible.
- NO_3 reduced to NO_2 by passing through a column of copperized Cd
- NO_2 reacts well with the diazotizing reagent (sulfanilamide) and NO_3 does not, thus explaining the need for reducing NO_3 to NO_2 for analysis using the Griess-Ilosvay method

4. Steam distillation with Devardas alloy (reductant) reduce NO_2 and NO_3 to NH_4

NH_4-N

Bremner (1959) stated soils contain a large amount of fixed (non-exchangeable) NH_4. Defined as the NH_4 that cannot be replaced by a neutral K salt solution present as NH_4 ions in interlayer positions of 2:1 type clay minerals.

Air-drying can lead to small but significant changes in NH_4-N

1. Steam distillation with MgO (alkaline reagent) color: indophenol blue
2. 2 M KCl (indophenol blue) phenol and NH_3 react to form an intense blue color
3. Ammonia gas sensing electrodes

Problems in N analysis:

- -accuracy is measured by the least precise measurement.
- -weight of the soil is the largest error (propagates through to +/- 0.01%N)

0.01% N = +/- 100 ppm (0.01* 10000)

total N in soils 0.10 = 1000 ppm +/- 100 ppm
inorganic N in soils 0.002 = 20 ppm +/- 1 ppm

Total N	Inorganic N	Organic N?
1000 ppm	20 ppm	980 ppm

1. Inorganic N is not determined on a percent basis because it is done on an aliquot basis.
2. Cannot subtract 20 from 1000 to get organic N (determined on a different basis).
3. Unrealistic because of the incompatibility of error terms.
4. Organic-N is difficult to determine (by subtraction, we have an extremely poor estimate).

Organic N

Procedures exist, but are unreliable and are not reproducible.

Mineralizable N

1. Leach with $CaCl_2$ - dissolves all the soluble N (NO_3 and NO_2)
2. Incubate the soil - over time - to determine the amount of NO_3 that has been mineralized (set period of time under set conditions)
3. Leach with $CaCl_2$ again (sample now has NO_3)
4. Determine concentration

Phosphorus Soil Index Procedures

Bray and Kurtz P-1

0.025 N HCl and 0.03N NH_4F (pH = 3.15)

Designed to remove easily acid soluble forms of P, largely calcium phosphates and a portion of the aluminum and iron phosphates. The NH_4F dissolves aluminum and iron phosphates by its complex ion formation with these metal ions in acid solution. This method has proved to be very successful in acid soils.

In view of the high efficiency of the fluoride ion in dissolving phosphate, Bray (1945) recommended the use of this reagent together with HCl as an extractant (effectively removed sorbed phosphate).

Al reacts with F and inactivates Al leaving P in solution. Use of NH_4F will increase extractable P, or stabilize P (restricting Al from precipitating with P because of the solubility constants).

Mehlich II

0.20 NH_4Cl, 0.2N CH_3COOH, 0.015N NH_4F and 0.012N HCl (pH = 2.5)

The concentrations of HCl and NH_4F used in Mehlich are half that used in Bray and Kurtz P-1. However this extracting solution also contains NH_4Cl and acetic acid which probably buffer the solution (i.e., keeps its acidic strength for a longer period of time). Therefore, it can dissolve more of the P in apatite.

Mehlich III

0.2N CH_3COOH, 0.015N NH_4F, 0.25N NH_4NO_3, 0.13N HNO_3, 0.001M EDTA (pH = 2.4)

Designed to be applicable across a wide range of soil properties ranging in reaction from acid to basic. Can also be used for exchangeable cations (Ca and Mg). Because this extractant is so acid, there is some concern that the soil can be dissolved, increasing exchangeable amounts.

Olsen
0.5N $NaHCO_3$ (pH = 8.5)

This extracting solution is used to extract phosphorus in calcareous soils. It will theoretically extract the phosphorus available to plants in high pH soils. This extractant decreases the concentration of Ca in solution by causing precipitation of Ca as $CaCO_3$; as a result, the concentration of P in solution increases.

Essentially, increase the activity of CO_3 in solution which reacts with Ca, and $CaCO_3$ precipitates.

Nelson et al. (1953) (Mehlich I and or "Double Acid")
0.05N HCl and 0.025N H_2SO_4 (pH<2.0)

Found to be effective in high P-fixing soils of North Carolina. H_2SO_4 was found to be more effective than HCl in dissolving Fe phosphates but that both were equal regarding Al phosphates.

Extractable P discussion:

The pH of the extracting solution is an indicator of what forms of P will be extracted. However, this should be used with caution as the shaking time is important in terms of reaching an equilibrium.

Susuki et al. (1963) noted that 0.1N HCl extractable P was positively correlated with Ca-P.

$NaHCO_3$ was negatively correlated with Ca-P on 17 Michigan soils (pH 4.8-7.8)

What would happen if Bray P-1 was used on a calcareous soil?

The lime in the calcareous soil would neutralize the acidity in the extracting solution thus decreasing its ability to extract the Fe and Al-P forms which would be available at that soils pH.

Calibrations for the Bray-Kurtz P-1, Mehlich III and Olsen soil tests (Tisdale, Nelson, Beaton and Havlin, 1993)

P sufficiency level	Bray-Kurtz P-1	Mehlich III	Olsen	Fertilizer P Recommendation	
				lb P_2O_5/ac	kg P/ha
Very low	<5	<7	<3	50	25
Low	6-12	8-14	4-7	30	15
Medium	13-25	15-28	8-11	15	8
High	>25	>28	>12	0	0

Total P ?

Analysis for total P in soils was abandoned in the early 1900's as scientists recognized that this analysis was not correlated with plant availability. For this reason various strengths of extracting solutions were evaluated for specific soils at selected soil pH that mirrored what the plant would find in soil solution. All of these are indices that determine orthophosphate concentrations (from the dissolution of precipitated forms). Attempts to correlate extractable P (x - procedure) with total P will result in meaningless information. Total P (strong acid digest) will in essence dissolve P forms that will not be available at that soils specific pH.

Nutrient Interactions

Bray and Nye:
K applications on soils with high K by mass action displace Al^{+++} which complexes with P inducing a net P deficiency (pH < 6.0)

P and Zinc
Zinc deficiencies attributed to the immobilization of zinc owing to the increase in the concentrations of P in the roots above the threshold values.
Depression of zinc concentrations in plant tissue by P (interaction occurred in the plant and not in the soil).

Source of N by P
NO_3^- uptake (increase pH)
NH_4^+ uptake (decrease pH)

Spectroscopy

Light is considered to be a stream of particles. The discrete particles or units of energy are called photons or quanta. A photon of blue light contains much more energy than a photon of red light.

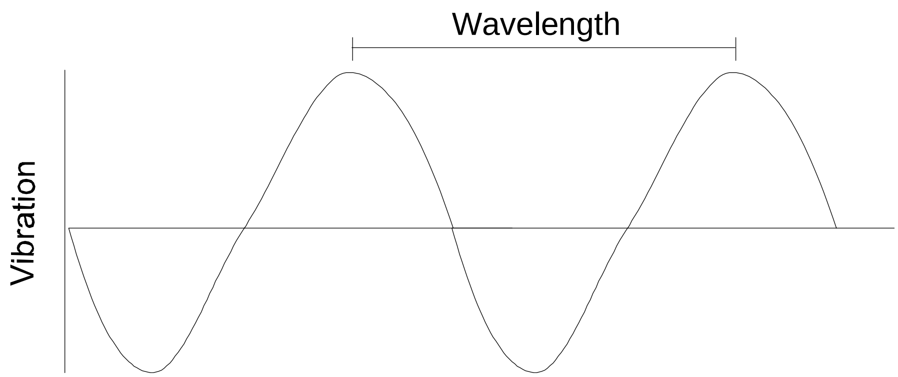
<u>Interaction of light with matter</u>
1nm = 1mu (millimicron) = 10A (angstrom) = 10^{-7} cm

The interaction of radiation with matter may result in the absorption of incident radiation, emission of fluorescence or phosphorescence, scattering into new directions, rotation of the plane of polarization, or other changes. Each of these interactions can provide useful information about the nature of the same in which they occur (Tinoco et al. 1978).

Color is characteristic of the spectrum (in the visible region) of light transmitted by the substance when white light (or sunlight) shines through it, or when light is reflected from it.

<0.01	Gamma (non particulate photons)	
0.01-10	X-Ray (photons)	
10-380	Ultraviolet	
Wavelength absorbed, nm	Absorbed Color	Transmitted Color (Complement)
380-450	Violet	Yellow-green
450-495	Blue	Yellow
495-570	Green	Violet
570-590	Yellow	Blue
590-620	Orange	Green-blue
620-750	Red	Blue-green
750-$1x10^{6}$	Infrared	
$1x10^{6}$-$1x10^{11}$	Micro and short radio waves	
>$1x10^{11}$	Radio, FM TV	

Wavelength: distance of one complete cycle
Frequency: the number of cycles passing a fixed point per unit time



λ = c/v

λ = wavelength in cm
v = frequency in sec^{-1} or hertz (Hz)
c = velocity of light in a vacuum ($3x10^{10}$ cm/sec)

Electromagnetic radiation possesses a certain amount of energy. The energy of a unit of radiation, called the **photon** is related to the frequency by **E = hv = hc/λ**

where E is the energy of the photon in ergs
h is Planck's constant 6.62 x 10^{-27} erg-sec

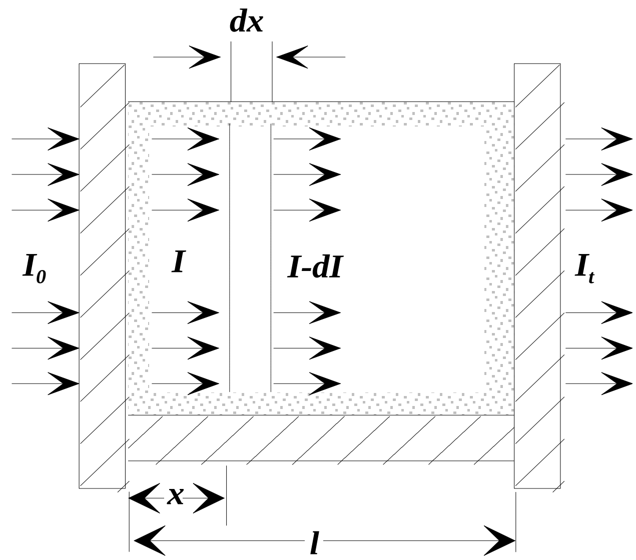
The shorter the wavelength or the greater the frequency, the greater the energy. Energy of a single photon (E) is proportional to its frequency (v) or inversely proportional to its wavelength.

If a molecule absorbs radiation, it is raised to a higher energy level, with the increase in energy being equal to the energy of the absorbed radiation (hλ).

The relative energy levels of the three transition processes are in the order electronic > vibrational > rotational.

If the electromagnetic force results in a change in the arrangement of the electrons in a molecule, we say that a transition to a new electronic state has occurred. The absorbed photon results in the excitation of the molecule from its normal or ground state, G, to a higher energy or excited electronic state, E. The excited electronic state has a rearranged electron distribution.

When considering absorbing substances that are either liquids, solids or gases, each will have a characteristic transmission of light. Suppose that light of intensity ***Io*** is incident from the left, propagates along the **x** direction and exits from the right with decreased intensity ***It.*** At any point ***x*** within the sample, it has intensity ***I***, which will decrease smoothly from left to right.

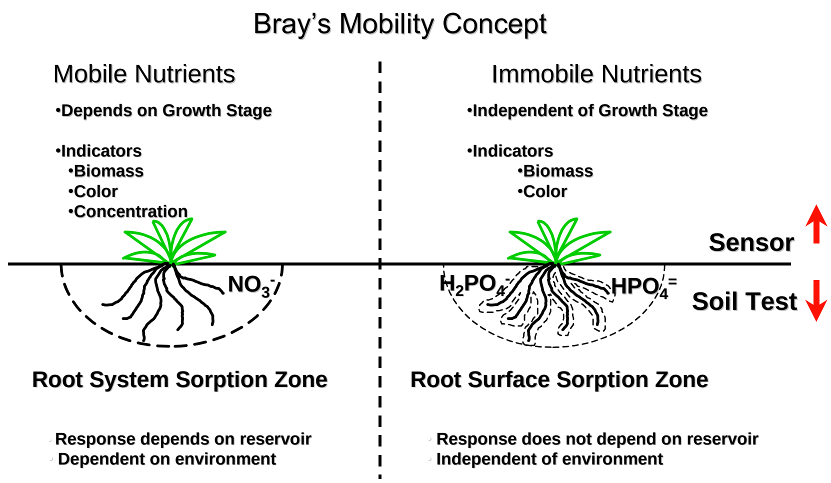


If the sample is homogeneous, the fractional decrease in the light intensity is the same across a small interval dx, regardless of the value of x. The decrease for a solution depends linearly on the concentration of the absorbing substance.

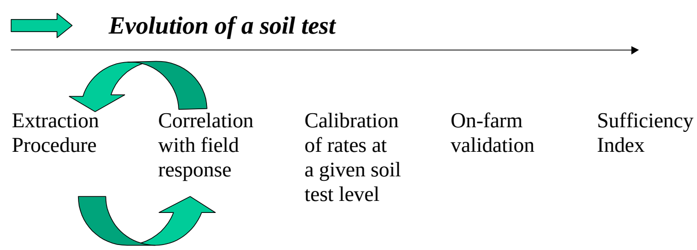
- Not all molecules can absorb in the infrared region
- The wavelength of absorption is a measure of the energy required for the transition
- Each molecule will have a complete absorption spectrum unique to that molecule, so a 'fingerprint' of the molecule is obtained

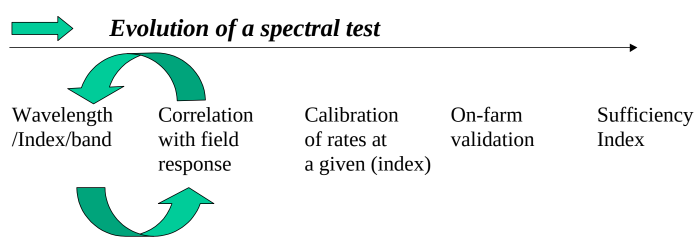
Soil Testing versus Non-destructive Sensor Based VRT

Soil Testing	Sensor Based VRT
low resolution	high resolution
Chemistry-Site specific	Site specific
Reliable and tested	untested
Years of correlation/calibration	new technology
Economical	high potential of being economical
Crop specific	untested
Variety specific	untested
Management specific row spacing/tillage	untested
Nutrient interactions	untested
NA	weed recognition
NA	time of day
NA	shadow/clouds
NA	direction of travel



Root system and root sorption zones as related to mobile and immobile nutrients and the use of soil and sensor tests.





Experimental Design/Soil Testing and Field Variability

Replication gradients: Do slopes (up and down or side to side) in fields adequately represent which direction a particular nutrient will increase or decrease? Are Blocks actually needed?

Number of Replications: If plot size remains large and greater than the field element size, increasing the number of replications will unlikely lead to increased power for detecting differences between treatments.

Plot Size: Because field variability has been demonstrated to be somewhere around 9 square feet, field experiments as we now know them must change. Common plot sizes are between 250 to 1000 square feet. Plant breeders have generally employed much smaller plot sizes and because of this, CV's from their work are generally smaller than that found in fertility/weed type trials.

10. MICRONUTRIENTS

Chlorine

Documented as essential element by Broyer et al. (1954). Deficiencies are rare, and appear to be limited to in-land regions that have not required K fertilization.

Chlorine is absorbed as Cl^-. Cl is mobile in the soil and in plants.

In Plants

Average concentration in plants ranges from 1 to 20 g kg^{-1} (0.1 to 2%), while the concentration required for optimum growth ranges from 150-300 mg kg^{-1} (0.015-0.03%).

Cl functions in plants mainly as a mobile anion in processes related to osmotic pressure regulation (stomatal openings) and charge compensation (as a counter ion in cation transport).

General crop requirement is about 1 unit Cl for 10,000 units of dry matter produced, or about 2-3 kg ha^{-1}. (Oklahoma receives about 11 lb Cl $acre^{-1}$ yr^{-1} annually in rainfall.)

Critical deficiency concentration for optimum growth is reported to range from 70 mg kg^{-1} in tomato to 1000 mg kg^{-1} in kiwi. Recent studies suggest the critical toxicity concentrations range from 3-5 g kg^{-1} in sensitive plant species and 20-40 g kg^{-1} in tolerant plant species.

Deficiency symptoms include reduced root growth, wilting and curling of leaves and leaflets, bronzing and chlorosis similar to that for Mn deficiency.

In Soils

Critical soil test level of 43.5 kg ha^{-1} of Cl in the upper 60 cm suggested by Fixen for identifying responsive soils.

Most common fertilizer source of Cl is muriate of potash (0-0-62), KCl.

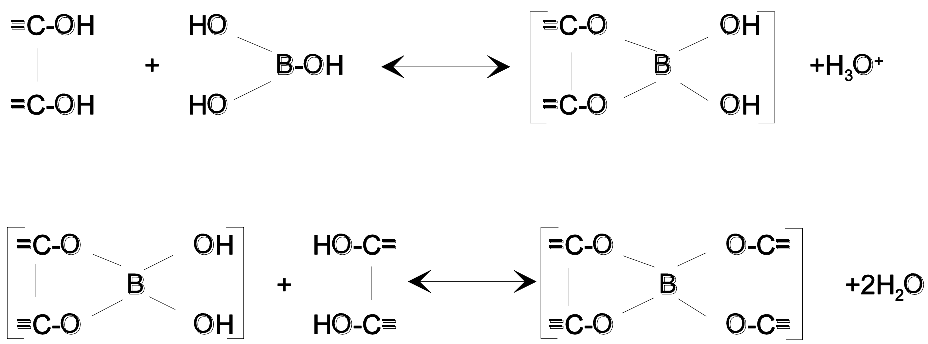
Boron

In plants

Critical deficiency concentration ranges from 5-10 ppm in monocotyledons to 50-70 ppm in dicotyledons, to as high as 100 ppm in latex producing plants such as dandelion.

The critical toxicity concentration is not much higher than the deficiency concentration. In corn it is about 100 ppm and cucumbers 400 ppm.

The main function of boron is in cell growth and formation. The action appears to be in binding sugars together in cis-diol ester linkages, resulting in B being strongly complexed in cell walls. An example of this is shown in the following generalized reactions.



Boron is immobile in plants.

In soils

Boron in aqueous solution is present mainly as undissociated boric acid, $B(OH)_3$. It dissociates according to the equation:

$B(OH)_3 + HOH \longrightarrow B(OH)^-_4 + H^+ \quad K_{eq} = 10^{-9.2}$

$[B(OH)^-_4][H^+]/[B(OH)_3] = 10^{-9.2}$
and, rearranging we have

$[B(OH)^-_4]/[B(OH)_3] = 10^{-9.2}/[H^+]$
taking the log of both sides, results in

$\log [B(OH)^-_4]/[B(OH)_3] = -9.2 - \log [H^+]$, or

$\log [B(OH)^-_4]/[B(OH)_3] = -9.2 + pH$

and at pH 7.2, $\log [B(OH)^-_4]/[B(OH)_3] = -2$, so there is 100 times less $B(OH)^-_4$ than $[B(OH)_3]$(the ratio is .01), verifying that $B(OH)_3$ is the predominate B species in the soil solution of agricultural soils. Hence, unlike all other nutrients plants obtain from the soil, B is apparently taken up as the uncharged $B(OH)_3$.

Boron is mobile in soils.

Molybdenum

In plants

Found in plants primarily as the oxyanion (oxidation state VI), but also as Mo (V) and (IV).

Mo is absorbed as $MoO_4^=$, since it is the dominant species above pH 4.5 (see Fig. 10.1 below, taken from Micronutrients in Agriculture)

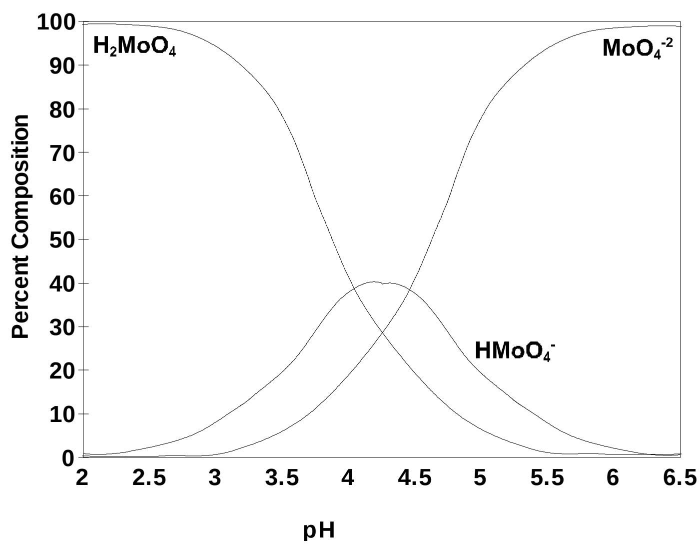


Figure 10.1. Relationship of molybdate ion species to pH.

Mo functions in electron transfer in plants, primarily in nitrate reductase (see Fig. 10.2 from Micronutrients in Agriculture) in non-legumes and nitrogenase (see Fig. 10.3 from Micronutrients in Agriculture) in legumes.

In each case N reduction is involved. Plants supplied with NH_4^+ have a much lower demand for Mo.

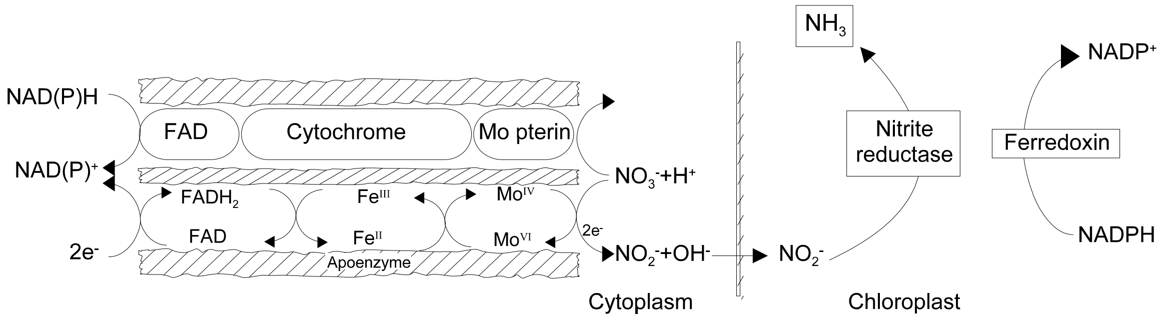


Figure 10.2. Structural model of the nitrate reductase with its two subunits. Each subunit contains three prosthetic groups: FAD, heme-Fe, and Mo-pterin. (Based on Campbell, 1988)

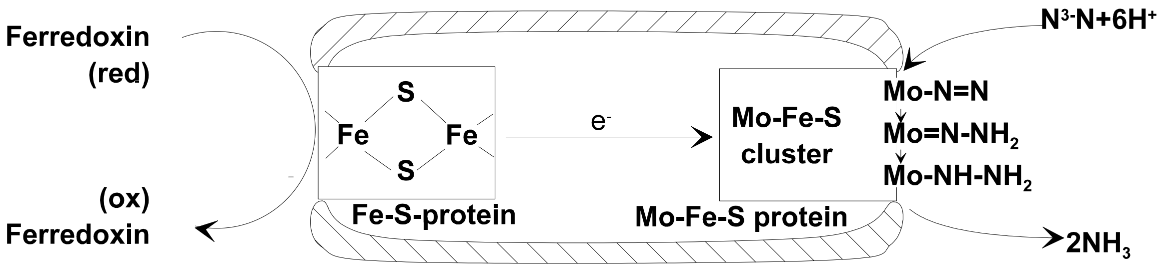


Figure 10.3. Model of the stepwise N_2 reduction by the Mo-containing nitrogenase.

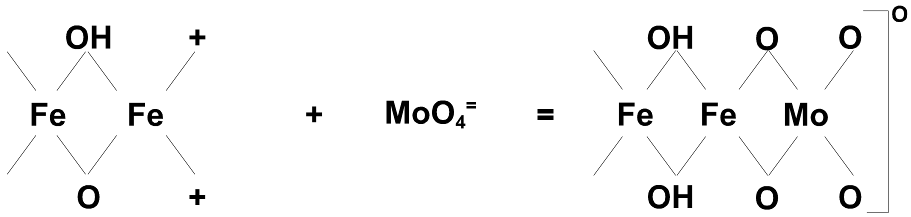
The critical deficiency level ranges from 0.1 to 1 ppm in leaves, whereas critical toxicity concentrations range from 100 to 1,000 ppm.

Mo is readily translocated and deficiency symptoms are normally found in the oldest leaves. For legumes the symptoms are like that for N deficiency. In non-legumes the condition of “whip tail”, where leaf blades are reduced and irregularly formed is common together with interveinal mottling, marginal chlorosis, and accumulation of NO_3.

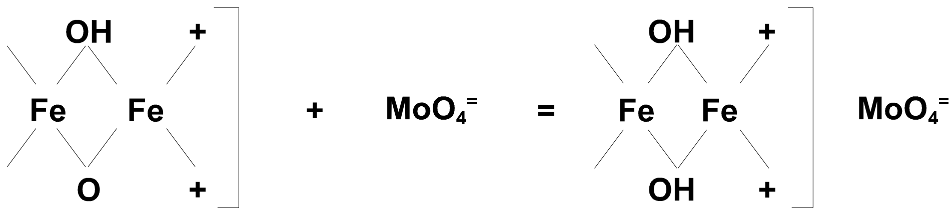
In Soils

The normal concentration of Mo is quite low, ranging from about 1 to 10 ppm.

Deficiencies are uncommon, but are more likely in acid than alkaline soils apparently because $MoO_4^{=}$ is strongly adsorbed to iron oxide surfaces in acid soils, either as a result of chemical bonding or simple anion exchange associated with pH dependent charges in acid soils.. Liming these acid soils increases the availability of Mo and is a common procedure for correcting Mo deficiency.



Bonding mechanisms



Exchange mechanisms

Iron

In Plants

The deficiency concentration of Fe in mature plant tissue is about 50 ppm. Total Fe may be much higher than this level, even in Fe-chlorotic plants because Fe in the plant is not always all metabolically active. HCl extractable Fe is sometimes assumed to be metabolically active and a better guide to plant sufficiency. Fe in plants is found in the Fe^{+++} state, any Fe^{++} is present only as a transitory state (free Fe^{++} is phytotoxic).

Fe functions as a co-enzyme, in important electron transfer enzymes, and the formation and component of enzymes that are precursors to chlorophyll. The two important categories of enzymes are the Fe-S proteins and the heme proteins.

Heme proteins are characterized by a tetrapyrrole ring structure that has Fe as the centrally coordinated metal. Fe is involved as a co-factor in the synthesis of protoporphyrin, which is the precursor to both heme and chlorophyll as depicted in Fig. 10.4.

The Fe-S proteins are formed when Fe is coordinated to the thiol group of cysteine, or inorganic S, or both (see illustration below).

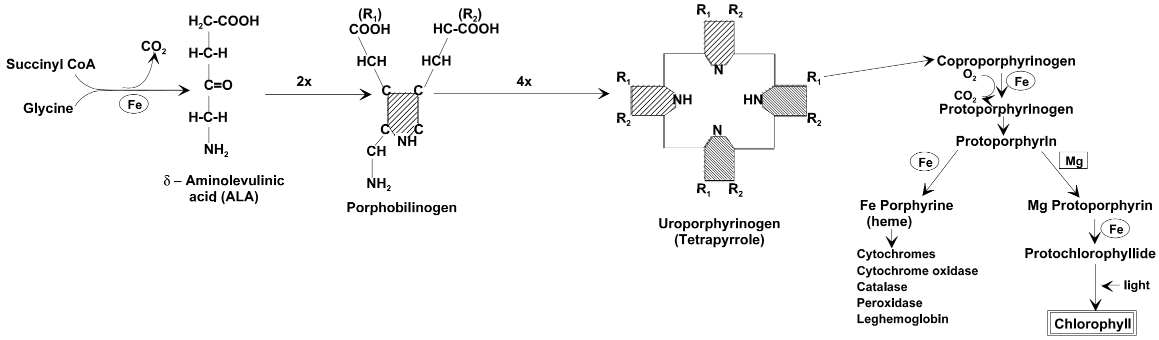
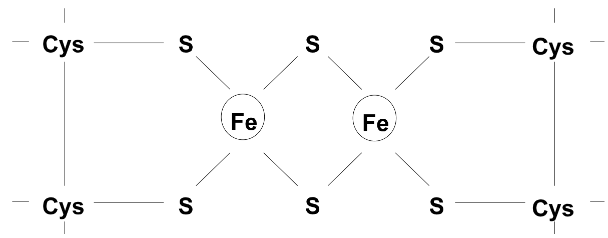


Figure 10.4. Role of Fe in biosynthesis of heme coenzymes and chlorophyll.

The best known Fe-S protein is ferredoxin, important in both nitrate reductase and nitrogenase. Other Fe-S proteins have important functions in the citric acid cycle, respiration, SO_4 and SO_3 reduction, and chlorophyll (see Fig. 10.5).



Because Fe is strongly bound it is not easily translocated and should be considered immobile in plants. The characteristic deficiency symptoms are interveinal chlorosis in the new leaves of growing plants.

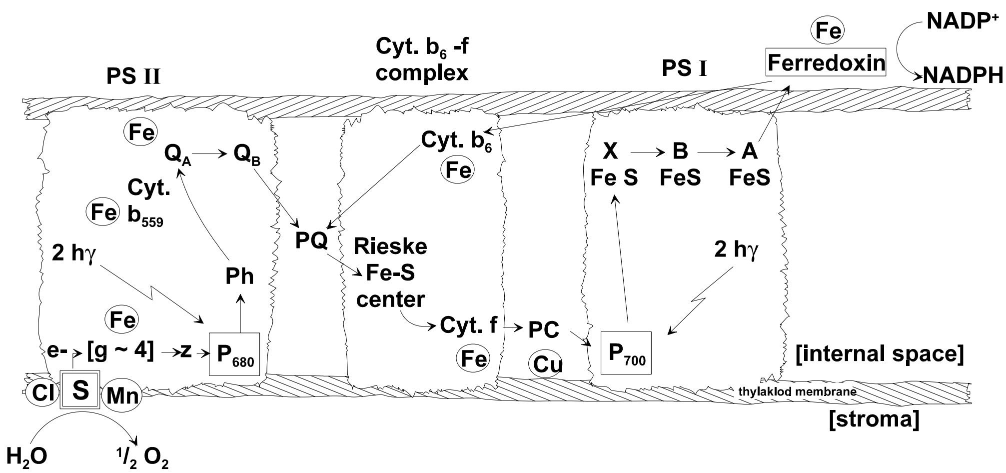


Figure 10.5. Role of Fe and other micronutrients in the photosynthetic electron transport chain. PS=photosystem (PS I, PS, II); S = water-splitting enzyme; g~4 = non-heme Fe-S group; Z = tyrosine residue-containing electron donor to P 680; P 680 = primary electron donor of PS I; Ph = primary electron acceptor pheophytin; QA = quinone-Fe complex; PQ = plastoquinone; Cyt = cytochrome; PC = plastocyanin; and X, B, and A = Fe4S4 proteins. Schematically drawn as Z scheme. (Based on Terry and Abadia, 1986; Rutherford, 1989.)

Iron in soil

Soils contain about 1 to 5% iron, which is many fold more than that required for plants, however, in aerobic environments Fe is mainly present in the Fe^{+++} oxidation state as iron oxide (written as either $Fe_2O_3 \cdot nH_2O$ or $Fe(OH)_3$) which is very insoluble. The amount of Fe^{+++} in aqueous solution is governed by

$Fe(OH)_3 \longleftrightarrow Fe^{+++} + 3(OH)$, for which the equilibrium condition is expressed in molar concentrations as

$$(Fe^{+++})(OH)^3 / Fe(OH)_3 = 10^{-39.4} \quad (1)$$

Since $Fe(OH)_3$ is a solid, it has an activity of unity (1) and the equation becomes

$$(Fe^{+++})\ (OH)^3 = 10^{-39.4} \quad (2)$$

and the value $10^{-39.4}$, instead of being called the equilibrium constant (K_{eq}), is called the solubility product constant (K_{sp}). The concentration of Fe^{+++} in solution is given by

$$Fe^{+++} = 10^{-39.4} / (OH)^3 \quad (3)$$

and at pH = 7.0,
$Fe^{+++} = 10^{-39.4} / (10^{-7})^3$; $=10^{-39.4} / 10^{-21}$; $= 10^{-18.4}$ moles/liter.

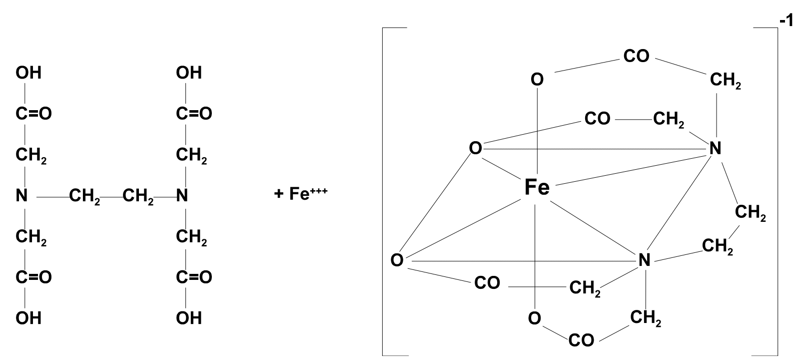
Since the atomic weight of Fe is 55.85, the concentration in ppm would be
55.85 g/mole x 1000 mg/g x $10^{-18.4}$ moles/liter =
55.85 x $10^{-15.4}$ mg/liter; = 55.85 x $10^{-15.4}$ ppm

The plant's dilemma: The concentration of Fe necessary to provide plants a sufficient amount of Fe by passive uptake has been suggested to be about 10^{-6} moles/liter. At pH 7 the soil supply, as identified by equation (3) is 12 orders of magnitude too small! Even at pH 5 the difference between supply and requirement is still 6 orders of magnitude too small (students should verify this by calculation).

Two things are obvious; (a) the plant cannot get enough Fe by passive uptake from the soil solution, and (b) there will be a 1000 fold decrease in supply of available Fe from $Fe(OH)_3$ in the soil with each unit increase in soil pH. Consequently, one should expect Fe deficiency to be most common in high pH soils and least in acid soils. This is in fact what is observed. But, how do plants get enough Fe, and why are not all plants subject to Fe chlorosis when grown in neutral and alkaline soils?

Part of the solution to the plant's dilemma of getting enough Fe from the soil is found in chemical reactions called metal chelation. This is the process whereby metals are bound in ring-like structures of organic compounds. The more rings in the structure that the metal is a part of, the stronger the metal is bound. The chemical forces involved are mainly coordinate bonds where the metal acts as a Lewis acid (electron acceptor) and the chelating material has functional groups (sometimes called ligands), like amino, hydroxyl, and phenolic groups that act as Lewis bases (electron donor). The transition metals seek to fill the d orbital to attain the electron configuration of the inert gas of that period, krypton. Heme and chlorophyll are examples of natural chelates that hold Fe and Mg as a centrally coordinated atom.

As an example of chelates, consider the common synthetic chelate EDTA. EDTA stands for the chemical compound ethylenediaminetetraacetic acid.



Note in the Fe-EDTA complex there are five rings formed with Fe, and that the complex has a single negative charge. As a result, the complex is mobile in the soil and so is the Fe it is carrying. Two other common synthetic chelates are DTPA (commonly used in micronutrient metal soil test extraction procedures) and EDDHA (a commercial chelate for supplying Fe in calcareous soils).

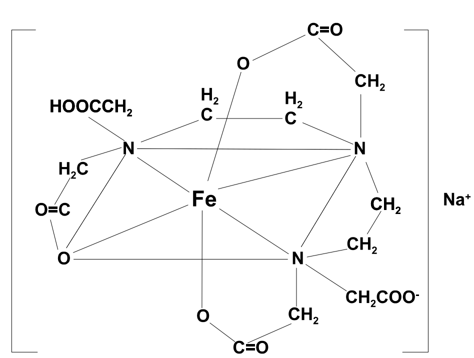


Figure 10.6. Sequestrene 330 Fe (DTPA) is monosodium hydrogen ferric diethylenetriamine pentaacetate, which has a molecular weight of 468.

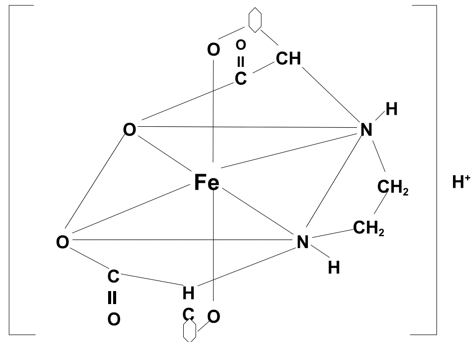


Figure 10.7. Chel 138 HFe (EDDHA) is hydrogen ferric ethylene bis (alpha-imino-2-hydroxy-phenyl-acetic acid), which has a molecular weight of 413.

Two important natural chelating compounds in plants are citrate and hydroxamate. Citrate is important as a carrier for the micronutrient metals Cu, Zn, Fe, and Mn. Hydroxamate is a siderophore (produced by micoorganisms) believed responsible for complexing Fe in calcareous soils and increasing its availability to plants.

The reaction of chelates with metals to form soluble metal chelates is given by the general equilibrium reaction

$$M + L = ML \tag{4}$$

Where M refers to the metal concentration, L the chelate (or Ligands) concentration, and ML the concentration of metal chelate. At equilibrium the relative amounts of each present are described in relation to the equilibrium constant as

$$ML / (M)(L) = K_{eq} \tag{5}$$

Since the equilibrium condition strongly favors the reaction to the right (equation 4), K_{eq} is called the formation constant K_f. The formation constants for citrate and hydroxamate are $10^{12.2}$ and 10^{32}, respectively.

The benefit of chelates for improving Fe availability can be demonstrated by considering just the reactions involved in chelates complexing Fe from $Fe(OH)_3$. If the reactions are considered simultaneously they can be written as follows for an equilibrium situation where a weak chelate such as citrate is present.

		Log$_{10}$ K
$Fe(OH)_3$ ————> Fe^{+++} + $3(OH^-)$		-39.4
Fe^{+++} + L ————> FeL		12.2
$3(OH) + 3H^+$ —————————> $3H_2O$		42
$Fe(OH)_3 + L + 3H^+$ ————> FeL		14.8

$Fe(OH)_3 + L + 3H^+$ ————> FeL $\quad 10^{14.8}$ (6)

Equation (6) was obtained by summing the equations (canceling components that appear as both reactant and product of the reactions) and the $\log_{10}$ of the solubility and formation constants. The concentration of products and reactants can be expressed for the general reaction in terms of the equilibrium constant as

$(FeL) / (L)(H^+)^3 = 10^{14.8}$
or in terms of (FeL) as
$(FeL) = 10^{14.8} \times (L)(H^+)^3$

If the soil pH is 7 and the concentration of citrate is 10^{-6} , then the concentration of FeL is

$(FeL) = 10^{14.8} \times (10^{-6})(10^{-7})^3$
$(FeL) = 10^{-12.2}$

Compared to the concentration of Fe^{+++} in solution from $Fe(OH)_3$ dissolving, which is $10^{-18.4}$, this is an improvement of $10^{6.2}$ ($10^{-12.2}$ / $10^{-18.4}$). In other words, the presence of even a weak chelating agent like citrate has improved the availability of iron a million fold!

One should be aware, that in the case of a metal nutrient like Fe, the concentration of FeL in the soil solution is mainly a function of the formation constant (K_f) and the concentration of L since the other factors are constant. For example, consider Eq. (5)

$ML / (M)(L) = K_{eq}$
This can be rewritten as
$ML = K_{eq} (M)(L)$

Where M is Fe^{+++}, and is a constant identified by the solution pH and K_{sp} for $Fe(OH)_3$. Since K_{eq} is also a constant, these can be combined into one constant, to give

$ML = K(L)$ (7)

Equation (7) identifies that any condition that results in increasing the concentration of L for complexing or chelating Fe will increase the concentration of FeL and thus the availability of Fe for the plant.

The two most obvious ways of increasing L will be by (1) drying the soil so the water soluble L will become more concentrated and, (2) producing more L in the soil solution. In fact, a common observation is that Fe chlorosis is lessened in susceptible plants when there are definite drying cycles as opposed to continuously moist soil. Also, Fe chlorosis can often be lessened by incorporating large amounts of decayed or decaying organic matter to the soil which will directly provide more L.

<u>Plant absorption of soil Fe (Dicotyledons)</u>

Until recently, the mechanisms responsible for allowing some species of plants to grow well in calcareous soils while others commonly exhibited iron chlorosis were not well understood. The observation that some dicots were “iron efficient” while others, even varieties within a species, were “iron inefficient” is explained by an adaptive response mechanism inherent in iron efficient plants. Characteristics of this mechanism, which is activated when plants are in an Fe stress situation are

1. Enhanced root-associated Fe^{+++} reduction
2. Enhanced H^+ efflux from roots
3. Accumulation of citrate in roots
4. Increased root hair development
5. Increased absorption of Fe

A description of the mechanism is illustrated in Fig. 10.8.

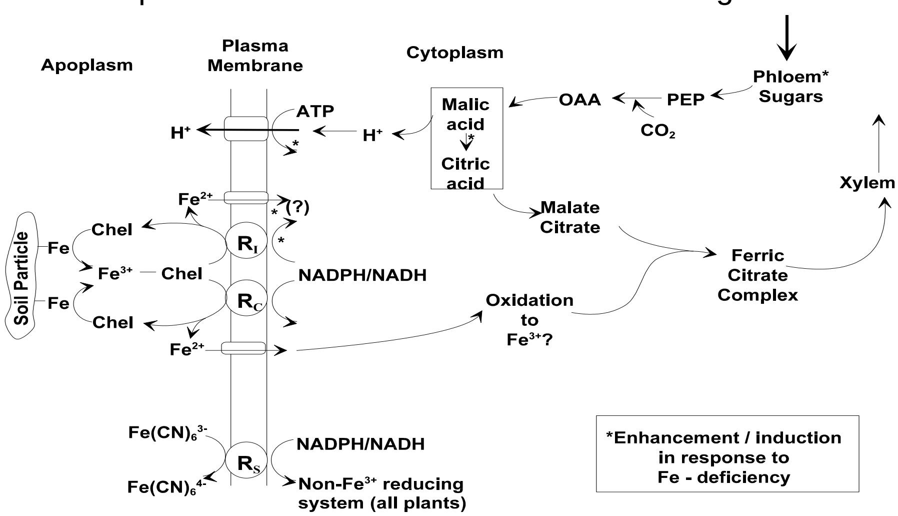


Figure 10.8. Ferric-chelate reduction-based model depicting the various physiological processes thought to be involved in the reduction of Fe(III) at the root-cell plasma membrane, and the subsequent absorption of Fe(II) ions into the root-cell of dicot and nongraminaceous monocot plants. Central to this model is the inducible Fe(III) reductase (Ri) in the plasma membrane that is induced in response to Fe deficiency. A constitutive Fe(III) reductase (Rc) is hypothesized to function under Fe-sufficient conditions.

Grasses

In grasses, Fe uptake is enhanced by a different mechanism, one that relies on the plant production of phytosiderophores. Phytosiderophore is a term used to describe plant produced chelates or complexing material that can increase the availability of Fe^{+++}. An illustration of this mechanism is provided in Fig. 10.9.

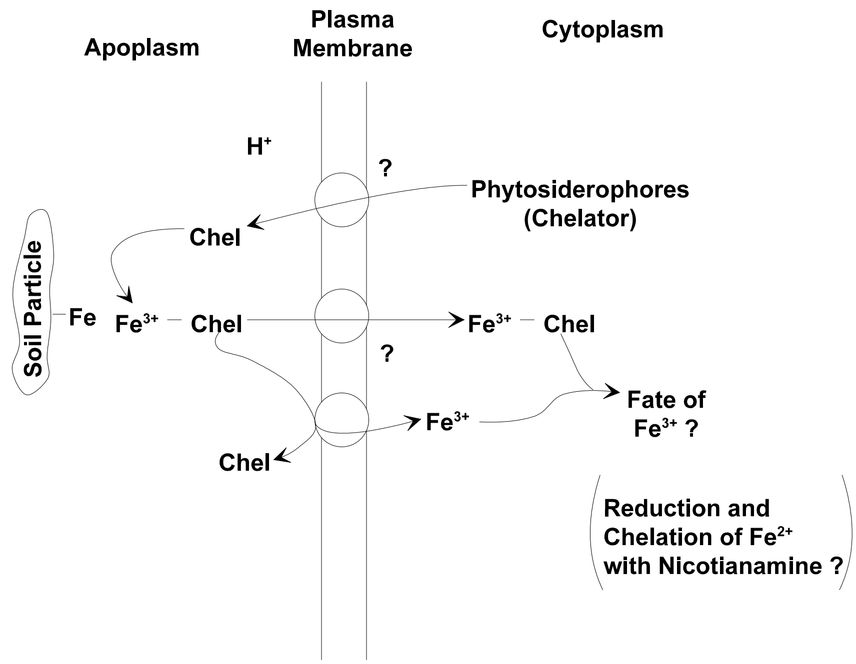


Figure 10.9. Phytosiderophore-based model for Fe absorption in grasses.

Manganese

In plants

Manganese is absorbed as Mn^{++}

The critical deficiency concentration is about 10 - 15 ppm.

Deficiency symptoms include “gray speck” in cereals, a condition that results when there is interveinal discoloration on the middle-aged leaves.

Mn functions in electron transfer processes and as a co-factor for some enzyme reactions. The most widely known function is probably its involvement in the Hill reaction of photosynthesis, wherein there is a $4e^-$ transfer that results in the splitting of water and release of O_2.

$$2H_2O + 4e^- \longrightarrow 4H^+ + O_2$$

In soils

Mn concentration in soils varies widely (20 to 3,000 ppm) depending upon parent material and the degree of soil weathering.

Mn is easily oxidized from the Mn^{++} to Mn^{+++} and Mn^{++++}, the Mn^{++} is not strongly chelated, while the Mn^{++++} may be strongly complexed. Oxides of the highest valence state are quite insoluble, hence availability can be greatly affected by redox potential. Mn uptake is improved in some plants if they undergo Fe stress and are able to respond by producing a reducing agent since it will reduce both iron and manganese to more soluble oxidation states.

Deficiencies are most common in highly weathered soils that have been recently limed.

Copper

In plants

The critical deficiency concentration is about 1 to 3 ppm.
Typical deficiency symptoms are chlorosis (white tip), necrosis, and die-back in the youngest leaves.

Cu is absorbed as Cu^{++} and is relatively immobile in the plant.

Because it undergoes oxidation-reduction reactions relatively easily, Cu is involved in electron transfer and enzyme systems much like Fe, most notably the oxidase enzymes.

In soils

Of the divalent cations, Cu^{++} is the most strongly complexed by organic matter. Deficiencies are most common in high organic (peat) soils because the Cu in the soil is bound too tightly for plants to extract adequate amounts.

As much as 98% of all the Cu^{++} in the soil solution may be present as organic complexes.

Zinc

In plants

The critical deficiency concentration is from 15 to 30 ppm, higher if leaf P is above normal.

Zn has only one oxidation state as an ion, Zn^{++}. Zn^{++} is immobile in both the plant and soil.

Zn functions as an ion for coupling enzymes and substrate. The most common Zn containing enzyme is alcohol dehydrogenase.

Deficiencies are manifested by a shortening of internodes to the extent it appears leaves are all emanating from the same point on stems (condition is called "rosetting"). In corn, chlorotic bands appear along the leaf midrib. Zn deficiency symptoms on older leaves is mainly a result of P toxicity (retranslocation of P is inhibited by Zn deficiency). Deficiencies are common in pecans and corn, but have not been reported for wheat even in very deficient soil.

In soil

Total content ranges from 10 to 30 ppm

Availability is closely linked to soil pH and organic matter content.

11. SPECIAL TOPICS

Method of Placement

1. Broadcast
   - N (in zero tillage on acid soils, not a good idea) - increased acidity.
   - Increased N needs in zero tillage (1. immobilization, 2. leaching)
   - P (in zero tillage - horizontal band)

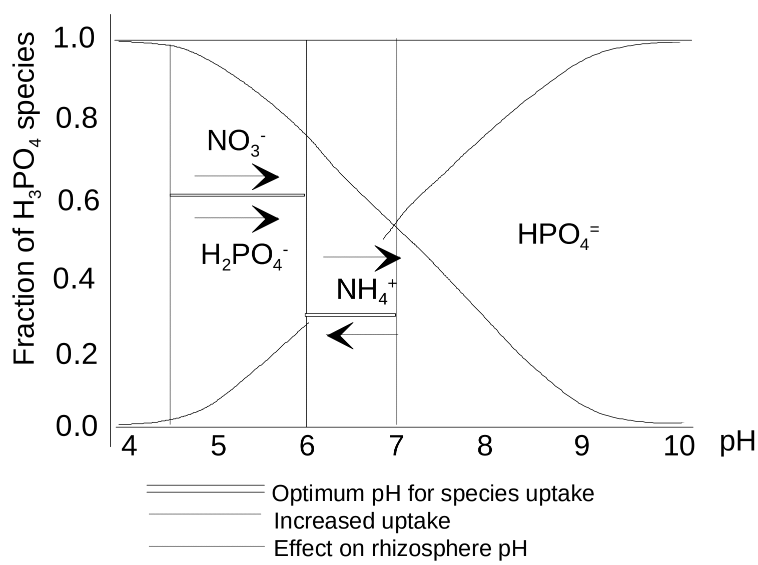
2. Band
   - Dual placement

Not a good idea on acid soils (banding P and N) - increased acidity will bring Al^{+++} and Mn^{++} into solution.

Works well in calcareous soils where increased acidity will increase micronutrient availability.

Plant needs for micronutrients can be satisfied with the localized band (synergistic effect of placing nutrients within an area, results in increased root growth within that zone: root probability).

Dual placement in calcareous soils can be beneficial when anhydrous ammonia is used as the N source and an ammonium form of N is taken up by the plant. Uptake of ammonium will result in a decreased rhizosphere pH thus enhancing P availability (H_2PO_4 : HPO_4 ratios).



3. Foliar

Foliar applications have generally been used for micronutrients where a severe deficiency warranted the expense of applying fertilizers via this method.

Topdress applications of UAN, via center pivot systems has become increasingly popular with time (apply the N when it is needed).

Acid neutralized ammonia: Anhydrous ammonia injected into the irrigation pipe followed by injections of H_2SO_4 to lower water pH. This method has not been used commercially, because of the fear associated with handling large quantities of industrial grade H_2SO_4. It does make sense when considering that AA is 1/2 the price per unit N compared to UAN.

Aqueous ammonia: Anhydrous ammonia bubbled into ditch irrigation systems without the use of H_2SO_4 (common in irrigated regions of Mexico).

Saline/Sodic Soils

Accumulated salts contain Na, Ca, Mg and Cl, SO_4, HCO_3 and CO_3. Na can be toxic to plants and acts as a dispersing agent, reducing soil drainage (slick spots).

Problem is caused by the dispersion of small size clay particles which plug soil water flow channels (destroys soil structure).

Fine textured soils with montmorillonitic clays may disperse when 15% of the exchange complex is dominated by Na.

Tropical soils high in Fe and Al oxides may require 40% Na saturation before dispersion is a problem.

Saline (Arid and semi-arid regions): Function of poor drainage accompanied by high evaporation rates (salts accumulate at the surface). Saline soils are generally 'man-made problem soils' where fertilizers have been applied and where poor drainage and or where poor quality (high salt content) water is used for irrigation. Over 2 %/yr of the arable land present in the world today is taken out of production due to salinity/sodicity problems

Sources of salt:
a. natural weathering (parent materials)
b. fertilizer
c. irrigation water
d. fossil salts (gypsiferous sediments)
e. rain (near the ocean)

Measurement:
EC (electrical conductivity) is the inverse of Resistance (ohms)
*note: water quality is measured in resistance, high purity = high resistance

a. Salinity is conventionally measured on aqueous extracts of saturated soil pastes
b. Crop tolerance to salinity is often related to the electrical conductivity or total electrolyte concentration of the saturation extract

Reagent: Sodium hexametaphosphate $(NaPO_3)_6$ 0.1%
(added to prevent precipitation of $CaCO_3$)

Saturation Extract: 200 to 400 g of soil (do not oven dry)
1. Weigh soil + container
2. Add distilled water until nearly saturated
3. Mix and allow to stand overnight
4. Weigh container + contents (record increase in weight)
5. Transfer to a Buchner filter funnel, apply vacuum and collect filtrate (if turbid, re-filter)
6. Add 1 drop of 0.1% $(NaPO_3)_6$ for each 25 ml of extract

Major solutes of interest: Ca, Mg, Na, K, CO_3, HCO_3 SO_4, Cl, NO_3 and H_3BO_3

Reading: Temperature compensation conductivity meter.
Ability of the soil solution to conduct electrical current

new units: dS/m (decisiemens per meter)
old units: mmho/cm (millimhos per cm)

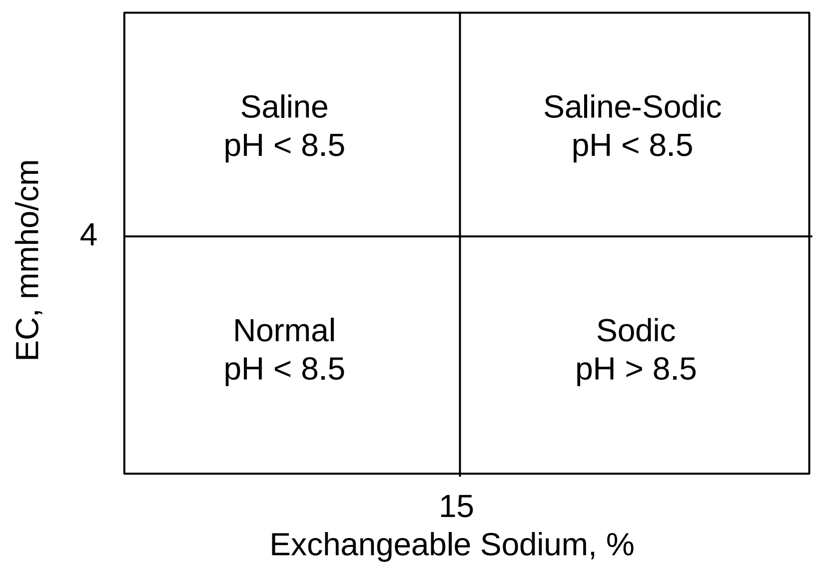
1 mmho/cm = 1dS/m

Plants must overcome solution osmotic potential to absorb water.
increased EC - increased OP --> results in decreased H_2O availability

OP = EC(-0.36)

Reclamation:

1. Saline
    a. wash with water (low salt content)
    b. must be leached below the root zone
2. Saline-Sodic
    a. replace Na on the exchange complex with Ca by adding gypsum
    b. wash with water
3. Sodic
    a. resolve sodic problem first (apply $CaSO_4$ to exchange for Na)
    b. wash with water
4. Normal



Reclamation:

All require long periods of time to reclaim and all have drainage problems. In each case, addition of organic matter (incorporation) will assist with drainage.

Early estimates of the relative sodium contents of water were based solely on their percent sodium content. Waters with high Na may produce relatively low exchangeable Na levels in soils if the total cation concentration is high (Bohn, p 225).

SAR (sodium adsorption ratio) was proposed to characterize the relative Na status of irrigation waters and soil solutions.

$SAR = [Na+] / ([Ca + Mg]/2)\ 1/2$

where all concentrations are in meq/liter.

The Ca + Mg is divided by two because most ion exchange equations express concentrations as moles/liter or mmoles/liter rather than meq/liter.

Allows us to gain information about the exchangeable cations without actually taking an actual measurement.

Amounts adsorbed are proportional to the amounts in soil solution (Donan Equilibrium Theory).
(measurement of soil solution and not exchange)

Stability Analysis

Linear regression of yield on the mean of all treatments (varieties) for each site and season. Original work employed a logarithmic scale.

Objective (Plant Breeding)

a. Mean yield of all varieties provided a quantitative grading of environments.
b. Varieties specifically adapted to good or poor environments were identified.

Objective (Soil Fertility)

a. To assess treatment response as a function of environment and to detect the benefits of using these analyses to complement conventional analysis of variance.

Eberhart and Russell, 1966

$$Y_{ij} = u_i + B_i I_j + e_{ij}$$

Yij = variety mean of the i^{th} variety and j^{th} environment
u_i = i^{th} variety mean over all environments
B_i = regression coefficient that measures the response of the i^{th} variety to varying environments
e_{ij} = deviations from regression of the i^{th} variety at the j^{th} environment
I_j = environmental index

Defined a stable genotype as one having deviations from regression = 0 and a slope of 1.0

Analysis of Variance: (Over Locations)
10 locations
10 varieties
3 reps

Source of Variation	df	
Total	299	
Environment (e-1)	9	
Rep(Environment) (r-1(e))	20	(error A)
Genotype (g-1)	9	
Genotype * Environment (g-1)(e-1)	81	
Residual Error	180	

df - degrees of freedom
G*E interaction

Stability analysis is essentially a method of partitioning the G*E interaction term assuming that environment could be quantified. In general, environment means in stability analysis are assumed to be a function of temporal variability and that genotype response was a direct function of that variable which influenced yield potential. This has most generally been attributed to high or low rainfall.

A major purpose of long-term fertility trials is to provide a measure of the effect of environment over time on the consistency of treatment effects. Assessing year X trt interactions in long-term fertility experiments is an issue when more than two or three years of data are present. Interpretation of year X treatment interactions using analysis of variance is difficult due to the number of factors affecting environment.

Initial use of regression to assess yield stability of genotypes across a wide range of environments was originally presented by Yates and Cochran (1938) and later followed by Finlay and Wilkinson (1963) and Eberhart and Russell (1966). The technique is useful in relating a measurement of environment which is usually the mean yield across all genotypes for each environment to performance of different genotypes tested. Eberhart and Russell, (1966) characterize a stable genotype as having a linear regression coefficient of one and deviations from regression equal to zero.

The extrapolation of some of these concepts to characterize stability of agronomic treatments instead of genotypes seems to be a practical application in separating the response of treatments as a function of environment over time. This assumes that the lack of consistency of treatment effects over time (a treatment X year interaction) can be interpreted as a linear function of the environment mean on the mean yield for a given treatment. Hildebrand (1984), stated that it is visually possible to compare treatments and to generalize these equation sets for various kinds of management practices, and further states that the environment mean measures treatment response to good or poor environments regardless of the reasons these environments were good or bad.

Stability Analysis for single-site-long-term experiments:

Analysis of Variance: (Split plot 'in-time')
10 years
10 treatments (N, P, K fertilization, Herbicide trt, etc)
3 reps

Source of Variation	df	
Total	299	
Replication	2	
Treatment	9	
Replication*Treatment	18	(error A)
Year	9	
Year*Treatment	81	
Residual Error	180	

df - degrees of freedom (weak test for treatment, 18 df)

Results:

K supply in a stress environment showed increases in yield. Why? This observation was the trt*environment interaction.

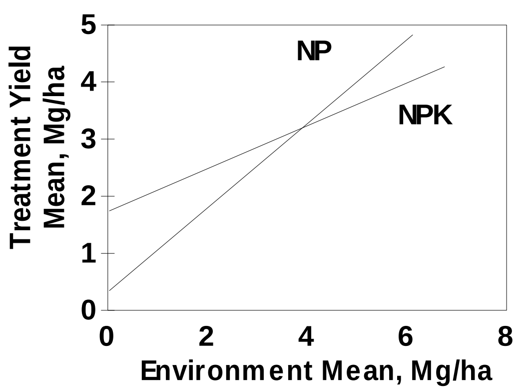
Anhydrous ammonia superior in stress environments. Why? NH_4 supply - immediate glutamine formation.

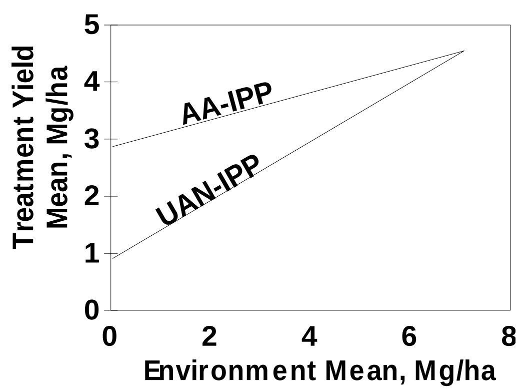
Stability Analysis: discussion

It is conceivably difficult to predict the environment mean since variety, rainfall, weed pressure and disease are variable from year to year. In an additive linear model like those used in conventional analysis of variance, the mathematical sums of squares accounted by year, treatment and year X treatment effects are removed from the random variation (residual error), yet year and year X treatment effects are seldom interpreted from a biological point of view. Limited biological interpretation of the lack of consistency of treatment effects over years (year X treatment interaction) decreases the value of conventional analysis in identifying treatment advantages as a function of environment.

The use of stability analysis implies that treatment is actually a linear function of temporal variability which would complement some of the limitations encountered in conventional analysis of variance. Hildebrand (1984) states that stability analysis explicitly incorporates variation in farmer management as well as in soils and climate to help agronomists evaluate responses to treatments and partition farmers into recommendation domains. In depth analysis of year X treatment interactions suggests that the researcher should view changed treatment response within the specific environment in which the treatment differences were observed. When considering 2 or 3 years of data, the year X treatment interaction can be easily separated into discrete components using specific comparisons by means of non-orthogonal contrasts. However, it is unlikely that biological interpretation of the year X treatment interaction will be achieved when faced with 10 or more years of data using conventional analysis. Alternatively, stability analysis is in effect somewhat restricted to long-term experiments and/or multilocation experiments since adequate degrees of freedom are needed to obtain meaningful regressions.

In general, differences in environment means for single-site long-term experiments can largely be attributed to moisture availability. This observation could assist in identifying potential differences between fertilizer treatments in either reduced or oxidized environments. Work by Olsen (1986) discusses the differences between ammonium and nitrate nutrition as related to energy use and factors which affect availability.





It is of some concern as to how residual treatment effects influence yield in succeeding cycles. If treatment response was a function of a particular environment, then it seems reasonable that detection of residual treatment effects will be affected by the previous environment. However, plots of grain yield by year did not reveal any evident patterns of residual treatment effects. Furthermore, in stability analysis the environment mean while random, is in effect ordered in succession thus confounding any detection of residual treatment effects if they existed. Nonetheless, conventional split plot in time analysis of variance models are no better in this regard since residual effects are also not evaluated. It should also be mentioned that stability analysis over locations versus one-site long-term experiments presents a problem of correlated yield results over time or autocorrelations in the data for the latter mentioned example.

When year X treatment interactions are detected in the conventional analysis of variance model, ensuing stability analysis provides a simple method of determining whether or not this interaction is a function of environment. Although this can also be achieved by partitioning the degrees of freedom in the year X treatment interaction from the analysis of variance model, stability analysis may provide a more direct method of assessing temporal variability in long-term experiments.

Recommendation strategies could possibly be refined by the added use of stability analysis when assessing agronomic treatment response over time. As issues of sustainability become increasingly important, stability analysis and relative stability may assist in our understanding of yield as a function of environment as well as identifying areas that warrant further investigation.

Soil Solution Equilibria

K° = equilibrium constant expressed in terms of activities
K°= (HL)/(H) (L)

What does K° mean?

- log K°, high positive number (dissociation will take place)
- log K°, high negative number (low solubility - slow dissociation)

$10^{-39.4}$ = (Fe) (OH)3/ $Fe(OH)_3$ indicates that Fe will stay in this form $Fe(OH)_3$

Example:

Activity of Al^{+++} (Xn) limited or controlled by gibbsite (Y)

$Al(OH)_3 + 3\ H^+ \longrightarrow Al^{+++} + 3\ H_2O$ Log K° = 8.04 (equilibrium activity constant) gibbsite

Gibbsite is the most abundant free hydroxide of Al in soils and occurs in large amounts in highly weathered soils (Bohn, p. 89)

$Al^{+++}/(H^+)^3 = 10^{8.04}$

Log Al^{+++} = 8.04 - 3pH
pH - 1/3 pAl = 2.68
-Log(H^+) - 1/3 log(Al) = 2.68

Redox Relationships

reduction: gain electrons
oxidation: lose electrons

H atom atomic wt.	= 1.007826
H ion (proton)	= 1.007277
electron	= 0.000549

Effect of redox on the stability of Fe and Al phosphates:

When soils are flooded, we can increase P availability in acid soils. The pH of a reduced soil generally rises toward neutral (7.0) which increases the solubility of Fe and Al phosphates. As pe + pH drops below 8.34 (depending on which iron oxides control iron and which minerals control Al^{+++}) strengite and variscite convert to vivianite. Rice plants (grown under reduced conditions) are able to obtain sufficient P in the presence of vivianite because in the immediate vicinity of the root, redox is higher than that of the bulk soil because O_2 is supplied through the stem to the roots. This is an example of how plants absorb P where vivianite suppresses the solubility of P in the bulk soil to very low levels (Lindsay, p 179).

Oxidation reduction reactions in soils

redox potential (p3) is expressed as (-log of electron activity) which is consistent with pH = - log(H^+)

1. Most soil systems consist of aqueous environments in which the dissociation of water H_2(g) or O_2(g) impose redox limits on soils.

$K° = (H_2(g))1/2/(H^+)(e^-)$

$\log K° = 1/2 \log H_2(g) - \log(H^+) - \log(e^-)$

The equilibrium constant for this reaction is defined as unity (Log K° = 0) for standard state conditions in which (H^+) activity = 1 mole/l and H_2(g) is the partial pressure of H_2(g) at 1 atmosphere.

since log K° = 0

pe + pH = 1/2 log H_2(g)

therefore when $H_2(g)$ = 1 atm, pe + pH = 0

This represents

* most reduced equilibrium conditions expected for natural aqueous environments.

On the oxidized side, redox limit of aqueous systems is given by the reaction

$H^+ + e^- + 1/2\ O_2(g) \longrightarrow 1/2\ H_2O$

Equilibrium expression for this reaction is $K° = (H_2O)^{½}(H^+)(e^-)(O_2(g))^{¼}$

The value of K° can be calculated from the standard free energies of formation (Appendix, Lindsay, 1979) and is equal to $10^{20.78}$. In dilute aqueous systems, the activity of water is very near unity, so the equilibrium expression in log form becomes

$-\log(H^+) - \log(e^-) - ¼ \log O_2(g) = 20.78$

$pe + pH = 20.78 + ¼ \log O_2(g)$

Therefore, when $O_2(g)$ is 1 atm, pe + pH = 20.78 which corresponds to most oxidized equilibrium conditions expected in natural aqueous environments. The parameter pe + pH provides a single term expression for defining redox status of aqueous systems. (range = 0 on reduced side (1 atm H_2) to 20.78 on the oxidized side (1 atm O_2))

pH expressed - log (H^+) activity
pe denotes - log (e^-) activity

Activity of Al^{+++} is at equilibrium with various Al minerals (gibbsite, etc) and is pH dependent (decreasing 1000x for each unit increase in pH).

When Al^{+++} is controlled by $Al(OH)_3$ amorphous rather than gibbsite, the activity of Al^{+++} is $10^{9.66}/10^{8.04} = 10^{1.62}$ or 42 times higher.

1.62(10x) = 41.68

Activity of Al^{+++} in soils is often below that of gibbsite due to the presence of various aluminosilicates.

Because silicon is removed from soils more rapidly than Al, weathering causes the eventual disappearance of aluminosilicates. The Fe and Al that are released generally precipitate as oxides and hydroxides (e.g., gibbsite which is present in highly weathered soils).

In aqueous solutions Al^{+++} does not remain as a free ion. It is normally surrounded by six molecules of water ($Al(H_2O)_6$).

As pH increases, protons are removed

Phosphorus

The figure on page 112 shows the relative fractions of different orthophosphoric acid species as a function of pH. The formation constant (log K°) relating two species is numerically equal to the pH at which the reacting species have equal activities.

$HPO_4^{=} + H^+ \longrightarrow H_2PO_4^-$ log K° = 7.2

$(H_2PO_4^-)/(HPO_4^{=})(H^+) = 10^{7.2}$

$\log (H_2PO_4^-)/(HPO_4^{=}) = \log K° - pH = 7.2 - pH$

When pH = log K° the activity ratio of the reacting species is unity. A decrease in pH of one unit increases the ratio $H_2PO_4^-/HPO_4^{=}$ by a factor of 10.

Some Rules of Thumb for Predicting the Outcome of Simple Inorganic Chemical Reactions Related to Soil Fertility

G.V. Johnson

For the general reaction:

$$An^{+} + Bm^{-} \Leftarrow = \Rightarrow AmBn \qquad (1)$$

Whether the reactant ions A and B combine to form a compound (usually a solid) may generally be predicted by the size of electrical charge in the ionic form. Generally, the higher the charge of either the cation or anion, the greater is the tendency for the compound or solid to be formed. When the solid is easily formed, only small concentrations of the reactants are necessary for the reaction to take place. Because of this, the compound or solid that forms is also quite insoluble (it will not easily dissolve in water), or it does not easily break apart (reaction to the left). Conversely, if the cation and anion are both single charged, then the compound (solid) is not as easily formed, and if it does form, it is quite soluble. Here are some examples:

1. Single charged ions forming soluble compounds.

$$Na^{+} + Cl^{-} \Leftarrow = \Rightarrow NaCl \qquad (2)$$

We all have experienced that NaCl, common table salt, is very soluble and easily dissolves in water. Once dissolved, the solid NaCl does not reform until the ions, $Na^{+} + Cl^{-}$, are present in high concentration. This happens when water is lost from the solution by evaporation and the solid finally reforms as NaCl precipitate.

2. Multiple charged ions forming insoluble compounds

When iron reacts with oxygen a very insoluble solid, rust or iron oxide, is formed. The reaction can be expressed as

$$2\ Fe^{3+} + 3\ O^{=} \Leftarrow = \Rightarrow Fe_2O_3 \quad \text{(rust)} \qquad (3)$$

With regard to solubility of inorganic compounds, we may expect the following:

I. When both the cation and anion are single charged, the resulting compound is usually very soluble. Examples are compounds formed from the cations H^+, NH_4^+, Na^+, K^+ and the anions OH^-, Cl^-, NO_3^-, H_2PO_4, and HCO_3^- (bicarbonate). Also, when the cation reacts with OH^- to form a base, the base is very strong (e.g. NaOH). When the anion reacts with H^+ to form an acid, the acid is a strong acid (e.g. HCl, HNO_3). The monvalent anions $H_2PO_4^-$, and HCO_3^-, which are products of multicharged ions that have already reacted with H+, are exceptions.

Except for H^+ and OH^-, whenever either the cation or anion is <u>single</u> charged and reacts with a <u>multiple</u> charged ion, the resulting compound is usually very soluble. Examples of multiple charged ions, common to soil fertility studies, are

a. the divalent cations Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}.
b. the divalent anions $SO_4^=$, $CO_3^=$ (carbonate), $HPO_4^=$, and $MoO_4^=$
c. the trivalent cation Fe^{3+}
d. the trivalent anion PO_4^{3-}

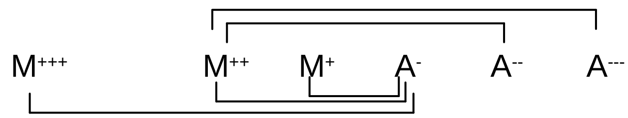
Accordingly, when either of the monovalent anions Cl^-, NO_3^- react with any of the cations Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, or Fe^{3+}, the solids are all quite soluble. Similarly, when any of the monovalent cations NH_4^+, Na^+, or K^+ reacts with any of the multicharged anions $SO_4^=$, $CO_3^=$, $HPO_4^=$, $MoO_4^=$, or PO_4^{3-}, the solids are all quite soluble.

II. If both the cation and anion are divalent, the resulting compound will be only sparingly soluble. An example is gypsum ($CaSO_4 . 2H_2O$).

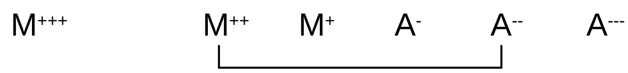
III. If one of the ions is divalent and the other is trivalent, the compound will be moderately insoluble. An example is tricalcium phosphate, $Ca_3(PO_4)_2$.

IV. If both the anion and cation are trivalent, the compound is very insoluble. An example is iron (ferric) phosphate, $FePO_4$.

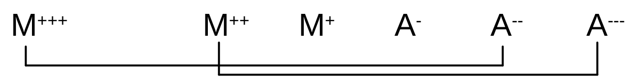
A summary of these general rules is illustrated in the following diagrams.



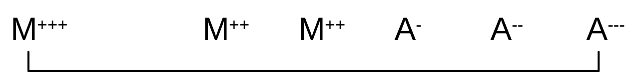
A. All compounds with a monovalent ion are soluble.



B. Compounds with both ions divalent are sparingly soluble.



C. Compounds with one divalent ion and one trivalent ion are moderately insoluble.



D. Compounds with both ions trivalent are very insoluble

References

Alexander, M.A., 1977. Introduction to soil microbiology. 2nd Edition. John Wiley & Sons, Inc. New York, NY.

Allison, Franklin E. 1966. The fate of nitrogen applied to soils. Adv. Agron. 18:219-258.

Altom, W., J.L. Rogers, W.R. Raun, G.V. Johnson and S.L. Taylor. 1996. Long-term rye-wheat-ryegrass forage yields as affected by rate and date of N application. J. of Prod. Agric. 9:510-516.

Aulakh, M.S., D.A. Rennie And E.A. Paul. 1984. The influence of plant residues on denitrification rates in conventional and zero tilled soils. Soil Sci. Soc. Am. J. 48:790-794.

Aylmore, L.A.G., Kavim Meshanul, and J.P. Quirk. 1967. Adsorption and desorption of sulphate ions by soil constituents. Soil Sci. 103:10-15.

Balba, Monem and Roger H. Bray. The application of the miterscherlich equation for the calculation of plant composition due to fertilizer increments. Soil Sci. Soc. Am. Proc. 20:515-518.

Barreto, H.J., and R.L. Westerman. 1985. YIELDFIT, Determining maximum economic fertilization rates using Mitscherlich, quadratic and square root functions. Comp. Software Series CSS-11. Okla. Agric. Exp. Stn.

Bear, F.E., A.L. Prince and J.L. Malcolm. 1945. Potassium needs of New Jersey soils. N.J. Agric. Exp. Stn. Bull. 721.

Blevins, R.L., M.S. Smith, G.W. Thomas and W.W. Frye. 1983. Soil properties unchanged after ten years of no-till corn. Agrichemical Age, October-November 276:420-43.

Bock, B.R., and D.E. Kissel. 1988. Ammonia volatilization from urea fertilizers. Bulletin Y-206. National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, AL.

Bohn, H.L., B.L. McNeal and G.A. O'Connor. 1979. Soil Chemistry. John Willey & Sons, Inc. New York, NY.

Bray, R.H., and LT. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. Soil Sci. 59:39-45.

Bray, Roger H. 1954. A nutrient mobility concept of soil-plant relationships. Soil Sci. 104:9-22.

Bremner, J.M. 1959. Determination of fixed ammonium in soil. J. Agric. Sci. 52:147-160.

Bremner, J.M. 1965. Inorganic forms of nitrogen. *In* C.A. Black et al. (ed.) Methods of soil analysis, Part 2. Agronomy 9:1179-1237. ASA and SSSA, Madison, WI.

Burford J.R., and J.M. Bremner. 1975. Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. Soil Biol. Biochem. 7:389-394.

Campbell, C.A., E.A. Paul and W.B. McGill. 1976. Effect of cultivation and cropping on the amounts and forms of soil N. p. 9-101. In W.A. Rice (ed.) Proc. Western Can. Nitrogen Symp., Calgary, Alberta, Canada, 20-21 January. Alberta Agriculture, Edmonton, Alberta, Canada.

Cate, R.B., Jr., and L.A. Nelson. 1965. A rapid method for correlation of soil test analyses with plant response data. North Carolina Agric. Exp. Stn. International Soil Testing Series Tech. Bull. No. 1.

Daigger, L.A., D.H. Sander, and G.A. Peterson. 1976. Nitrogen content of winter wheat during growth and maturation. Agron. J. 68:815-818.

Doran, J.W., and M.S. Smith. 1987. Organic matter management and utilization of soil and fertilizer nutrients. In J.J. Mortvedt (ed.) Soil fertility and organic matter as critical components of production systems. Soil Sci. Soc. Am. SSSA Special Pub. No. 19. Madison, WI.

Eberhart S.A., and W.A. Russell. 1966. Stability parameters for comparing varieties. Crop Sci. 6:36-40.

Ernst, J.W., and H.F. Massey. 1960. The effects of several factors on volatilization of ammonia formed from urea in the soil. Soil Sci. Soc. Am. Proc. 24:87-90.

Fenn, L.B., and D.E. Kissel. 1976. The influence of cation exchange capacity and depth of incorporation on ammonia volatilization from ammonium compounds applied to calcareous soils. Soil Sci. Soc. Am. J. 40:394-398.

Finlay, K.W., and G.N. Wilkinson. 1963. The analysis of adaptation in a plant breeding programme. Aust. J. Agric. Res. 14:742-754.

Ferguson, R.B., D.E. Kissel, J.K. Koelliker and Wes Basel. 1984. Ammonia volatilization from surface-applied urea: Effect of hydrogen ion buffering capacity. Soil Sci. Soc. Am. J. 48:578-582.

Follett, R.F. and B. McConkey. 2000. The role of cropland agriculture for C sequestration in the Great Plains. Great Plains Soil Fertility Conference Proceedings.

Fox, R.L., R.A. Olson and H.F. Rhoades. 1964. Evaluating the sulfur status of soils by plant and soil tests. Soil Sci. Soc. Amer. Proc. 28:243-246.

Francis, D.D., J.S. Schepers and M.F. Vigil. 1993. Post-anthesis nitrogen loss from corn. Agron. J. 85:659-663.

Fried, Maurice and L.A. Dean. 1951. A concept concerning the measurement of available soil nutrients. Soil Sci. 73:263-271.

Gillman. G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. Aust. J. Soil Res. 17:129-139.

Graham, E.R. 1959. An explanation of theory and methods of soil testing. Mo. Agric. Exp. Stn. Bull. 734.

Harper, L.A., R.R. Sharpe, G.W. Langdale, and J.E. Giddens. 1987. Nitrogen cycling in a wheat crop: soil, plant, and aerial nitrogen transport. Agron. J. 79:965-973.

Hauck, R.D., and J.M. Bremner. 1976. Use of tracers for soil and fertilizer nitrogen research. Adv. Agron. 28:219-266.

Hildebrand, Peter E. 1984. Modified stability analysis of farmer managed on-farm trials. Agron. J. 76:271-274.

Kamprath, E.J., W.L. Nelson, and J.W. Fitts. 1956. The effect of pH, sulfate and phosphate concentrations on the adsorption of sulfate by soils. Soil Sci. Soc. Am. Proc. 20:463-466.

Kanampiu, F.K., W.R. Raun and G.V. Johnson. 1997. Effect of nitrogen rate on plant nitrogen loss in winter wheat varieties. J. of Plant Nutr. 20(2&3):389-404.

Kohl, D.H., G.B. Shearer and B. Commoner. 1973. Variation of 15N in corn and soil following applications of fertilizer nitrogen. Soil Sci. Soc. Am. Proc. 37:888-892.

Lindsay, Willard L. 1979. Chemical equilibria in soils. John Wiley & Sons. New York, NY.

McLean, E.O. 1977. Contrasting concepts in soil test interpretation: sufficiency levels of available nutrients versus basic cation saturation ratios. In T.R. Peck, J.T. Cope and D.A. Whitney (eds.) Soil testing: correlating and interpreting the analytical results. ASA Special Pub. No. 29. Madison, WI.

Moll, R.H., E.J. Kamprath and W.A. Jackson. 1982. Analysis and interpretation of factors which contribute to efficiency of nitrogen utilization. Agron. J. 74:562-564.

Nelson, W.L., A. Mehlich, and E. Winters. 1953. The development, evaluation, and use of soil tests for phosphorus availability. Agronomy 4:153-188.

Olsen, S.R. 1986. The role of ammonium nutrition in higher yields. p. 6 14. In J. Havlin (ed.) Proc. Great Plains Soil Fertility Workshop. Denver, CO. Kansas State Univ., Manhattan, KS.

Olson, R.V. and C.W. Swallow. 1984. Fate of labeled nitrogen fertilizer applied to winter wheat for five years. Soil Sci. Soc. Am. J. 48:583-586.

Olson, R.A., K.D. Frank, P.H. Grabouski and G.W. Rehm. 1982. Economic and agronomic impacts of varied philosophies of soil testing. Agron. J. 74:492-499.

Olson, R.A., and L.T. Kurtz. 1982. Crop nitrogen requirements, utilization and fertilization. In Frank J. Stevenson (ed.) Nitrogen in agricultural soils. Agron. Monogr. 22. ASA, CSSA and SSSA, Madison, WI.

Parr, J.F., and R.I. Papendick. 1978. Factors affecting the decomposition of crop residues by microorganisms. In ______ (ed.) Crop Residue Management Systems. ASA, CSSA, SSSA. Madison, WI.

Pearson, R.W., F. Abruna, and, J. Vicente-Chandler. 1962. Effect of lime and nitrogen applications on downward movement of calcium and magnesium in two humid tropical soils of Puerto Rico. Soil Sci. 93:77-82.

Perry, A.M. 1983. Estimating the greenhouse effect. Science 222:1072.

Polemio, M., and J.D. Rhoades. 1977. Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soils. Soil Sci. Soc. Am. Proc. 32:488-492.

Ranney, R.W. 1969. An organic carbon-organic matter conversion equation for Pennsylvania surface soils. Soil Sci. Soc. Amer. Proc. 33:809-811.

Raun, W. R., H. J. Barreto, and R. L. Westerman. 1993. Use of stability analysis for long-term soil fertility experiments. Agron. J. 85:159-167.

Sanchez, C.A., A.M. Blackmer, R. Horton and D.R. Timmons. 1987. Assessment of errors associated with plot size and lateral movement on nitrogen-15 when studying fertilizer recovery under field conditions. Soil Sci. 144:344-351.

Shearer, Georgia, and J.O. Legg. 1975. Variations in the natural abundance of 15N of wheat plants in relation to fertilizer nitrogen applications. Soil Sci. Soc. Amer. Proc. 39:896-901.

Thomas, Grant W. 1982. Exchangeable cations. *In* A.L. Page, R.H. Miller and D.R. Keeney (eds.) Methods of soil analysis. Part 2, 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Tisdale, Samuel L., Werner L. Nelson, James D. Beaton and John L. Havlin. 1993. Soil fertility and fertilizers. Fifth Edition. MacMillan Publishing Co. New York, NY.

Tinoco, Ignacio, Kenneth Sauer and James C. Wang. 1978. Physical chemistry, principles and applications in biological sciences. Prentice-Hall, Inc. Englewood Cliffs, New Jersey.

Varvel, G.E., and Todd Andrews Peterson. 1991. Nitrogen fertilizer recovery by grain sorghum in monoculture and rotation systems. Agron. J. 83:617-622.

Vigil, M.F., and D.E. Kissel. 1991. Equations for estimating the amount of nitrogen mineralized from crop residues. Soil Sci. Soc. Am. J. 55:757-761.

Vose, P.B. Introduction to nuclear techniques in agronomy and plant biology. 1980. Pergammon Press Inc., Elmsford, NY.

Wallace, Arthur, Garn A. Wallace and Jong W. Cha. 1990. Soil organic matter and the global carbon cycle. J. of Plant Nutr. 13:459-466.

Wittwer, S.H. 1985. Carbon dioxide levels in the biosphere: effects on plant productivity. CRC Critical Reviews in Plant Sciences 2:171-198.

Wuest, S.B., and K.G. Cassman. 1992. Fertilizer-nitrogen use efficiency of irrigated wheat: I. Uptake efficiency of preplant versus late-season application. Agron. J. 84:682-688.

Yates F, and W.G. Cochran. 1938. The analysis of a group of experiments. J. Agric. Sci. 28:556-580.

$1000000 = 10^6$ = mega
$1000 = 10^3$ = kilo
$100 = 10^2$ = hecto
$10 = 10^1$ = deka
$0.1 = 10^{-1}$ = deci
$0.01 = 10^{-2}$ = centi
$0.001 = 10^{-3}$ = milli
$0.000001 = 10^{-6}$ = micro
$0.000000001 = 10^{-9}$ = nano

Appendix Table 1. Conversion factors and relationships between English and metric units.

Yield and Rate

lb/ac * 1.12 = kg/ha
bu/ac * 67.2 = kg/ha (60 lb test weight)
bu/ac * 0.0672 = Mg/ha (60 lb test weight)
1 Mg/ha = 14.88 bu/ac (60 lb test weight)

Area

1 hectare = 10000 m^2	
1 acre = 43560 ft^2	
1 acre (ac) = 0.405 hectares (ha)	1 ha = 2.47 ac

Length

1 inch (in) = 2.54 centimeters (cm)	1 cm = 0.393 in
1 foot (ft) = 30.48 centimeters (cm)	
1 mile (mi) = 1.609 kilometers (km); 1 mile=5280ft	1 km = 0.621 mi
1 yard (yd) = 0.914 meters (m)	1 m = 1.094 yd
1 $mile^2$ (mi) = 259 hectares (ha)	

Volume

1 gallon (gal) = 3.785 liters (l)	1 l = 0.264 gal
1 quart (qt) = 1.057 liters (l)	1 l = 0.964 qt

Mass

1 kilogram (kg) = 1000 grams (g)	
1 Megagram (Mg) = 1000 kilograms (kg)	
1 ounce (oz) = 28.35 grams (g)	1 g = 0.03527 oz
1 pound (lb) = 0.454 kilograms (kg)	1 kg = 2.205 lb
1 ton (2000 lb) = 907 kilograms (kg)	

Temperature

Centrigrade (°C) = 5/9 (°F - 32)
Fahrenheit (°F) = (9/5 °C) + 32

NH_3 +

→ H_2SO_4	→	$(NH_4)_2SO_4$ ammonium sulfate	20%N
→ HNO_3	→	NH_4NO_3 ammonium nitrate	33%N
→ CO_2	→	$(NH_2)_2CO$ urea	45%N
→ H_3PO_4	→	$NH_4H_2PO_4$ ammoniated phosphates 11-48-0 18-46-0	11-18%N
→ HNO_3/rock phosphate	→		nitric phosphates

Haber-Bosch: (Germany, 1910)

High temp (1200°C)
High pressure (200-1000 atm)
(magnetite, Fe_3O_4) catalyst

Methane → Anhydrous Ammonia

$$3CH_4 + 3O_2 + 2N_2 \longrightarrow 4NH_3 + 3CO_2$$

12. NUTRIENT CYCLES

NITROGEN

Form taken up by plant:	NH_4^+, NO_3^-
Mobility in soil:	NH_4^+: no; NO_3^-: yes NO_3^- water soluble, not influenced by soil colloids
Mobility in plant:	Yes
Deficiency symptoms:	Chlorosis in older leaves, under severe deficiency lower leaves are brown, beginning at the leaf tip and proceeding along the midrib.
Soil pH where deficiency will occur:	None due to nitrate's mobility
Role of nutrient in plant growth:	N assimilation into amino acids for protein and amino acid synthesis, component of chlorophyll, vegetative growth
Enzymes that require N:	Nitrate reductase, nitrite reductase, nitrogenase
Role of nutrient in microbial growth:	Necessary for the synthesis of amino acids
Concentration in plants:	Wheat 1.7 - 3.0% Grain 2.0% Forage 3.0 % Straw Corn 2.7 - 3.5% Soybeans 4.2 - 5.5% Grain sorghum 3.3 - 4.0% Peanuts 3.5 - 4.5% Alfalfa 4.5 - 5.0% Bermudagrass 2.5 - 3.0%
Effect of pH on availability:	
Precipitated forms (low pH):	*none*
Precipitated forms (high pH):	*none* *at pH>8, no nitrification; at pH>7, NO_2^- accumulates*
Interactions with other nutrients:	Si: enhances leaf erectness, thus neutralizing the negative effects of high nitrogen supply on light interception (leaf erectness usually decreases with increasing nitrogen supply); P: symbiotic legume fixation needs adequate P or a N deficiency

can result; Mo: component of nitrogenase therefore could have Mo induced N deficiency in N_2 fixing legumes (especially under acid soils conditions); Fe: necessary for nitrogenase and ferredoxin (electron carrier), legume hemoglobin, deficiency reduces nodule mass, and nitrogenase;

Fertilizer sources: ammonium sulfate, anhydrous ammonia, ammonium chloride, ammonium nitrate, ammonium nitrate-sulfate, ammonium nitrate with lime, ammoniated ordinary superphosphate, monoammonium phosphate, diammonium phosphate, ammonium phosphate-sulfate, ammonium polyphosphate solution, ammonium thiophosphate solution, calcium nitrate, potassium nitrate, sodium nitrate, urea, urea-sulfate, urea-ammonium nitrate, urea-ammonium phosphate, urea phosphate.

References:

Burford, J.R., and J.M. Bremner. 1975. Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. Soil Biochem. 7:389-394.

Marschner, Horst. 1995. Mineral Nutrition in Higher Plants. Academic Press, London.

Tisdale, S.L., W.L. Nelson, J.D. Beaton, and J.L. Havlin. 1993. Soil Fertility and Fertilizers. MacMillan Publishing Co., New York, N.Y.

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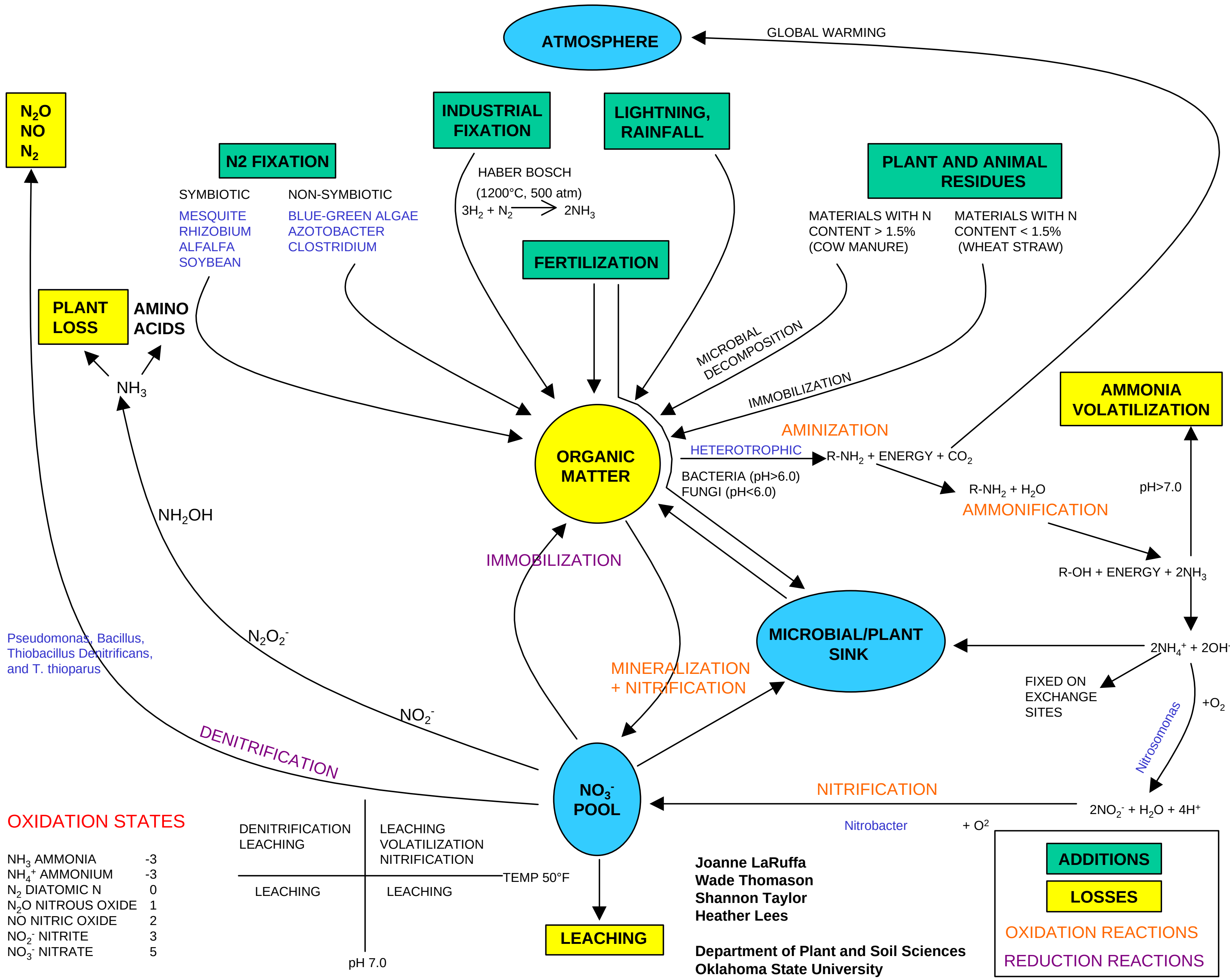

ATMOSPHERE
GLOBAL WARMING
N2O
NO
N2
INDUSTRIAL FIXATION
LIGHTNING, RAINFALL
N2 FIXATION
PLANT AND ANIMAL RESIDUES
HABER BOSCH
(1200°C, 500 atm)
3H2 + N2 → 2NH3
SYMBIOTIC
NON-SYMBIOTIC
MESQUITE
RHIZOBIUM
ALFALFA
SOYBEAN
BLUE-GREEN ALGAE
AZOTOBACTER
CLOSTRIDIUM
MATERIALS WITH N CONTENT > 1.5% (COW MANURE)
MATERIALS WITH N CONTENT < 1.5% (WHEAT STRAW)
FERTILIZATION
PLANT LOSS
AMINO ACIDS
NH3
MICROBIAL DECOMPOSITION
IMMOBILIZATION
AMMONIA VOLATILIZATION
AMINIZATION
HETEROTROPHIC
R-NH2 + ENERGY + CO2
ORGANIC MATTER
BACTERIA (pH>6.0)
FUNGI (pH<6.0)
R-NH2 + H2O
AMMONIFICATION
pH>7.0
NH2OH
IMMOBILIZATION
R-OH + ENERGY + 2NH3
MICROBIAL/PLANT SINK
Pseudomonas, Bacillus, Thiobacillus Denitrificans, and T. thioparus
N2O2-
2NH4+ + 2OH-
MINERALIZATION + NITRIFICATION
FIXED ON EXCHANGE SITES
+O2
Nitrosomonas
NO2-
DENITRIFICATION
NO3- POOL
NITRIFICATION
2NO2- + H2O + 4H+
Nitrobacter
+ O2
OXIDATION STATES
NH3 AMMONIA -3
NH4+ AMMONIUM -3
N2 DIATOMIC N 0
N2O NITROUS OXIDE 1
NO NITRIC OXIDE 2
NO2- NITRITE 3
NO3- NITRATE 5
DENITRIFICATION
LEACHING
LEACHING
VOLATILIZATION
NITRIFICATION
TEMP 50°F
LEACHING
LEACHING
pH 7.0
LEACHING
Joanne LaRuffa
Wade Thomason
Shannon Taylor
Heather Lees
Department of Plant and Soil Sciences
Oklahoma State University
ADDITIONS
LOSSES
OXIDATION REACTIONS
REDUCTION REACTIONS

PHOSPHORUS

Form taken up by plant: $H_2PO_4^-$, $HPO_4^=$

Mobility in soil: None; roots must come in direct contact with orthophosphate P

Mobility in plant: Yes

Deficiency symptoms: Lower leaves with purple leaf margins
Deficiency pH range: *<5.5 and >7.0*

Toxicity symptoms: None
Toxicity pH range: *Non toxic (optimum availability pH 6.0-6.5)*

Role of nutrients in plant growth: Important component of phospholipids and nucleic acids (DNA and RNA)

Role of nutrient for microbial growth: Accumulation and release of energy during cellular metabolism

Concentration in plants: 1,000 – 5,000 ppm (0.1 –0.5%)

Effect of pH on availability: $H_2PO_4^-$ at pH < 7.2
HPO_4^{2-} at pH > 7.2

Interactions with other nutrients: P x N, P x Zn at high pH, in anion exchange P displaces S, K by mass action displaces Al inducing P deficiency (pH<6.0)

Phosphorus fertilizer sources: Rock phosphate, phosphoric acid, Ca orthophosphates, ammoniumphosphates, ammonium poly-phosphates, nitric phosphates, K phosphates, microbial fertilizers (phosphobacterins) increase P uptake

Additional categories:

Mineralization/immobilization: C:P ratio of < 200: net mineralization of organic P; C:P ratio of 200-300: no gain/loss of inorganic P; C:P ratio of >300: net immobilization of inorganic P

P fixation: Formation of insoluble Ca, Al, and Fe phosphates

$$Al(OH)_3 + H_2PO_4^- \rightarrow Al(OH)_2HPO_4$$

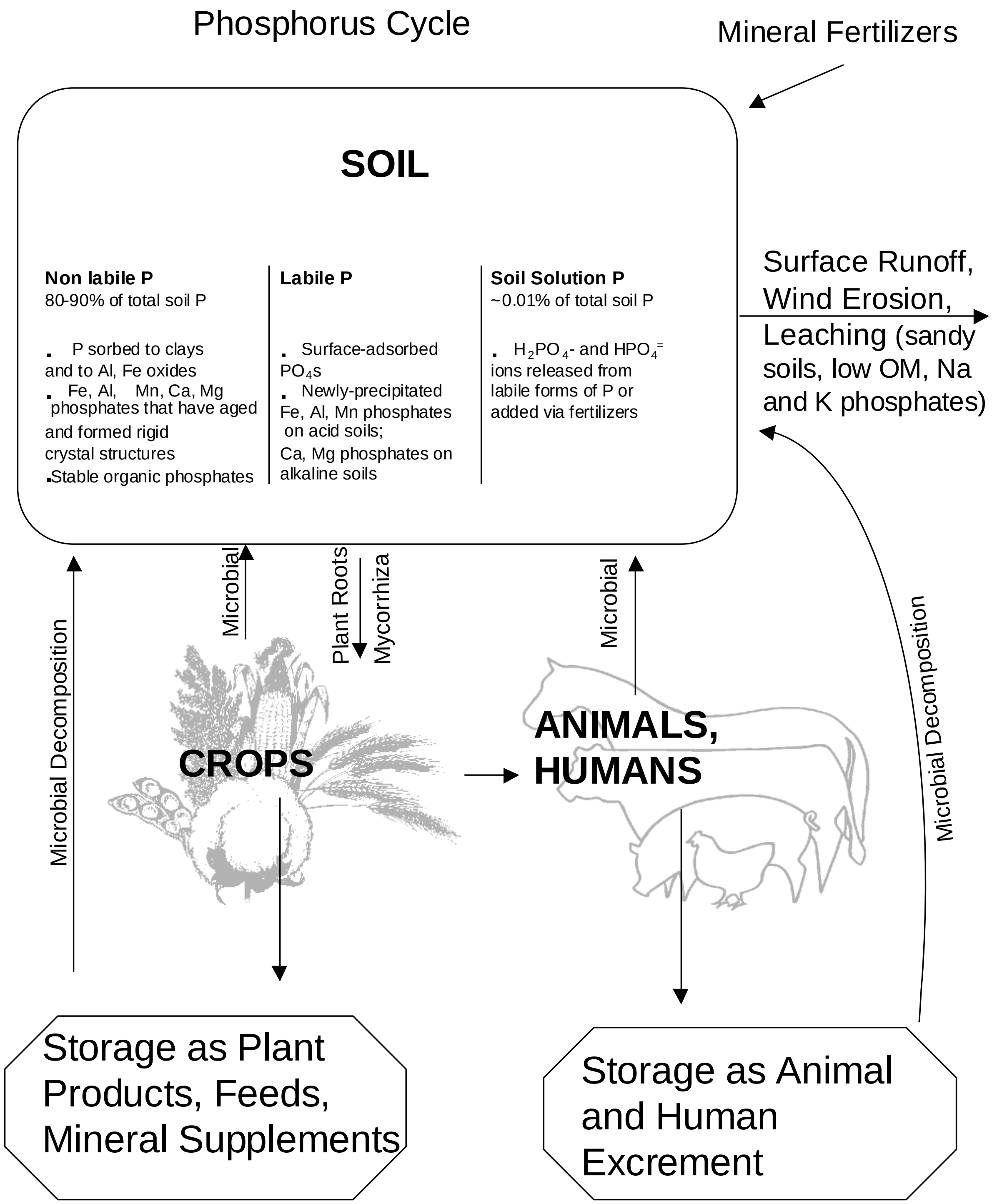
(Soluble) (Insoluble)

Organic P sources:	Inositol phosphate (Esters of orthophosphoric acid), phospholipids, nucleic acids, phosphate sugars
Inorganic P sources:	Apatite and Ca phosphate (unweathered soils) and Fe and Al sinks from P fixation (weathered soils)
Waste:	Poultry litter (3.0 to 5.0%), steel slag (3.5%), electric coal ash (<1.0%)
Total P levels in soil:	50 – 1500 mg/kg
Solution concentration range:	< 0.01 to 1.0 ppm
Applied fertilizer:	< 30% recovered in plants, more P must be added than removed by crops

References:

Alexander, M., 1977. Introduction to Soil Microbiology. 2nd Edition. John Wiley and Sons, NY.
Brady, N.C., 1990. The Nature and Properties of Soils. 10th Edition. Macmillan Publishing Co., NY.
Brigham Young University. 1997. The Phosphorus Cycle. http://ucs.byu.edu/bioag/aghort/214pres/geochem.htm
Harrison, A.F., 1987. Soil Organic Phosphorus. A Review of World Literature. C.A.B. p.39.
Pierre, W.H., 1948. The Phosphorus Cycle and Soil Fertility. J. Amer. Soc. of Agron., 40:1-14.
Pierzynski, G.M., Sims, J.T., and Vance, G.F., 1994. Soil and Environmental Quality. Lewis Publishers, FL.
Stewart, J.W.B., and Sharpley, A.N., 1987. Controls on Dynamics of Soil and Fertilizer Phosphorus and Sulfur in Soil Fertility and Organic Matter as Critical Components of Production Systems, SSSA Spec. Pub. No.19, 101-121.
Tiessen, H., 1995. Phosphorus in the Global Environment – Transfers, Cycles and Management. John Wiley and Sons, NY.
Tisdale, S.L., Nelson, W.L., Beaton, J.D. and Havlin, J.L., 1993. Soil Fertility and Fertilizers. Macmillan Publishing Co., NY.

Authors: Clyde Alsup and Michelle Armstrong, 1998, Asrat Shiferaw 1994, Jerry Speir, 1996


Phosphorus Cycle
Mineral Fertilizers
SOIL
Non labile P
80-90% of total soil P
. P sorbed to clays and to Al, Fe oxides
. Fe, Al, Mn, Ca, Mg phosphates that have aged and formed rigid crystal structures
.Stable organic phosphates
Labile P
. Surface-adsorbed PO4s
. Newly-precipitated Fe, Al, Mn phosphates on acid soils;
Ca, Mg phosphates on alkaline soils
Soil Solution P
~0.01% of total soil P
. H2PO4- and HPO4= ions released from labile forms of P or added via fertilizers
Surface Runoff,
Wind Erosion,
Leaching (sandy soils, low OM, Na and K phosphates)
Microbial Decomposition
Microbial
Plant Roots
Mycorrhiza
Microbial
Microbial Decomposition
CROPS
ANIMALS,
HUMANS
Storage as Plant Products, Feeds, Mineral Supplements
Storage as Animal and Human Excrement

POTASSIUM

Form taken up by the plant:	K^+
Mobility in the soil:	No
Mobility in the plant:	Yes
Deficiency symptoms:	Since K is mobile in the plant, visual deficiency symptoms usually appear first in the lower leaves, and progress to the top as the severity of the deficiency increases. Necrotic lesions on broadleaf plants, chlorotic and necrotic leaf margins on grasses, straw lodging in small grains, and stalk breakage in corn.
Role of nutrient in plant growth:	Enzyme activation, carbohydrate transportation, amino acid synthesis, starch synthesis, water relations, stomatal opening and closing, transpiration, photosynthesis, mass flow in absorpton, energy relations, ATP synthesis, translocation of assimilates, nitrogen uptake, protein synthesis, grain formation, tuber development, nutrient balancing, chlorophyll, disease and insect resistance, strengthening of roots and stems.
Role of nutrient in microbial growth:	Fulfillment of biological requirements similar to other organisms.
Enzymes:	Enzyme activation is regarded as the most important function of potassium. Over 80 plant enzymes require K for activation.
Concentration in plants:	5,000 to 60,000 μg/g (0.5 – 6.0%)
Distribution in the soil:	
Mineral:	5,000 – 25,000 μg/g
Non-exchangeable:	50 – 750 μg/g
Exchangeable:	40 – 600 μg/g
Soil solution:	1 – 10 μg/g

Effect of pH on availability: In very acid soils, toxic amounts of exchangeable Al^{3+} and Mn^{2+} create an unfavorable root environment for uptake of K^+. The use of lime on acid soils low in exchangeable K^+ can induce a K^+ deficiency through ion competition.

Interactions with other nutrients: K^+ enhances NH_4^+, NO_3^- and Cu^{2+} uptake, K^+ decreases Ca^{2+} and Mg^{2+} in plant tissue, Ca^{2+} and Mg^{2+} decreases K^+ in plant tissue, K^+ reduces B uptake, K^+ reduces Fe^{2+} toxicity, K^+ enhances Mn^{2+} uptake when Mn is deficient and decreases uptake when Mn is present in toxic amounts, Na^+ is capable of substituting for K^+. K^+ reduces Mo uptake, high NH_4^+ with inadequate K^+ may cause toxicity symptoms.

Fertilizer sources: Potassium Chloride (KCl); Potassium Sulfate (K_2SO_4); Potassium Magnesium Sulfate (K_2SO_4, $MgSO_4$); Potassium Nitrate (KNO_3); Potassium Phosphates (KPO_3, $K_4P_2O_7$, KH_2PO_4, K_2HPO_4); Potassium Carbonate (K_2CO_3), Potassium Bicarbonate ($KHCO_3$), Potassium Hydroxide (KOH); Potassium Thiosulfate ($K_2S_2O_3$), Potassium Polysulfide (KS_x).

References:

Alexander, M.A. 1977. Introduction to Soil Microbiology. 2nd Edition. John Wiley & Sons, Inc. New York, NY pp. 382-385.

Dibb, D.W. and W.R. Thompson, Jr. 1985. Interaction of potassium with other nutrients. pp. 515-533 in R.D. Munson (ed.) Potassium in agriculture. Am. Soc. Agron.- Crop Sci. Soc. Am.- Soil Sci. Soc. Am. Madison, WI.

Kramer, P.J. and J.S. Boyer. 1995. Water relations of plants and soils, 2nd Edition. Academic Press, Inc., San Diego, CA. pp. 263-264.

Raven, P.H., R.F. Everet, and S.E. Eiichhorn. 1986. Biology of Plants, 4th Edition. Worth Publishing, Inc., New York, NY. p. 519.

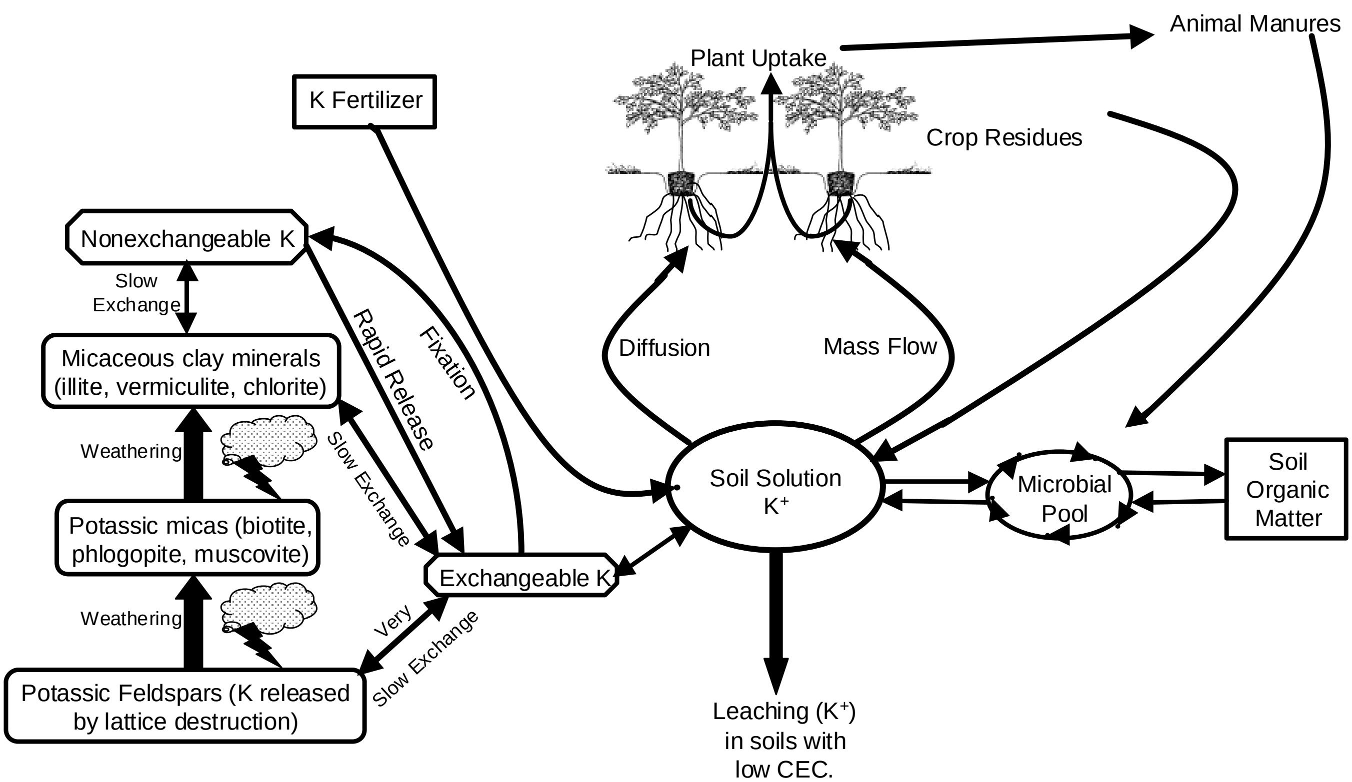
Salisbury, F.B. and C.W. Ross. 1985. Plant physiology, 3rd Edition. Wadsworth Publishing Co., Belmont, CA. p. 108.

Tisdale, S.L., W.L. Nelson, and J.D. Beaton. 1985. Soil fertility and fertilizers, 4th Edition. Macmillan Publishing Co., New York, NY pp. 249-291.

Tisdale, S.L., W.L. Nelson, J.D. Beaton, and J.L. Havlin. 1993. Soil fertility and fertilizers, 5th Edition. Macmillan Publishing Co., New York, NY pp. 230-263.

Authors: Dallas Geis 1994, Michael Goedeken 1996, Todd Heap and Matt Barnes 1998

Potassium Cycle



IRON

Forms taken up by plants:	Fe^{+2} (Ferrous), while Fe^{+3} (Ferric) is reduced to Fe^{+2} at the root surface before it is absorbed.
Mobility in soil	No
Mobility in plant	No
Deficiency symptom in plant	Interveinal chlorosis
Role in Plant nutrition	Iron is a component of cells, proteins, and enzymes. It is involved in nitrogen fixation, respiration and photosynthesis.
Typical concentration in plant tissue	20-300 ppm
Fe Soil Test	Chelation with EDDHA (ethylenediamineedi-o-hydroxyphenylacetic acid) Fe is 100% complexed with EDDHA over a broad range of soil pH.
Fertilizer sources	Foliar application of FeEDDHA or $FeSO_4 \cdot 7H_2O$
Oxidation/Reduction	Oxidation $Fe^{+2} + 1/4O_2 + H^+ \rightarrow Fe^{+3} + ½\ H_2O$ Reduction $Fe^{+3} + e^- \rightarrow Fe^{+2}$
Fe^{+3} Forms of Iron	$Fe(OH)_3$ amorphous $Fe(OH)_3$ (soil) Hematite Fe_2O_3 Goethite FeOOH Soil $Fe(OH)_3$ is usually the most soluble form of iron in soils and, therefore, typically controls the solubility of iron in aerobic soils.
Fe^{+2} Forms of Iron	A common iron mineral in nature is pyrite (FeS_2). Pyrite is often associated with bituminous coal and other ores. Bacterial oxidation of pyrite generates acid and is the cause of acid mine drainage. $FeS_2 + 31/2O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+$. Fe^{+2} hydrolyzes to form hydrolysis products common under reduced conditions. $FeOH^+$ predominates in solution at pH< 6.75, while $Fe(OH)_2^0$ prdeominates at pH >9.3.

Magnetite (Fe_30_4) is a stable mineral under reduced conditions

Microbial use of iron

Many organisms use Fe^{+3} as an electron acceptor such as some fungi and and chemoorganotrophic or chemolithtropic bacteria. This bacterial reduction of ferric to ferrous is a major way iron is solubilized. Reduction takes place under anaerobic conditions (waterlogged). Shewenella putrefaciens is one organism capable of reducing iron. Oxidation occurs under aerobic conditions. At neutral pH, organisms such as Gallionella ferruginea or Leptothrix oxidize iron. Under acidic conditions, Thiobacillus ferrooxidans is the primary organism responsible for iron oxidation. This organism is typical in acid mine drainage areas.

References:

Brock, T. D.; M. T. Madigan; J. M. Martinko; J. Parker. (1994). Biology of Microorganisms. Prentice Hall Englewood Cliffs, NJ.

Lindsay, W. L. (1979). Chemical Equilibria in Soils. John Wiley & Sons, NY.

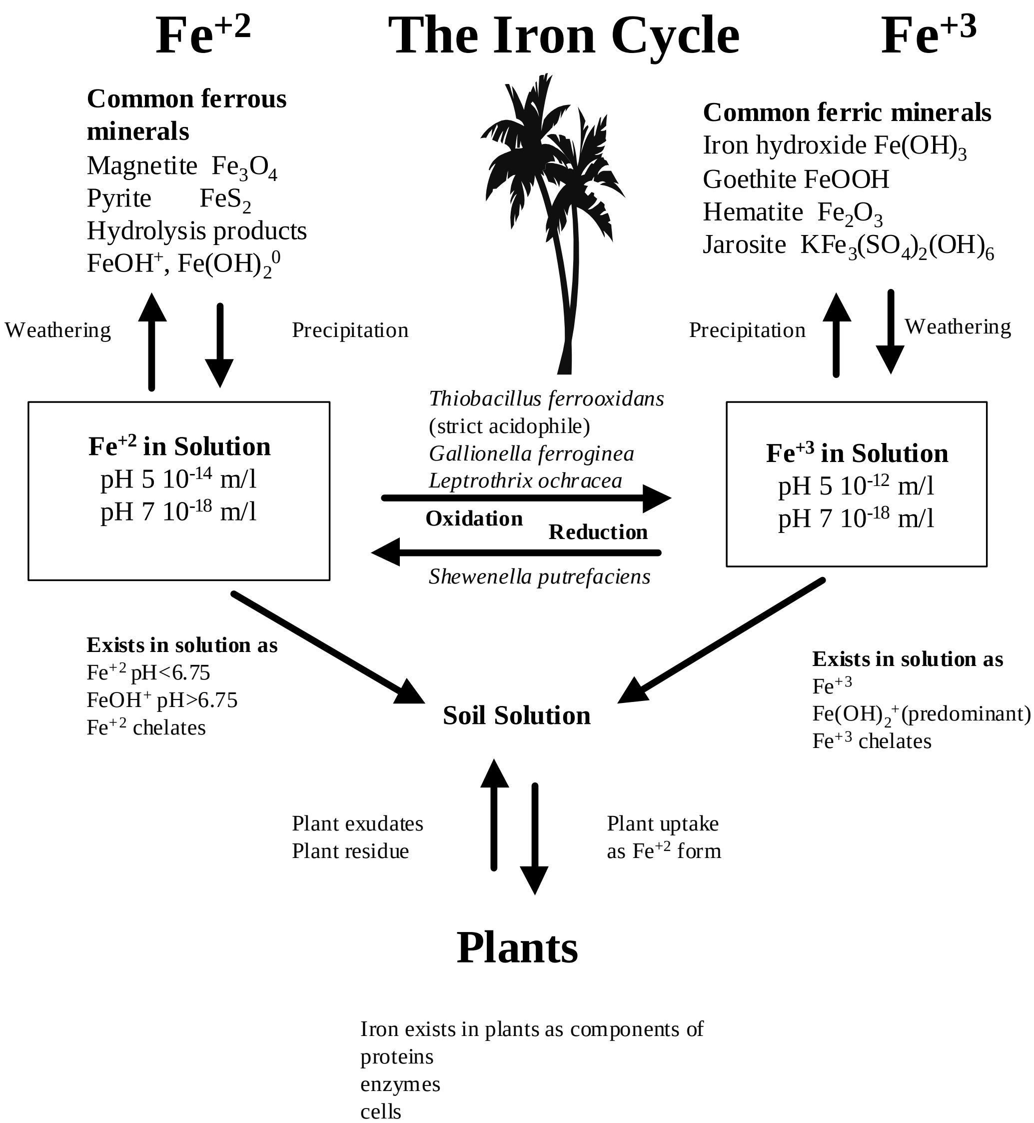
Raun, W. R.; G. V. Johnson; R. L. Westerman. (1998). Soil-Plant Nutrient Cycling and Environmental Qualtiy. Plant & Soil Sciences 5813 class notes.

Tisdale, S. L.; W. L. Nelson; J. D. Beaton; J. L. Havlin. (1985). Soil Fertility and Fertilizers 5th edition. MacMillan Publishing Co. NY.

Walsh, L. M.; J. D. Beaton. (1973). Soil Testing and Plant Analysis. Soil Science Society of America, Inc. Madison, WI.

Authors: Fred Kanampiu 1994, Jing Chen, Jason Yoder 1996 and Libby Dayton 1998

The Iron Cycle



SULFUR

Form taken up by plants:	SO_4^{2-}, SO_2^{-} (low levels adsorbed through leaves)
Mobility in plant:	Yes
Mobility in soil:	Yes
Deficiency symptoms:	Leaves chlorotic (upper leaves), reduced plant growth, weak stems
Role of nutrient in plant and microbial growth	Synthesis of the S-containing amino acids cystein, cystine, and methionine; Synthesis of other metabolites, including CoA, biotin, thiamine, and glutathione; Main function in proteins is the formation of disulfide bonds between polypeptide chains; Component of other S-containing substances, including S-adenosylmethionine, formylmethionine, lipoic acid, and sulfolipid; About 2% of the organic reduced sulfur is in the plant is present in the water soluble thiol (-SH) fraction; Vital part of ferredoxin; Responsible for the characteristic taste and smell of plants in the mustard and onion families; Enhances oil formation in flax and soybeans; Sulfate can be utilized without reduction and incorporated into essential organic structures; Reduced sulfur can be reoxidized in plants
Enzymes needing sulfur:	Coenzyme A, ferredoxin, biotin, thiamine pyrophosphates, urease and sulfotransferases
Concentration in plants:	0.1 and 0.5% of the dry weight of plants
Effect of pH on availability:	pH<6.5, AEC increases with decreasing pH
Interaction with other nutrients:	Associated with salts and exchangeable cations, can be replaced by phosphorus on exchange sites
Fertilizer sources:	Organic matter, ammonium bisulfite, ammonium nitrate-sulfate, ammonium phosphate-sulfate, ammonium polysulfide,

ammonium sulfate, ammonium thiosulfate, ferrous sulfate, gypsum, magnesium sulfate, potassium sulfate, pyrites, potassium-magnesium sulfate, potassium thiosulfate, potassium polysulfide, sulfuric acid (100%), sulfur, sulfur dioxide, single superphoshate, triple superphosphate, urea-sulfur, urea-sulfuric acid and zinc sulfate

References:

Hartmann, H.T., Kofranek, A.M., Rubatzky, V.E., Flocker, W.J. (1988). Plant Science. 2nd ed. Prentice Hall. Englewood Cliffs, N.J.

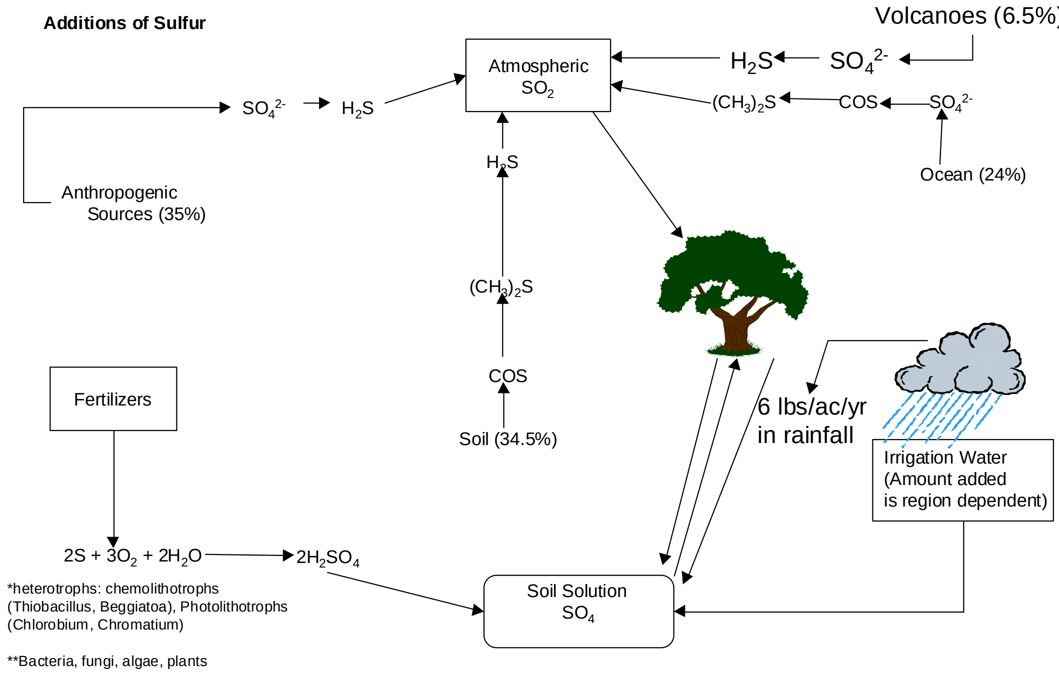
Marschner, H. (1995). Mineral Nutrition of Higher Plants. 2nd ed. Institute of Plant Nutrition Univ. Hohenheim. Academic Press. San Diego, Ca.

Tisdale, S.L., Nelson, W.L., Beaton, J.D., and Havlin, J.L. (1993). Soil Fertility and Fertilizers. 5th ed. Macmillan Pub. Co. New York, NY.

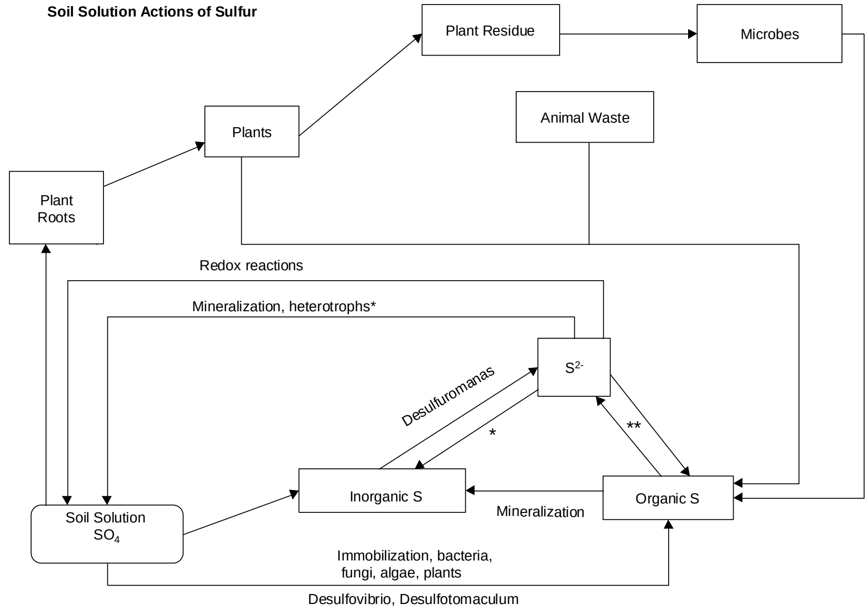
Vaughan, D., Malcolm, R.E. (1985). Soil Organic Matter and Biological Activity. Martinus Nijhoff/Dr W. Junk Publishers, Dordrecht.

Authors: Xin Li, Dale Keahey and Jeremy Dennis

Additions of Sulfur

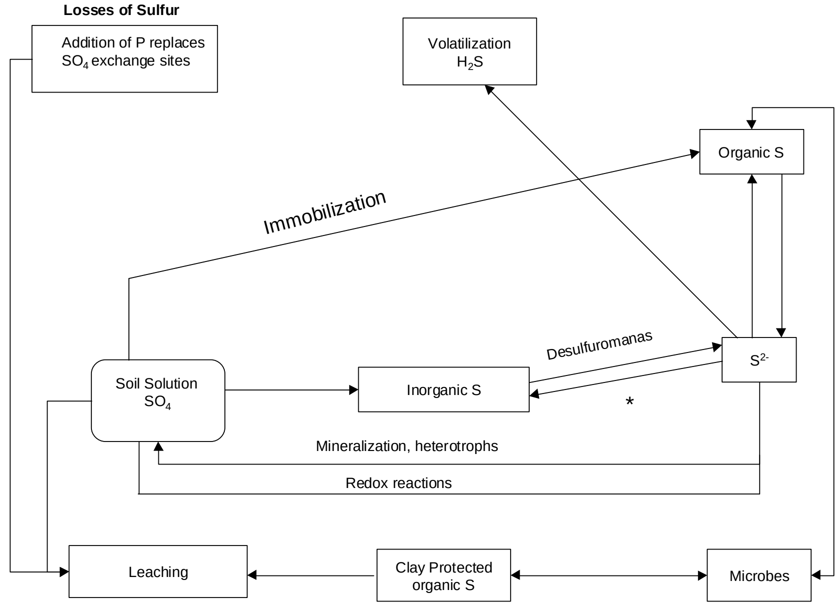


Soil Solution Actions of Sulfur



pH > 7 less sulfate adsorbed by plants

Losses of Sulfur



CARBON

Form taken up by the plant: CO_2

Mobility in soil: CO_2 mobile in soil pore space.
HCO_3^- mobile in soil solution.

Mobility in plant: --

Deficiency symptoms: --

Toxicity symptoms: --

Role in plant growth: Basic energy source and building block for plant tissues. Converted through photosynthesis into simple sugars. Used by plants in building starches, carbohydrates, cellulose, lignin, and protein. CO_2 given off by plant respiration.

Role in microbial growth: Main food of microbial population. Utilization by microbes is closely related to C:N ratio.

Concentration in plants: --

Effect of pH on availability: None

Interactions with other nutrients: 10:1 C:N ratio needed for stable soil organic matter. High C:N ratios lead to nitrogen immobilization. Low C:N ratios lead to nitrogen mineralization. N rates in excess of those required for maximum yield can lead to increased soil organic carbon.

Fertilizer sources: Crop residues, green manures and animal wastes can be significant sources of soil organic carbon.

References:

Detwiler, R.P., and C.A.S. Hall. 1988. Tropical Forests and the global carbon cycle. Science. 239:42-47.

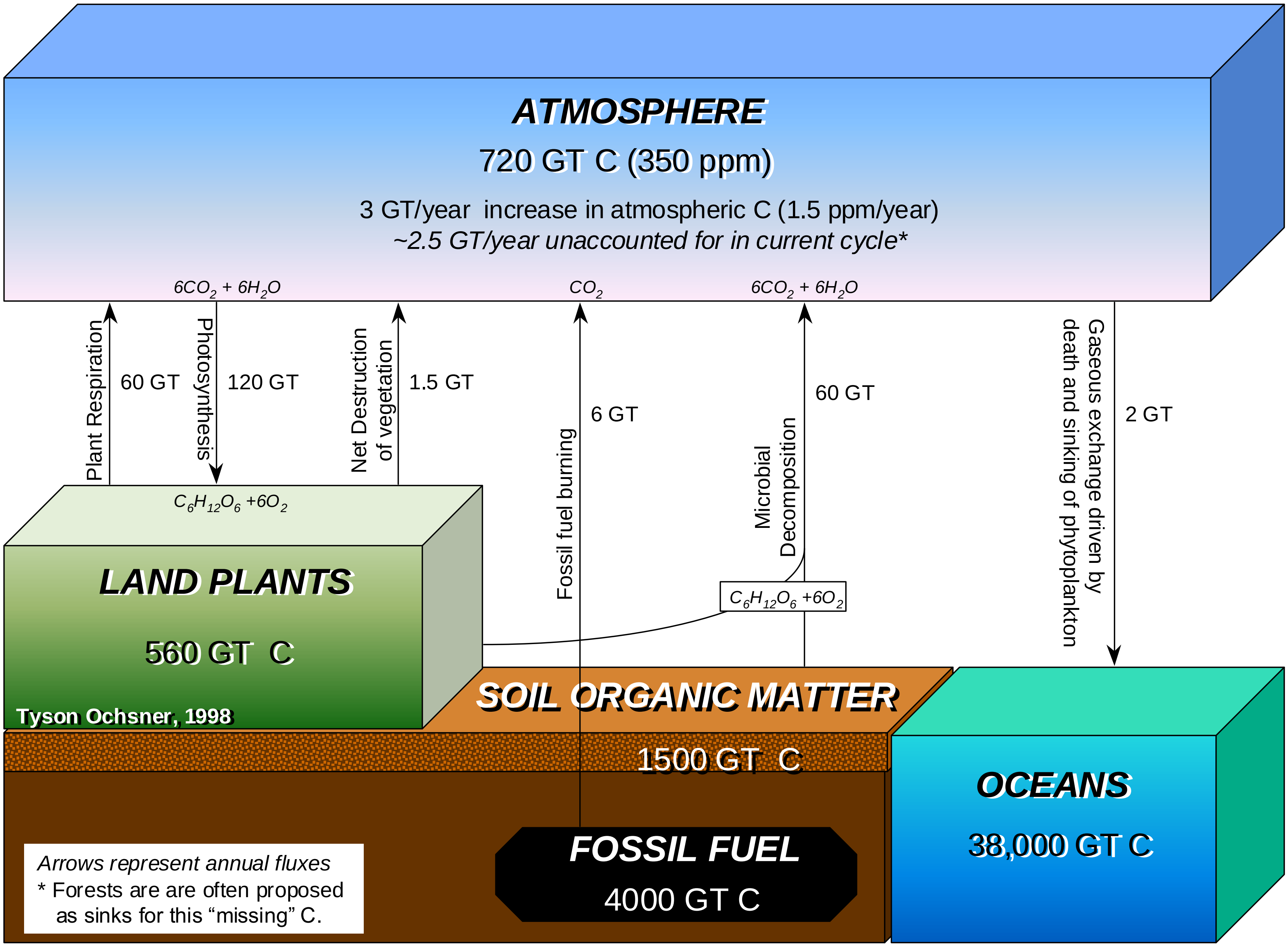
Dixon, R.K., S. Brown, R.A. Houghton, A.M. Solomon, M.C. Trexler, and J. Wisniewski. Carbon pools and flux of global forest ecosystems. Science. 263:185 190.

Gillis, A.M. 1991. Why can't we balance the globe's carbon budget?. Bioscience. 41:442-447.

Schlesinger, W.H. 1998. "Chapter 2: An overview of the carbon cycle". Soil processes and the carbon cycle. Boca Raton, Fla: CRC Press, c1998.

Wallace, A., G.A. Wallace, and J.W. Cha. 1990. Soil organic matter and the global carbon cycle. Journal of Plant Nutrition. 13:459-466

Author: Tyson Ochsner


ATMOSPHERE
720 GT C (350 ppm)
3 GT/year increase in atmospheric C (1.5 ppm/year)
~2.5 GT/year unaccounted for in current cycle*
$6CO_2 + 6H_2O$
CO_2
$6CO_2 + 6H_2O$
Plant Respiration
60 GT
Photosynthesis
120 GT
Net Destruction of vegetation
1.5 GT
Fossil fuel burning
6 GT
Microbial Decomposition
60 GT
Gaseous exchange driven by death and sinking of phytoplankton
2 GT
$C_6H_{12}O_6 + 6O_2$
$C_6H_{12}O_6 + 6O_2$
LAND PLANTS
560 GT C
Tyson Ochsner, 1998
SOIL ORGANIC MATTER
1500 GT C
OCEANS
38,000 GT C
FOSSIL FUEL
4000 GT C
Arrows represent annual fluxes
* Forests are are often proposed as sinks for this "missing" C.

CALCIUM

Form taken up by plants:	Ca^{+2}
Mobility in soil:	No, slight mobility in soil solution
Mobility in plant:	Movement occurs in xylem to the leaves (one way ticket)
Role of nutrient in plant growth:	Required for cell wall rigidity, cell division of meristems and root tips, normal mitosis, membrane function, acts as a secondary messenger, aids in storage of phosphates in vacuoles, actively involved in photosynthesis and found in the endoplasmic reticulum
Role in microbial growth:	Needed for Rhizobium and Azotobacter
Concentration in plants:	Fresh weight of plants typically contains 0.1-5.0%, can contain up to 10% dry weight in leaves before plant experiences toxicity
Content present in soils:	Tropical soils: 0.1-0.3% Temperate soils: 0.7-1.5% Calcareous soils: >3.0% Largely dependent on parent material of soil and rainfall
Deficiency symptoms:	First seen in the younger leaves of plants, loss in plant structure, under extreme deficiencies gel-like conditions, root development no longer takes place, stunted plant growth
Effect of pH on availability:	Depends on mineral
Interactions with other nutrients:	Since Ca^{+2} is so directly related to pH in solution, it effects all of the other nutrients. When NO_3-N is applied to soil, Ca^{+2} absorption increases in the plant. Increases in Ca^{+2} in soil decreases Al^{+3} in acid soils, as well as decreasing Na^{+} in sodic soils. Increases in Ca^{+2} taken up by plants cause deficiencies of Mg^{+2} and K^{+}. MoO_4^{-2} and $H_2PO_4^{-}$ availability increases with increases in Ca^{+2} concentrations.

Sources of Calcium: Lime (CaO) ($Ca(OH)_2$), Calcite ($CaCO_3$), Dolomite ($CaMg(CO_3)_2$, Gypsum ($CaSO_4 \cdot 2H_2O$), any Phosphorus fertilizer, Anorthite ($CaAl_2Si_2O_3$), biotite, apatite, augite & hornblende.

References:

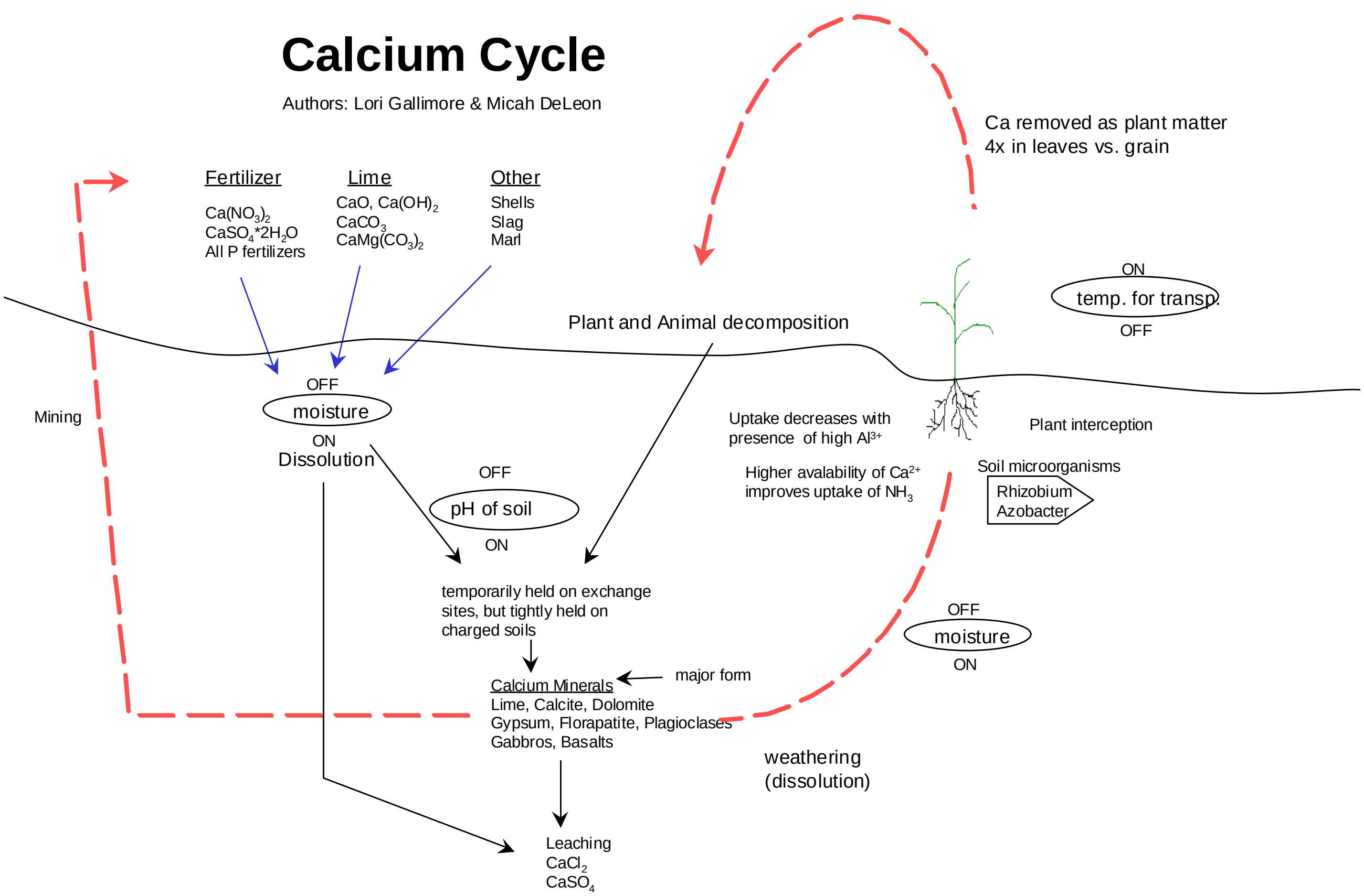
Amjad, Z. (ed.) 1998. Calcium Phosphates in Biological and Industrial Systems. Klower Academic Press. Boston, MA.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. John Wiley & Sons. New York, NY. pp. 86-102.

Marschner, H. 1995. Mineral Nutrition of Higher Plants. Academic Press. New York, NY. pp. 285-298.

Tisdale, S.L., Nelson, W.L., Beaton, J.D. and Havlin, J.L. 1993. Soil Fertility and Fertilizers. Macmillan Publishing Company. pp. 289-296.

Authors: James Johnson, Derrel White, Lori Gallimore and Micah DeLeon



MAGNESIUM

Form taken up by plant:	Mg^{++}
Mobility in Soil:	yes/no
Mobility in Plant:	yes as Mg^{++} or Mg Citrate
Deficiency Symptoms:	Interveinal chlorosis, necrosis, general withered appearance, leaves are stiff and brittle and intercostal veins are twisted.
Deficiencies:	pH 5.0 is best for Mg availability. A higher or lower pH depresses Mg uptake. High K and Ca levels also interfere with uptake.
Where deficiencies occur:	Highly leached humus acid soils or on sandy soils which have been limed heavily (due to Ca^{2+} competition). sometimes on soils high in K; Mg deficiencies are indicated by soil test index values less than 100 lbs/A.
Toxicity Symptoms:	none
Toxicities:	Grass Tetany when K/(Ca+Mg)> 2.2
Role of Mg in Plant Growth:	Responsible for electron transfer in photosynthesis; Central element of chlorophyll molecule (6-25% of total plant Mg); Required for starch degradation in the chloroplast; Involved in regulating cellular pH; Required for protein synthesis; Required to form RNA in the nucleus; Mg-pectate in the middle lamella
Role of Nutrient in Microbial Growth:	Important for phosphorus metabolism; Helps to regulate the colloidal condition of the cytoplasm.
Concentration in plants:	0.15% - 0.35% (1500-3500 ppm)
Effect of pH on Availability:	Highest Mg availability at pH 5.0.
Precipitated forms at low pH:	$MgCl_2$, $MgSO_4$, $Mg(NO_3)_2$
Precipitated forms at high pH:	MgO, $MgCO_3$, $Mg(OH)_2$, $MgCa(CO_3)_2$
Interactions with other nutrients:	Uptake of K^+, NH_4^+, Ca^{2+}, Mn^{2+} by plant limits Mg^{2+} uptake; H^+ (low pH) can limit

Mg^{2+} uptake; Mg salts increase phosphorus adsorption

Fertilizer Sources: Dolomite ($MgCa(CO_3)_2$) (most common); Magnesium sulfate ($MgSO_4 \times H_2O$) (Kieserite); Magnesium oxide ($Mg(OH)_2$) (Brucite); Magnesite ($MgCO_3$); Magnesia (MgO); Kainite ($MgSO_4 \times KCl \times 3H_2O$); Langbeinite ($2MgSO_4K_2SO_4$); Epsom Salts ($MgSO_4 \times 7H_2O$)

Additional categories:

Location in Plants: In corn, 34% of total Mg is in grain

Radioactive Isotopes:

^{23}Mg $t_{1/2} = 11.6$ sec
^{27}Mg $t_{1/2} = 9.6$ min
^{28}Mg $t_{1/2} = 21.3$ hr

Enzymes that require Mg++: Magnesium is a co-factor for many enzymes. This includes enzymes involved in glycolysis, carbohydrate transformations related to glycolysis, Krebs cycle, the monophosphate shunt, lipid metabolism, nitrogen metabolism, “phosphate pool” reactions, photosynthesis, and other miscellaneous reactions.

Examples: ATPase (phosphorylation), phosphokinases; RuBP carboxylase (photosynthesis); Fructose 1,6-phosphatase (starch synthesis in chloroplasts); Glutamate synthase (ammonia assimilation in the chloroplasts); Glutathione synthase; PEP carboxylase

Ionic Radius: 0.78 Angstroms

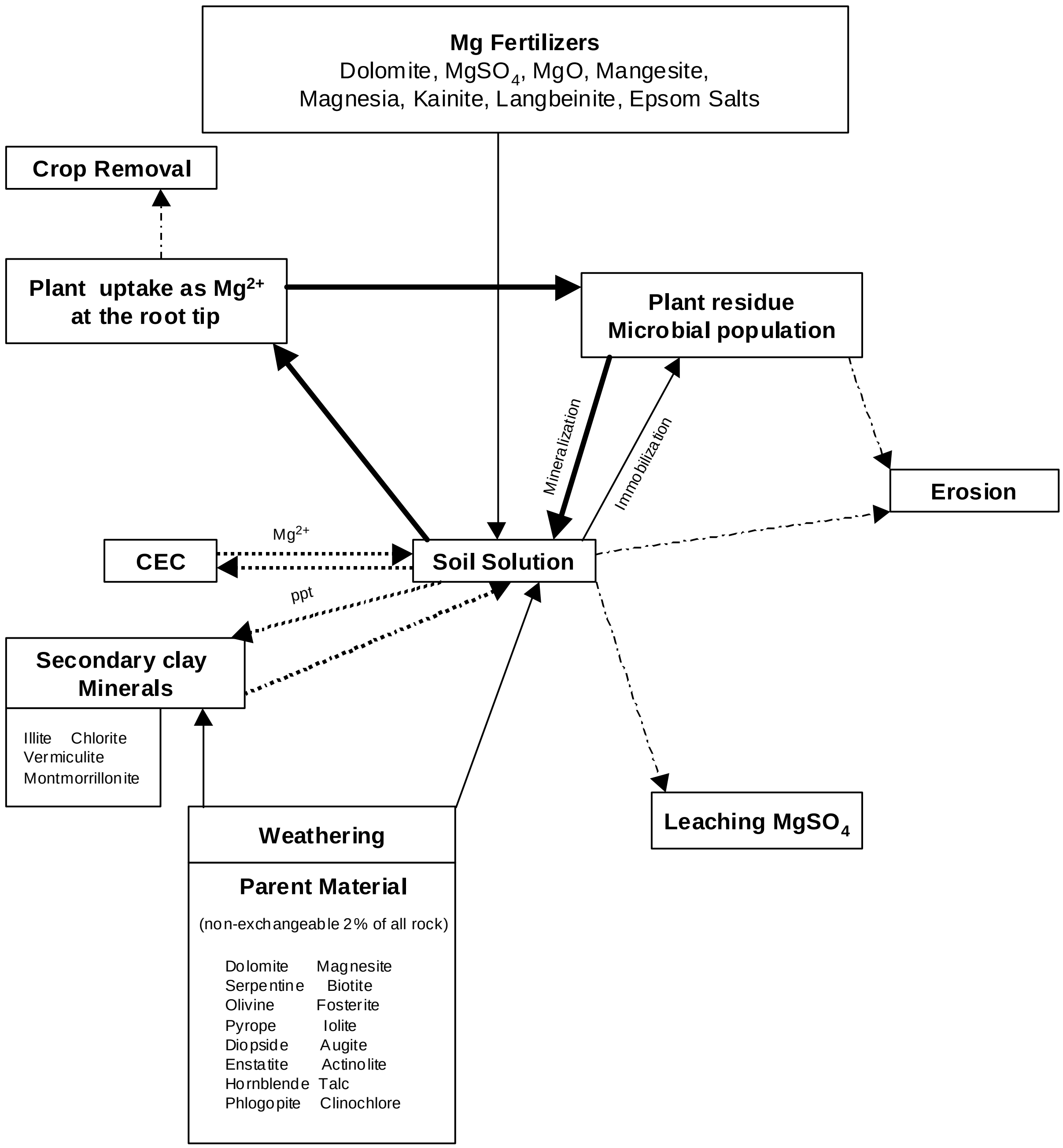
Hydration Energy: 1908 J mol^{-1}

References:

Ball, Jeffrey. 1994. Magnesium Cycle. As presented to SOIL 5813.
Jacob, A. 1958. Magnesium - the fifth major plant nutrient. Staples Press Limited, London.
Johnson, G.V., W.R. Raun, and E.R. Allen. 1995. Oklahoma Soil Fertility Handbook. 3rd ed. Okla. Plant Food Educational Society and Okla. State Univ. Dept. of Agronomy, Stillwater, OK.
Lauchli, A. and R.L. Bieleski (editors). 1983. Inorganic Plant Nutrition. Springer-Verlag, Berlin.
Marschner, H. 1986. Mineral Nutrition of Higher Plants. 2nd ed. Academic Press, London.
Mengel, K. and E.A. Kirkby. 1978. Principles of Plant Nutrition. International Potash Institute, Bern.
West Virginia Univ. 1959. Magnesium and agriculture symposium. Morgantown, WV.

Authors: Jeffrey Ball, Mark Everett and Rick Kochenower

Magnesium Cycle



BORON

Form taken up by plant: $H_3BO_3^0$

Mobility in soil: Yes

Mobility in plant: No

Deficiency symptoms: Boron deficient plants exhibit a wide range of deficiency symptoms, but the most common symptoms include necrosis of the young leaves and terminal buds. Structures such as fruit, fleshy roots and tubers may exhibit necrosis or abnormalities related to the breakdown of internal tissues.

Interactions with O.M.: Boron is complexed by O.M. and can be a major source of B to plants. Mineralization of O.M. releases boron to soil solution. The mineral source of boron in soils is Tourmaline, which is a very insoluble borosilicate mineral.

Effect of pH on availability: Boron availability decreases with increasing pH. Overliming acid soils can cause boron deficiency because of interaction with calcium.

Role of Soil characteristics Boron is generally less available on sandy soils in humid regions, because of more leaching. This is especially true in acid soils with low O.M. Boron availability increases with increasing O.M. Most alkaline and calcareous soils contain sufficient Boron because the primary boron minerals have not been highly weathered and, more important, B products of weathering (H_3BO_3) have not been leached out as in humid region soils.

Role of Boron in plants: Cell growth and formation. The action appears to be in binding sugars together. Indirect evidence also suggests involvement in carbohydrate transport.

Concentrations in Soil: Total Boron in soils is small (20-200 ppm)

Deficiency levels in plants: Monocots: 5-10 mg/kg

Dicots: 50-70 mg/kg

Toxic levels in plants: Corn: 100 mg/kg
Cucumber: 400 mg/kg

Toxic levels in soil & water: Boron can be toxic on some alkaline soils when soil test or extractable boron exceeds 5 ppm. Irrigation water that contains > 1ppm boron can also produce toxicity.

Boron availability index: Soil test is "hot water soluble" B
- <0.3 ppm boron
- 0.3-0.5 ppm boron
- > 0.5 ppm boron
- >5.0 ppm boron

Boron fertilizers:
Borax: ($Na_4B_4O_7\ 10H_2O$) 10-11% B
Boric acid (H_3BO_3) 17 % B
Colemanite ($Ca_2B_6O_{11}\ 5H_2O$) 10 % B
Sodium pentaborate ($Na_2B_{10}O_{16}10H_2O$) 18%B
Sodium tetraborate ($Na_2B_4O_7\ 5H_2O$) 14 % B
Use low rates, generally < 3 lbs/acre. Do not reapply without soil testing.

Other Sources of B: Animal wastes: 0.01 to 0.09 lb/ton of waste @ 72-85% moisture.

References:

Mortvedt, J.J. 1972. Micronutrients in Agriculture. Soil Science Society of Americia, Madison, Wisconsin.

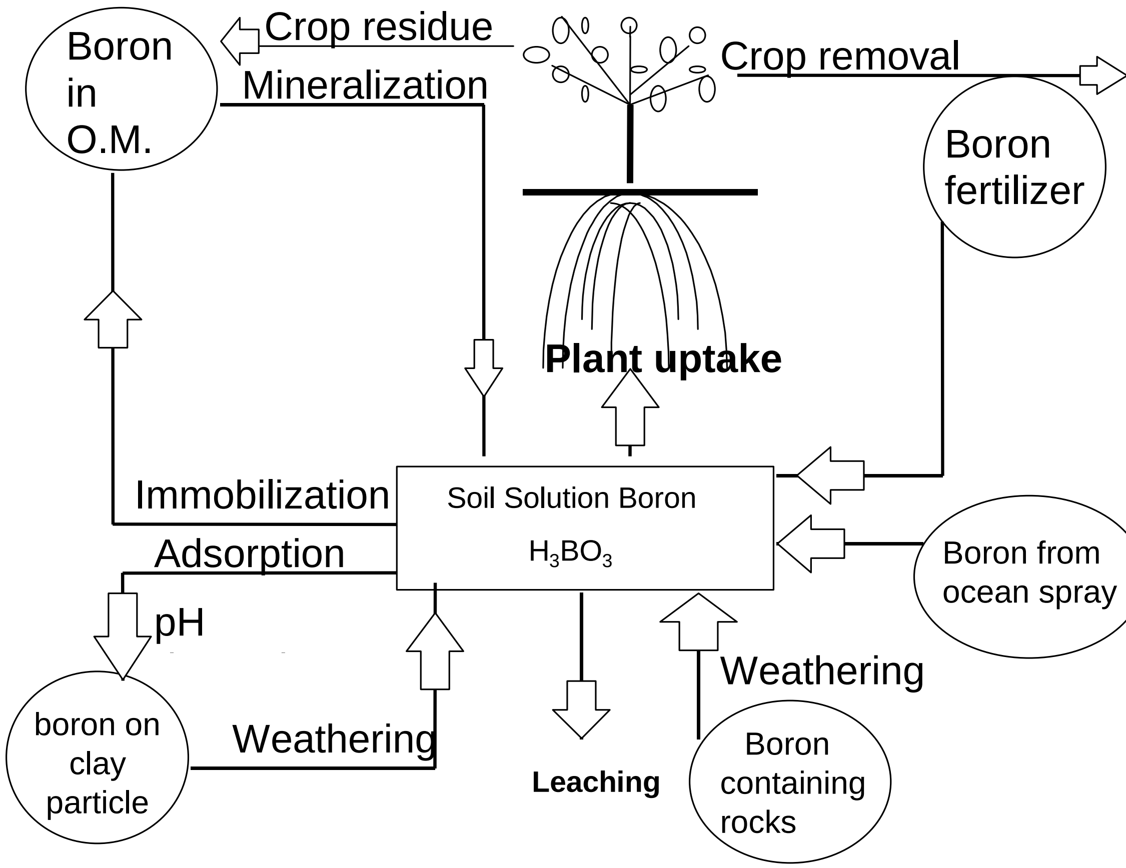
Philipson, Tore. 1953. Boron in Plant and Soil with special regard to Swedish Agriculture. Acta Agriculturae Scandinavica. III:2.

Raun, W.R., G.V. Johnson, and S.L. Taylor. 1996. Soil-Plant Relationships, Oklahoma State University Agronomy 5813 class notes.

Taiz, Lincoln and Eduardo Zeiger. 1991. Plant Physiology.

Tisdale S.L., W.L. Nelson, J.D. Beaton, and J.L. Havlin. 1993. Soil Fertility and Fertilizers. 5th ed. MacMillan Publishing Co. New York, NY.

Authors: Andrew Bennett and Jason Kelley



MANGANESE

Form taken up by the plant: Absorbed by plants as Mn^{2+} from the soil, or Mn^{2+} from foliar sprays of $MnSO_4$, or foliar chelates as MnEDTA.

Mobility in soil: Relatively immobile; concentration in soils generally ranges from 20 to 3000 ppm and averages 600 ppm; total soil Mn is an inadequate predictor of Mn availability; Mn is highest in the surface horizon, minimal in the B horizon, and generally increases in the C horizon; Mn^{2+} can leach from soils over geological time, particularly acid spodizols.

Mobility in plant: Relatively immobile; Mn moves freely with the transpiration stream in the xylem sap in which its concentration and ionic form may vary widely; Mn accumulated in leaves cannot be remobilized while that in roots and stems can.

Deficiency symptoms: Interveinal chlorosis (yellowish to olive-green) with dark-green veins first showing up in the younger leaves; patterns of chlorosis can be easily confused with Fe, Mg, or N deficiencies; under severe deficiencies, leaves develop brown speckling and bronzing in addition to interveinal chlorosis, with abscission of developing leaves; characterizations—gray speck of oats, marsh spot of peas, speckled yellows of sugar beets, stem streak necrosis in potato, streak disease in sugar cane, mouse ear in pecan, and internal bark necrosis in apple; most common micronutrient deficiency in soybeans; deficiencies are common in cereal grains, beans, corn, potatoes, sugar beets, soybean and many vegetables; some crops are more sensitive to deficiencies; may cause susceptibility to root rot diseases such as “take-all” in wheat.

deficiency at pH (.7.0) Mn tends to become limiting at a high pH.

Toxicity symptoms: Sometimes observed on highly acidic soils; crinkle leaf of cotton.

Toxic at pH (< 5.5)

Toxicity occurs in low pH soils (<5.5).

Role of Mn in plant growth:

Water splitting role in photosynthesis resulting in evolution of O_2; redox reactions; decarboxylation and hydrolysis reactions; dehydrogenase and transferase reactions; can substitute for Mg^{2+} in many phosphorylating & group-transfer reactions; influences auxin in plants; activates many enzymes involved in the metabolisms of organic acids, phosphorus, and nitrogen (in dispute); activator in enzymes involved in carboxylic acid cycle and carbohydrate metabolism, but frequently replaced by Mg.

Enzymes

Mn-containing protein in photosystem II involved in H_2O splitting; Mn-containing superoxide dismutases catalyze the dismutation of the toxic superoxide; often implicated as affecting purple acid phosphatases which catalyze the hydrolysis of phosphoric acid monoesters and anhydrides, but more recent evidence suggest a dominant role by Fe; affects indole acetic acid oxidase; C4 plants—requirement for NAD-malic and phosphoenolpyruvate (PEP) carboxykinase (two of three alternate forms of decarboxylating enzymes); C4 plants—NADP-malic enzyme (third type of decarboxylating enzyme) requires either Mn^{2+} or Mg^{2+} ; C4 plants—phosphoenolpyruvate (PEP) carboxylase requires either Mn^{2+} or Mg^{2+}; earlier evidence of a role in nitrate and nitrite reductase activity has been disputed; excess causes depression of net photosynthesis by inhibiting the RuBP carboxylase reaction; excess Mn^{2+} is sequestered in the vacuole to prevent saturation of ATPs which require Mg for normal functioning.

Role of Mn for microbial growth:

Used by many microbes in biological oxidation; Bacteria—Arthrobacter, Bacillus; Fungi—Cladisporium, Curvularia.

Concentration in plants:

Typically ranges from 20 to 500 ppm ; concentrations <20 ppm generally cause

	deficiencies, and >500 ppm cause toxicities, but vary with crop, culture, and tissue.
Effect of pH on availability:	Mn decreases 100-fold for each unit increase in pH; concentration of Mn^{2+} in solution is increased under acid, low-redox conditions; high pH also promotes the formation of less available organic complexes; activity of soil microorganisms that oxidize soluble Mn to unavailable forms reaches a maximum near pH 7.0; liming and burning can produce alkaline conditions causing deficiency; high pH favors oxidation to Mn^{+4}, from which insoluble oxides are formed (MnO_2, Mn_2O_3, and Mn_3O_4); pH < 6.0 favors reduction of Mn and formation of more available divalent form Mn^{+2}
precipitated forms (low pH)	Typically precipitated as Mn and Fe oxides, often as concretions.
precipitated forms (high pH)	Complexation occurs with organic matter at high pH; precipitated as Mn carbonates and MnOH.
Other factors:	Poor aeration increases Mn availability; soil waterlogging will reduce O_2 and lower redox potential, which increases soluble Mn^{2+}; dry soils allow rapid oxidation and deficiency may result; local accumulation of CO_2 around roots increases Mn availability; high organic matter (particularly if basic soil) forms unavailable chelated Mn^{2+} compounds, particularly in peat and muck soils; pronounced seasonal variations, with wet weather increasing Mn^{2+} and warm, dry weather encouraging the formation of less available oxidized forms; some deficiencies are caused by soil organisms oxidizing Mn^{2+} to Mn^{3+} ; Mn- efficient and Mn-inefficient plants
Interactions with other nutrients:	High levels of Cu, Fe or Zn can reduce Mn uptake; high levels of Mn can reduce Fe concentrations and induce Fe deficiencies and vice versa; ratio of Fe to Mn should be between 1.5 to 2.5; Mn and Al toxicities frequently occur together on acid soils

Fertilizer sources: Manganese sulfate ($MnSO_4*4H_2O$, 26-28%)—most common; Manganese oxide (MnO, 41-68%); Manganese chloride ($MnCl_2$, 17%); Organic complexes (5-9%); Synthetic chelates (MnEDTA, 5-12%)

References:

Adriano, D.C. 1986. Trace elements in the terrestrial environment. Springer-Verlag. New York, NY.

Boyles, F.W. Jr, and W.L. Lindsay. 1986. Manganese phosphate equilibrium relationships in soils. Soil Sci. Soc. Am. J. 50: 588-593.

Davis, J.G. 1996. Soil pH and magnesium effects on manganese toxicity in peanuts. Journal of Plant Nutrition. 19:535-550.

Graham, R. D., R.J. Hannam, and N.C. Uren. 1988. Manganese in soils and plants. Kluwer Academic Pub. Dordrecht, Netherlands.

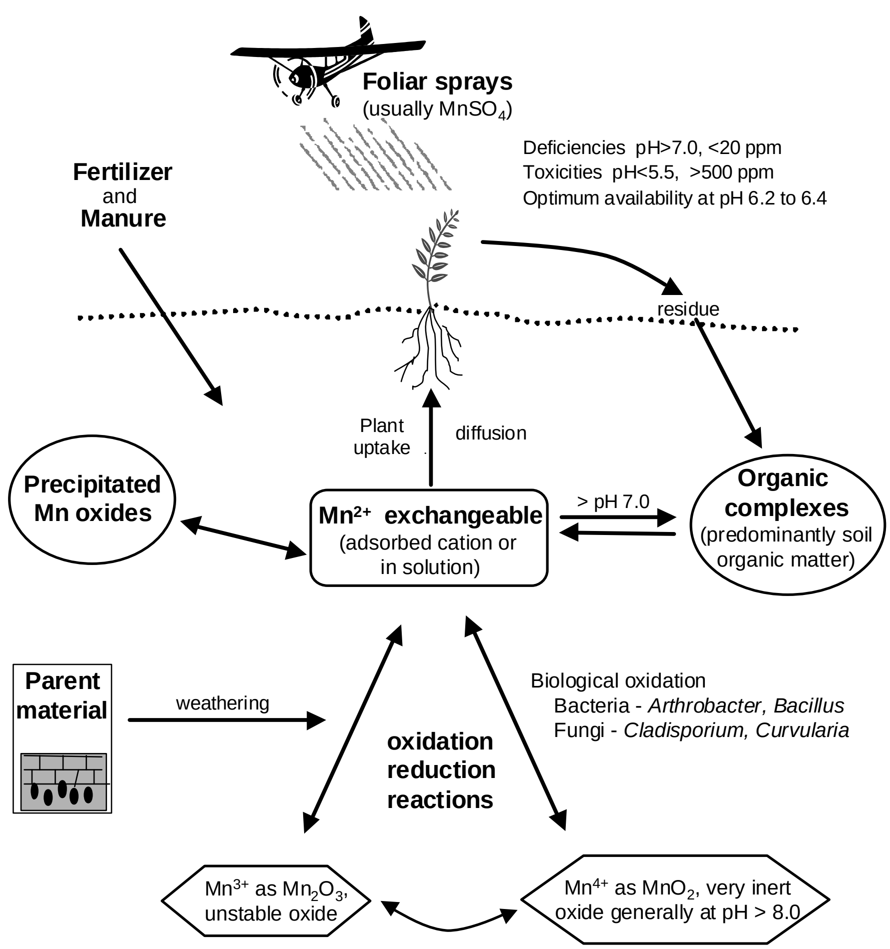
Marschner, H. 1995. Mineral nutrition of higher plants. Academic Press. 2nd Ed. London, New England.

Stevenson, F.J. 1986. Cycles of soil: carbon, nitrogen, phosphorus, sulfur, micronutrients. John Wiley & Sons. New York, NY.

Tisdale, S.L., W.L. Nelson, J.D. Beaton, J.L. Havlin. 1993. Soil fertility and fertilizers. MacMillan Publishing Co. 5th Ed. New York, NY.

Authors: John Koemel, Robert Zupancic and Johnny Roberts

Manganese Cycle



COBALT

Plant available forms:	Co^{2+}, Co^{3+}, $Co(OH)_3^-$, organic chelates of Co [6]; plant uptake increases as pH decreases. [2]
Role in plant nutrition:	Micronutrient, required for symbiotic nitrogen fixation by Rhizhobium bacteria in root nodules. No conclusive evidence of requirement by higher plants. [1] [2] [8] [9]
Plant Mobility:	Intermediate mobility. [2]
Plant Deficiency symptoms:	Necrosis of leguminous plants with deficient soil nitrogen and cobalt. [8]
Role in animal nutrition:	Vitamin B_{12} nutrition. [2]
Enzymes:	Cyanocobalamin (Vitamin B_{12}), essential metal for humans and mammals. [4]
Mammalian toxicity:	Critical organs include skin, heart, and respiratory tract. Reported toxicity occurred in miners that worked in cobalt rich ore, developed dermatitis, cardiomyopathy, and hard metal lung disease. [4]
Mobility in soil:	Low mobility of inorganic Co, High mobility of organic chelates of Co. [6]
Common soil types with deficiencies:	Acidic and highly leached sandy soils, calcareous soils, and peat soils. [2] [9]
Interactions with other nutrients:	Co^{2+} ion is strongly adsorbed on Mn nodules and goethite, and adsorption increases with pH. [6] [7] High adsorption by Fe and Mn oxides. [2] [6]
Concentrations:	
Earth's crust:	25 mg kg^{-1} [5], 40 mg kg^{-1} [3]
Soil:	1-50 mg kg^{-1} [7], 1-40 mg kg^{-1} [3], 0.1-70 mg kg^{-1} [6]
Plants:	0.05-0.5 mg kg^{-1} [3] 0.02-0.5 mg kg^{-1} [9]
Fertilizer sources:	Foliar feeding of Co solution [6], $CoSO_4$ and cobaltized superphosphate (trace amounts of $CoSO_4$). [9]

Geologic Sources: Associated with mafic and ultramafic deposits. Primary Co minerals are cobaltite (CoZnS-FeAsS) and skutterudite ($CoAs_3$-$NiAs_3$). Primary minerals with trace levels of Co include: olivine, hornblende, augite biotite, ilmenite, and magnetite. [2]

Industrial uses: Metal alloys, used for hard metal alloys due to high melting point, strength, and resistance to oxidation. Formerly added to beer (cobalt chloride) to improve the quality of beer froth. [4] Used in paints, enamels, and inks as a pigment, and as a catalyst in the petroleum industry. [1]

References:

Adriano, D.C. 1986. Trace elements in the terrestrial environment, Springer-Verlag, New York.

Alloway, B.J. 1990. Heavy metals in soils, Blackie Press, Glasgow.

Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1985. Soil Chemistry, 2nd Ed., John Wiley, New York.

Gerhardsson, Lars, and Staffan Skerfving. 1996. Concepts on biological markers and biomonitoring for metal toxicity. In Toxicology of metals, L.W. Chang, L. Magos, and S. Tsuguyoshi, Eds., CRC Press, Boca Raton, FL.

Huheey, J.E. 1983. Inorganic chemistry: Principles of structure and reactivity, 3rd Ed. Harper Collins Publishers, New York.

Kabata-Pendias, A., and H. Pendias. 1992. Trace elements in soils and plants, 2nd Ed., CRC Press, Boca Raton, FL.

Khattak, R.A. and A.L. Page. 1992. Mechanism of manganese Adsorption on soil constitiuents. In Biogeochemistry of trace metals, D.C. Adriano, Ed., Lewis Publishers, Boca Raton, FL.

Saliisbury, F.B., and C.W. Ross. 1992. Plant Phisiology, 4th Ed., Wadsworth, Belmont, CA.

Tisdale, S.L., W.L. Nelson, J.D. Beaton. 1985. Soil Fertility and Fertilizers, 4th Ed., MacMillan Publishsers, New York.

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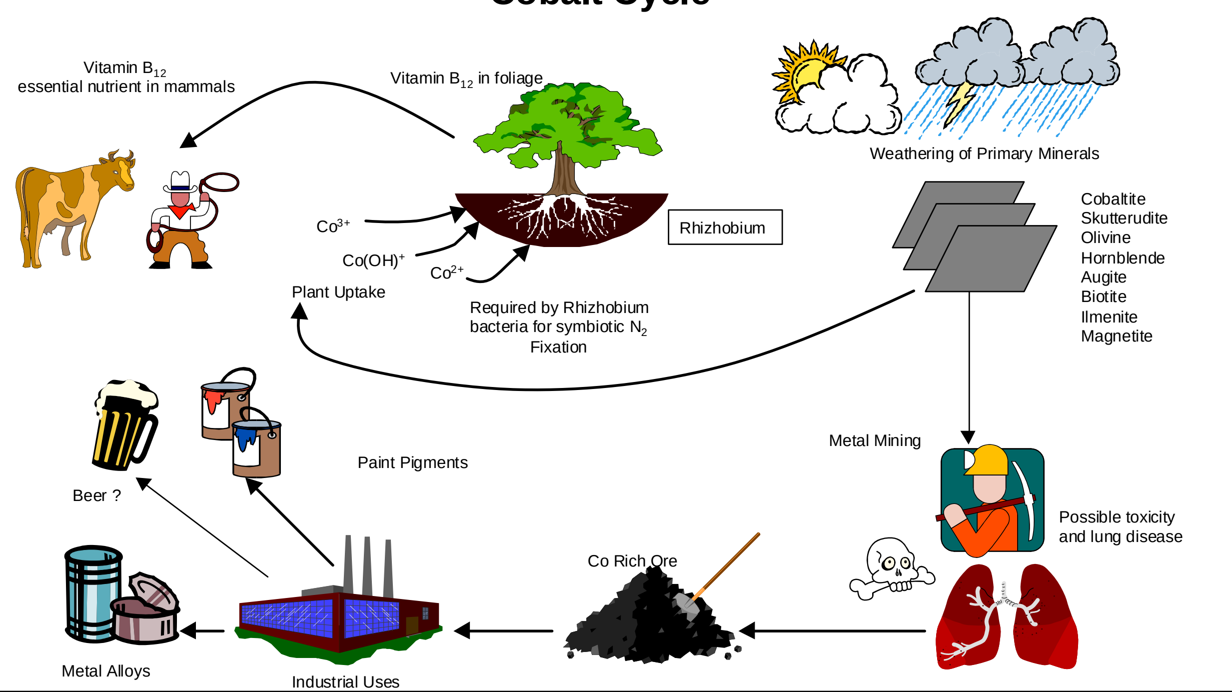
Cobalt Cycle



CHLORINE

Form taken up by the plant:	Cl^-
Mobility in the soil:	Mobile
Mobility in the plant:	Mobile
Deficiency Symptoms:	pH unknown. Reduced growth, wilting, development of necrotic and chlorotic spots on leaves, with leaves eventually attaining a bronze color. Roots become stunted in length but thickened or club shaped near the tips. Acts as a counter ion during rapid K^+ fluxes, contributes to turgor of leaves. Deficiency occurs in soils, <2ppm.
Toxicity Symptoms:	pH unknown. Can reduce yield and quality of crops. High levels will increase total leaf water potential and cell sap osmotic potential in wheat. Improves moisture relations in some crops. Leaves of tobacco and potatoes become thickened and tend to roll when excessive Cl concentrations occur. Storage quality of potato tubers are adversely affected by surplus uptake of Cl.
Role of Nutrient in Plant Growth:	Stimulates splitting of water in photosynthesis, essential for roots, cell division in leaves and as an osmotically active solute. Winter Wheat: Suppresses take-all, stripe rust, tan spot. Wheat: Suppresses leaf rust and tan spot. Oats: Suppresses leaf rust Corn: Suppresses stalk rot
Role of nutrient for microbial growth:	Unknown
Concentration in Plants:	Normal concentration is 0.2 - 2.0 % of dry matter. Cereal grain concentrations are 10-20 ppm, sugarbeet leaves 100-200 ppm. Tobacco plants require concentrations in soil of 10-15 ppm. <70-700 ug/g in tissue is deficient.
Effect of pH on availability:	Non adsorbed at pH >7 Non specific adsorption pH <7 No effect on availability

Interactions of Cl with other nutrients: Uptake of NO_3 and SO_4 can be reduced by the competitive effects of Cl. Lower protein concentrations in winter wheat are attributed to strong competitive relationships between Cl and NO_3 when Cl levels are high. Negative interaction between Cl and NO_3 has been attributed to competition for carrier sites at root surfaces.

Fertilizer sources:

Source	%Cl
Ammonium Chloride	66
Calcium Chloride	65
Potassium Chloride	47
Magnesium Chloride	74
Sodium Chloride	60

Origins of Cl in Soil and Plants: Most Cl in soil comes from salt trapped in parent material, marine aerosols, and volcanic emissions. Most often found in apatite, hornblende, and some feldspars. Nearly all soil Cl has been in the oceans at least once and returned to land by uplift and subsequent leaching of marine sediments or by oceanic salt spray carried in rain or snow. Sea spray near coastal regions provides about 100 kg/ha/yr and for inland regions accumulations are 1-2 kg/ha/yr. For inland regions these amounts are adequate since no deficiencies have been reported. Salt droplets and dust particles can be absorbed by plant leaves in adequate amounts for plant requirements.

Other: In recent years water softening, industrial brines, and road deicing have contributed significant amounts of Cl to local areas. Irrigation water that is highly mineralized, salt water spills associated with extraction of oil, natural gas, some coal deposits and improper disposal of feedlot wastes can supply Cl to soil. Wind erosion of salt evaporites can also affect enrichment of soils.

Forms in soil: Most Cl exists as soluble salts of NaCl, $CaCl_2$, or $MgCl_2$.

Behavior in Soil: Cl anion is very soluble in most soils. It is rapidly cycled through soil systems due to mobility (except in extremely acid soils). Exchangeable Cl can occur in acid, kaolinitic soils which have pH dependent positive charges. In humid climate zones Cl is leached through the soil system and in Arid to Semi-arid zones it is concentrated in the soil horizon.

Accumulations of Cl in Soil: Accumulates where internal drainage of soils is restricted and in shallow groundwater where Cl can move by capillary action into the root zone and be deposited at or near the soil surface.

Effects: Primary effect is an increase of osmotic pressure of soil water and thereby lowers the availability of water to plants.

References:

Bohn, H.L., B.L. McNeal and G.A. O'Connor. 1979. Soil Chemistry, Wiley-Interscience, New York, 219, 232, 286 pp.

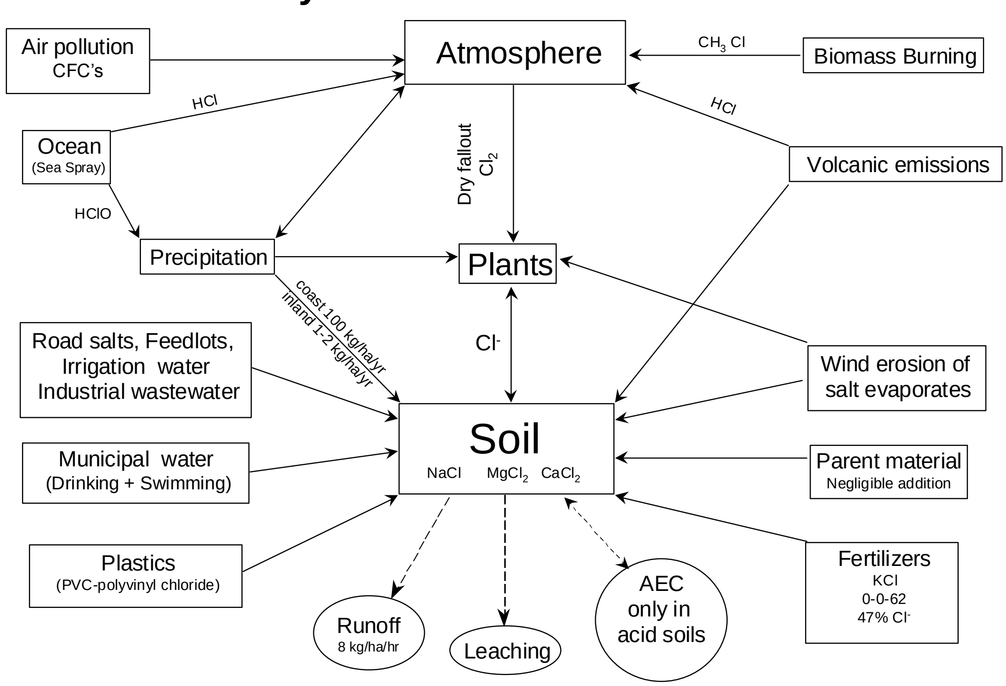
Pendias-Kabata, Alina and Henryk Pendias. 1992. Trace Elements in Soils and Plants. 2nd ed. CRC Press, Florida, 251-252pp.

Salisbury, Frank B. and Cleon W. Ross. 1992. Plant Physiology, 4th ed. Wadsworth Inc., California, 120, 129, 133, 135, 148, 215, 217 pp.

Tisdale, S.L., W.L. Nelson, J.D. Beaton and J.L. Havlin. 1993. Soil Fertility and Fertilizers. 5th ed. Macmillan, New York, 73-75, 342-344 pp.

Authors: David Gay, Justin Carpenter, Mark Wood and Curt Woolfolk

Chlorine Cycle



COPPER

Form taken up by the plant:	Cu^{2+}
Mobility in the soil:	Immobile, pH dependent, forms strong complexes with organic matter, oxides of Fe, Al, Mn, phenolic carboxyl., and hydroxyl groups, and clay minerals. Undergoes specific adsorption. Can be isomorphically substituted for Fe or Mn. Cu can leach through the soil profile in humus-poor, acidic peat, or in very acidic mineral soils, such as those around Ni and Cu smelters. Concentration of natural Cu in soil is 34 to 55 ppm.
Mobility in the plant:	Immobile
Deficiency symptoms:	Stunted growth, terminal dieback first in young shoots, necrosis of the apical meristem, bleaching of young leaves, impaired lignification of cell walls; impaired pollen formation and fertilization, delayed flowering and maturation, shortened internodes, stem deformation, yellowing, curling of leaves, seed and fruit growth dramatically reduced
Toxicity symptoms:	Stunting, reduced shoot vigor, reduced branching, thickening, poorly developed and discolored roots, leaf chlorosis resemble Fe deficiencies
Role of nutrient in plant growth:	Copper can not be replaced by any other metal ion in its involvement in enzymes. It is required for synthesis of quinones in chloroplasts, and makes up the electron transporter, plastocyanin in PSII
Enzymes containing Cu:	Superoxide Dimutase (CuZnSOD), Cytochrome oxidase, Ascorbate oxidase, Phenol Oxides, Tryosinase, Laccase, Diamine oxidase, Plastocyanin, Amine oxidase, Stellacyanin
Role in microbial growth:	Used in electron transport

Concentration in plants: 2-30 ppm dry weight (Adriano, 1986); 5-20 ppm (Tisdale, 1985)

Effect of pH on availability:

High pH (> 7.0) Formation of hydrolysis products which adsorb to exchange sites (lower availability), $CuOH^+$ is the primary form

Middle pH (6.9 - 7.0) Predominate form is $Cu(OH)_2{}^0$

Low pH (< 6.0) Exchange sites taken up by Al^{3+} and H^+ allowing the Cu^{2+} form to remain soluble

Interactions with other nutrients: Nitrogen and phosphorus (especially where Cu deficiencies exist), sulfur, iron, zinc, manganese, and molybdenum

Fertilizer sources: Copper sulfate, copper nitrate, copper chelate, copper ammonium phosphate, copper carbonate, animal waste, copper hydroxide, copper acetate, copper oxalate, copper oxychloride, copper polyflavanoids, copper-sulfur frits, copper-glass fusions, chalcanthite, azurite, malachite, chalcopyrite, chalcocite, covellite, tenorite, cuprite (Loneragan, 98)

References:

Adriano, D.C. 1986. Trace Elements in the Terrestrial Environment. Springer-Verlag, New York, NY.

Alloway, G.J. 1995. Heavy Metals in Soils. John Wiley and Sons, Inc., New York, NY.

Brady, N.C. 1990. The Nature and Property of Soils. MacMillan Publishing Co., New York, NY.

Committee on Medical and Biological Effects of Environmental Pollutants. 1977. Copper. National Academy of Sciences, Washington, D.C.

Hung, J.J. 1984. Effects of pH and other solution parameters on the Activities of Cadmium, Copper, and Zinc Cations in Soil Solutions. University Microfilms International, Ann Arbor, Michigan

Loneragan, L.F., A.D. Robson, R.D. Graham, eds. 1981. Copper in Soils and Plants. Academic Press, Sydney, Australia.

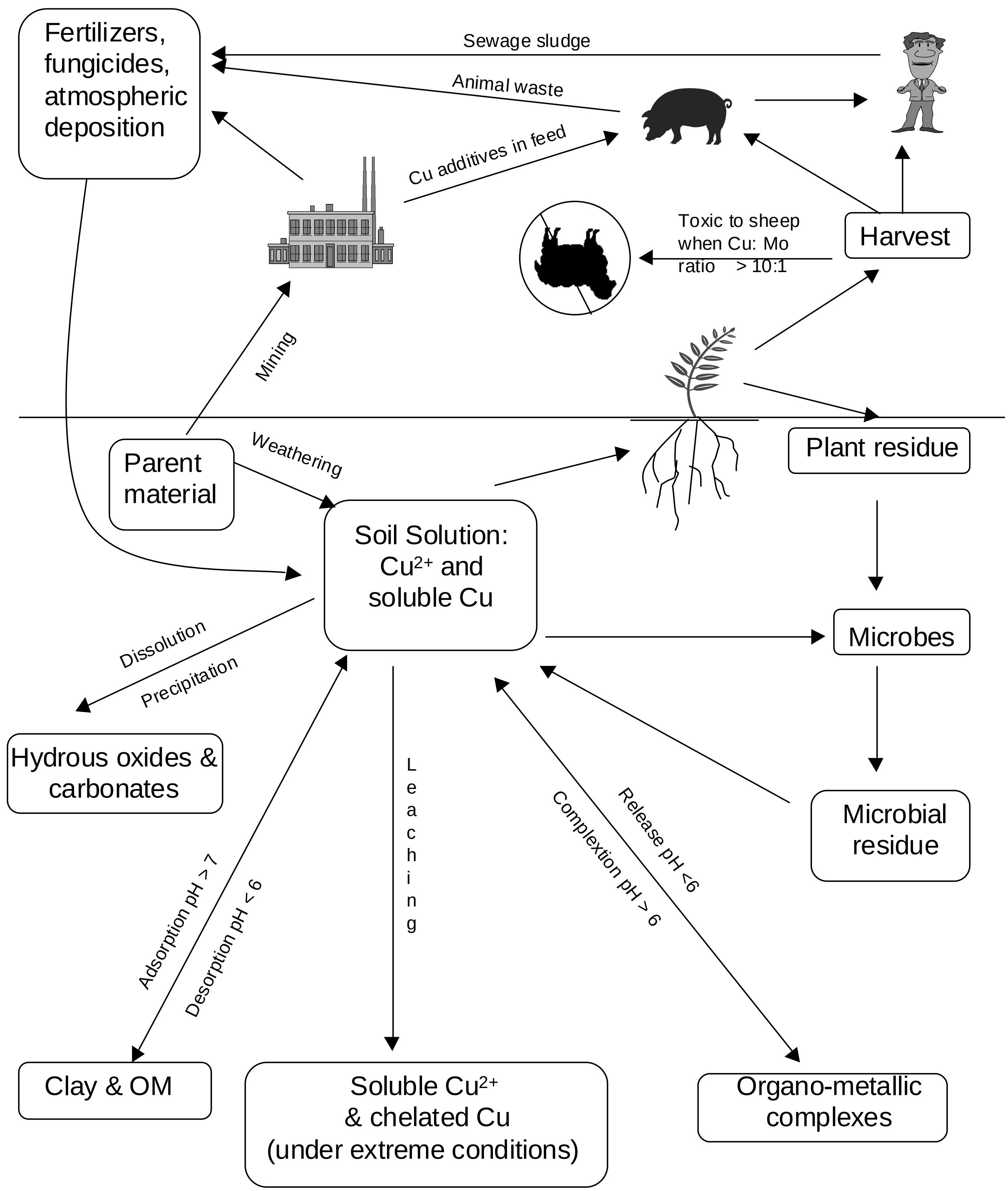
Narschner, Horst. 1986. Mineral Nutrition of Higher Plants. Academic Press, Inc., San Diego, CA.

Nriagu, J.O. 1979. Copper in the Environment, Part 1 and 2. John Wiley and Sons, Inc., New York, NY.

Stevenson, F.J. 1986. Cycles of Soil Carbon, Nitrogen, Phosphorus, Sulfur, and Micronutrients. John Wiley and Sons, Inc., New York, NY.

Authors: Tracy Johnston, Gary Strickland and Shawn Zupancic

Copper Cycle



ZINC

Form taken up by plant: Zn^{2+} at pH < 7.7; $Zn(OH)^{+}$ at pH > 7.7 (less available to plants).

Mobility in soil: No (Low solubility): Soluble by chelation by mobile ligands. Highly soluble at pH < 6.

Mobility in Plants: Low: Mobility in plants does not coincide with water flow. Zn is absorbed by plants as Zn^{2+} and transported as citrate, malate and malonate complexes.

Deficiency found in: Acidic, sandy soils with high leaching, calcareous soils pH>8.0, exposed subsoil horizons (erosion), Deficiency symptoms are purple margins similar to phosphorus deficiency, but also inward toward the center of leaves (purple blotching), and brown spots on rice leaves. Deficiency is rarely observed in wheat. Zn deficiency can be corrected by application of 2.5-25 kg/ha of $ZnSO_4$ (depending on soil pH and texture) or 0.3-6 kg/ha as chelates in broadcast or band application. Foliar application of 0.5-2.0% $ZnSO_4*7H_2O$ effective for fruit trees for the growing season; 2% solution is used for seed soaking. Soil application corrects Zn deficiency for 2-5 years.

Toxicity symptoms: Most plant species have high tolerance to excessive amounts of Zn. However, on acid and heavily sludged soils Zn toxicity can take place. Zn toxicity symptoms as follow: Inhibited root elongation, photosynthesis in leaves, depresses RuBP carboxylase activity, chlorosis in young leaves due to induced deficiency of Fe^{2+} and/or Mg^{2+}. Zn^{2+} has ion radius similar to Fe^{2+} and Mg^{2+}, which creates unequal competition for these elements when zinc supply is high. The critical toxicity level in leaves is 100-300 mg per kg of dry weight.

Role of Zn in the plant:

1. Component of ribosomes.
2. Carbohydrate metabolism

a) a cofactor of carbonic anhydrase, which converts CO_2 into HCO_3^-

b) activity of photosynthetic enzymes: ribulose 1,5 bisphosphate carboxylase (RuPPC)
c) Chlorophyll content decreases and abnormal chloroplast structure occurs when Zn is deficient
d) Sucrose and starch formation by activating aldolase and starch synthetase
3. Protein metabolism: Stabilizes DNA and RNA structures
4. Membrane integrity: Stabilizes biomembranes and neutralizes free oxigen radicals, as a part of superoxide dismutase
5. Auxin metabolism: Controls tryptophane synthetase, which produces tryptophane, a source for IAA
6. Reproduction: Flowering and seed production are depressed by Zn deficiency.

Role of Zn in microbial growth: Indispensability of Zn in metabolism of living organisms, microflora also is highly dependent on concentrations of zinc present. Some heterotrophs can tolerate high concentration of Zn and behave as bioaccumulators of Zn, among them Zoogloea-producing bacteria, Ephiphytic bacteria, Nonsporing bacteria. Different genera of Green Algae respond differently to Zn contamination. *Microspora, Ulothrix, Hormidium,* and *Stigeoclonium* are resistant to high Zn concentrations, whereas genera such as *Oedogonium* and *Cladophora* are rather sensitive to the presence of Zn.

Concentration in plants: Depending on genotype, Zn concentration varies in the range 25-150 ppm (0.0025-0.015% of dry weight) of Zn sufficient plant.

Concentration in soils: 10-300 ppm (0.001-0.03%). Concentration of total Zn increases with depth, whereas extractable Zn content decreases. Concentration of Zn in the upper horizon also depends on organic matter content, which can hold up to 13% Zn. In soils, 30-60% Zn can be found in iron oxides, 20-45% in the lattice of clay minerals, and 1-7% on clay exchange complex. Highest Zn concentration is in solonchaks – saline soils in Asia, lowest in light textured soils with low organic matter.

Origin in soils: Zinc composition of soils defined by parent material. Magmatic rocks have 40 and 100 mg/kg Zn in granites and basalt, respectively. Sedimentary rock composition varies in the range 10 to 30 mg/kg in sandstones and dolomites, and 80-120 mg/kg in clays,

Effect of pH on availability: pH is the most important parameter of Zn solubility. General equation for soil Zn is

$$pZn = 2pH - 5.8$$

The form of Zn predominant at

- $pH<7.7$ – Zn^{2+}
- $pH>7.7$ – $ZnOH^{+}$
- $pH<7.7$ – $Zn(OH)_2$

Interaction of Zn with other nutrients: Increase in available P content can considerably decrease availability of Zn in the soil due to the high antagonism between these two elements. However, some authors suggest that symptoms considered as a Zn deficiency are actually P toxicity. Presence of other nutrients such as iron, copper, manganese and calcium may also inhibit Zn uptake by plants, probably due to the competition for the carrier sites on roots. Application of high rates of NPK fertilizers can aggravate Zn deficiency.

Fertilizer sources: Zinc sulfate with 25-36%Zn, Zinc oxide – 50-80% Zn, Zinc Chloride - 48% Zn, Zinc Chelate – 9-14.5% Zn, and manure are used in agriculture.

Soil Test: For available Zn determination four extractants are generally used:
0.1*M* HCL, EDTA-$(NH_4)_2CO_3$, Dithizone - NH_4OAC, and DTPA-TEA.
Soil content of Zn of 2ppm (0.0002%) and higher are sufficient for most of the crops, <2 ppm is deficient for pecans, <0.8 ppm is deficient for corn. When Zn concentration is less than 0.3 ppm, deficiency symptoms are observed in less sensitive crops such as cotton, wheat, soybean, etc.

References:

Allowey, B.J. (ed.). 1990. Heavy Metals in Soils. John Wiley and Sons. New York.

Johnson, G.V., W. R. Raun, H.Zang, and J.A. Hattey. 1997 Oklahoma Soil Fertility Handbook. 4th ed. Department of Agronomy Oklahoma State University.

Kabata-Pendias, A., H. Pendias. 1991. Trace elements in soils and plants. 2nd ed. CRC Press Boca Raton Ann Arbor London.

Nriagu, J.O. (ed.). 1980. Zinc in the Environment. John Wiley and Sons. New York.

Prasad, R., and J.F. Power. 1997. Soil Fertility Management for Sustainable Agriculture. CRC Press LLC. New York.

Raun, W.R., G.V. Johnson, R.L. Westerman. 1997. Soil - Plant Nutrient Cycling and Environmental Quality. Oklahoma State University.

Robson, A.D. (ed.). 1993. Zinc in Soils and Plants. Kluwer Academic Publishers. Australia.

Marschner, H. 1995. Mineral Nutrition of Higher Plants. 2nd ed. Academic Press. London.

Tisdale, S.L., W.L. Nelson, J. D. Beaton, and J.L. Havlin. 1993. Soil Fertility and Fertilizers. 5th ed. MacMillian. USA.

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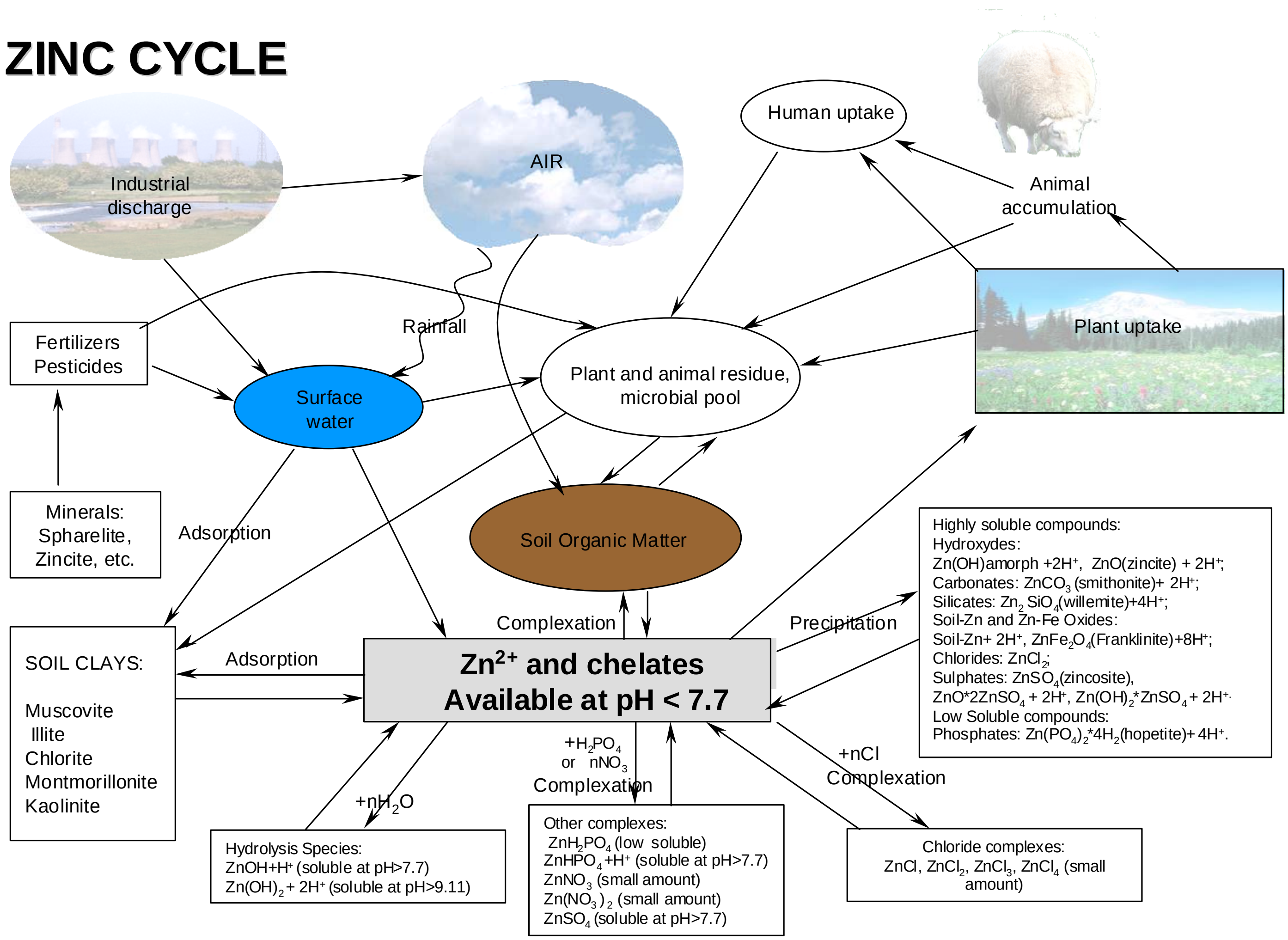


MOLYBDENUM

Form taken up by plants:		MoO_4^{2-}
Mobility in soil:		Immobile. Solution concentrations below 4 ppb transfer by diffusion. Above 4 ppb by mass flow.
Mobility in plant:		It is readily translocated and deficiency symptoms generally appear in the whole plant.
Deficiency symptoms:		Deficiency symptoms are closely related to N metabolism because Mo is needed for nitrogenase. General deficiency symptoms are varied between plants and range from yellowing, stunting, interveinal mottling and cupping of older leaves followed by necrotic spots at the tips and margins.
Deficiencies occur in:		Soils with low pH and high Fe and Al oxides. Deficiency usually resolved by addition of lime.
Plants most susceptible to deficiencies:		Legumes, Brassica sp., Lycopersicon esculentum, *Beta vulgaris,* Crucifers, Citrus
Toxicity symptoms:	PLANTS	Not readily toxic and marked toxicity is not known in the field. When it does occur, toxicity symptoms are yellow or orange-yellow chlorosis, with some brownish tints that start in the youngest leaves. Further symptoms include moribund buds, thick stems, development of auxillary buds and succulent older leaves. However, when toxicity does occur, it is normally found in high pH soils in the western regions of North America and Australia.
	ANIMALS	Toxicity occurs in livestock when they intake feeds and forages with high Mo content of 10-50 ppm. Ruminant animals are particularly sensitive and develop the disease molybdenosis.
Role of Mo in plants:		Needed in nitrate reductase for the reduction of NO_3^- to NO_2^-, biological nitrogen fixation, influences nitrogen content in plants, aids in

purine catabolism, aids in oxidation of sulfite to sulfate, influences the utilization of carbohydrates, and promotes root flavonoids.

Role of Mo for microbes: Needed in nitrogenase for fixation of N_2 by Rhizobium, Azotobacter, Rhodospirillum, Klebsiella, and blue-green algae.

Enzymes that require Mo: Nitrate reductase, molybdoenzyme, nitrogenase, sulfite oxidase, Xanthine oxidase, and aldehyde oxidase.

Effect of pH on availability:
Precipitated forms at low pH $FeMoO_4$, $PbMoO_4$
Precipitated forms at high pH $CaMoO_4$

Soil solution forms: MoO_4^{2-}, $HMoO_4^-$, H_2MoO_4 (MoO_4^{2-} is the most dominant species.)

Concentration in soil: Average concentration is about 2 ppm and ranges between 0.2 and 5 ppm.

Interactions with other nutrients: P additions increase Mo uptake by replacements on the exchange complex and release to solution. S depressed Mo uptake by direct competition on root adsorption sites. Mo, with Mn, affects Fe uptake in tomatoes.

Fertilizer sources: $Na_42MoO_4 \cdot 2H_2O$ (39%), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (54%), MoO_3 (66%), and MoS_2 (60%).

References:

Adriano, D. C. 1986. Trace elements in the terrestrial environment. Springer-Verlag New York Inc. pp. 329-361.

Barber, S.A. 1995. Soil nutrient bioavailability: a mechanistic approach. 2nd Edition. John Wiley & Sons Inc. New York, NY. pp. 345-352.

Bohn, H.L, B.L. McNeal, and G. A. O'Connor. 1985. Soil chemistry. 2nd Edition. John Wiley & Sons Inc. New York, NY. pp. 226, 308.

Brady, N.C. 1990. The nature and properties of soil. 10th Edition. Macmillian. New York, NY. pp. 381-398.

Brown, J.C., Ambler, J.E., Chaney, R.L. and Foy, C.D. 1972. Micronutrients in agriculture. SSSA, Inc. Madison, WI. pp. 401-402.

Gupta, U.C. 1997. Molybdenum in agriculture. Cambridge University Press. United Kingdom.

Gupta, U.C. and J. Lipsett. 1981. Molybdenum in soils, plants, and animals. Advances in Agronomy 34:73-115.

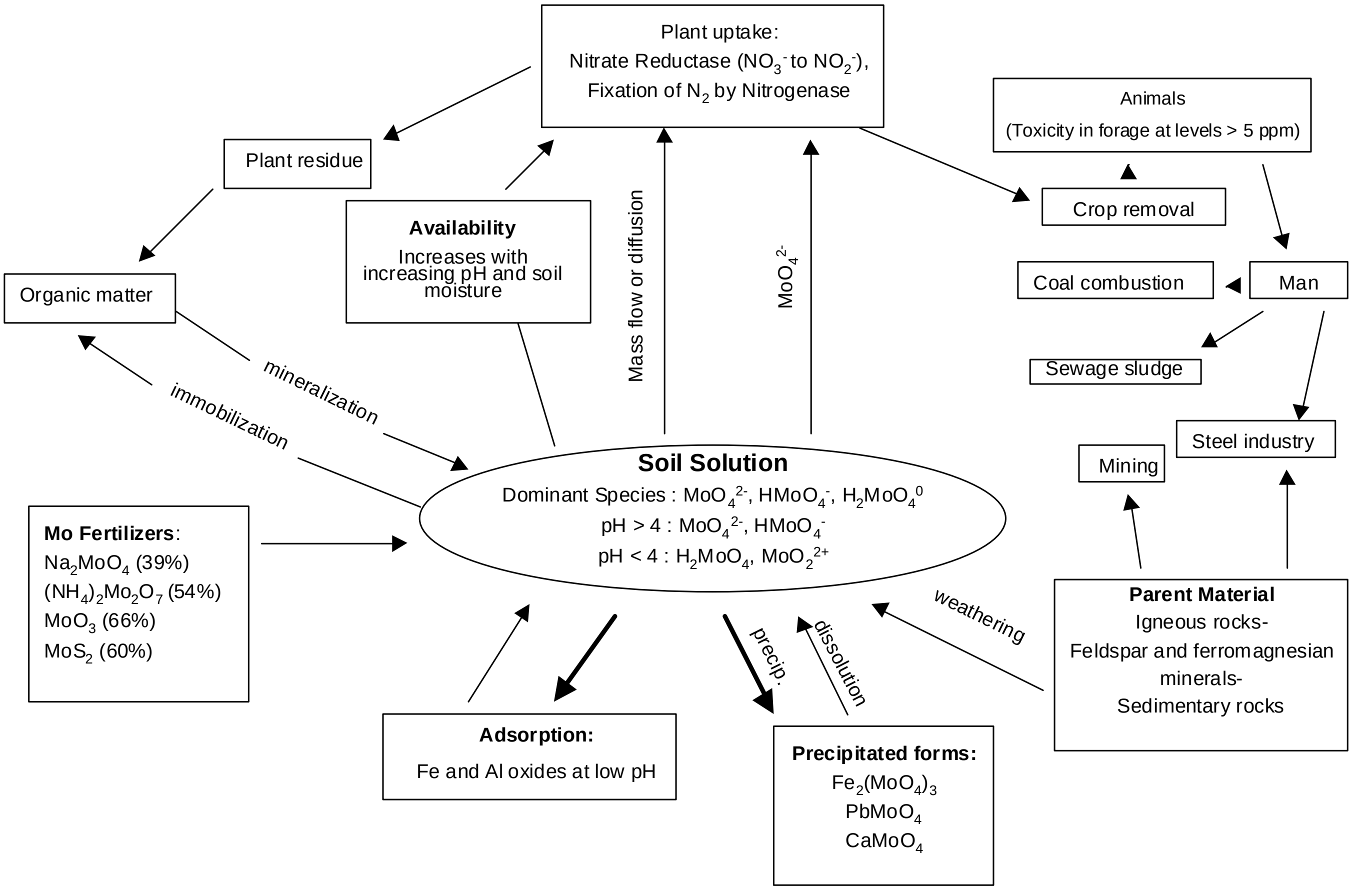
Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley & Sons. New York, NY. pp. 365-372.

Stevenson, F.J. 1986. Cycles of soil. John Wiley & Sons Inc. New York, NY.

Tisdale, S.L., W.L. Nelson, and J.D. Beaton. 1985. Soil fertility and fertilizers. 5th Edition. Macmillian. New York, NY. pp. 378-381.

Authors: Matt Rowland and Renee' Albers 1998, Steven Phillips and Eric Hanke

Molybdenum Cycle



ALUMINUM

Form taken by plants:	Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$
Mobility in soil:	Mass flow at low pH (< 5.5). Otherwise immobile.
Mobility in plants:	No
Deficiency symptoms:	Unknown.
Toxic forms:	Al^{3+}, aluminum hydroxides, "Al_{13}" hydroxy-polymer.
Toxicity symptoms for plants:	<u>Phytotoxicity</u> (monomeric Al forms): Limited root branching and rooting depths. Browning of root tips. Inhibited shoots growth. Phosphorus deficiency symptoms. <u>Rhyzotoxicity</u> (polymeric Al forms): Impaired germination of seeds.
Toxicity for humans:	Neurotoxicity. Impaired motor functions. Aggravation of Alzheimer disease and parkinsonism.
Toxicity for wildlife:	Forest die-backs in North America and Europe (red spruce, various firs, pines, sugar maple). Al accumulator plants are toxic to herbivores. Embriotoxicity for oysters. Neurotoxicity for mammals.
Al as a nutrient in plant growth:	Very low Al levels can benefit some plants. Otherwise unknown.
Effect of pH on availability:	Availability of inorganic complexes of Al is greatest at low pH (< 5.5). Organic complexes of Al is released at high pH (> 7.0)
Soluble species:	Al^{3+} pH < 5.5 $Al(OH)^{2+}$ pH 4.7 – 6.5 $Al(OH)_2^{+}$ pH 6.5 – 8.0 $Al(OH)_4^{-}$ pH > 8.0
Precipitated forms:	$AlPO_4$, Al_2SiO_5 , $Al_2(OH)_6$ (gibbsite)
Anions ameliorating toxicity:	PO_4^{3-}, F^{-}, SO_4^{2-}, hydroxides, organic carboxylates.

References:

Bertsch, P.M., and Bloom, P.R., 1996. Aluminum. In: Methods of Soil Analysis. Part 3, Chemical Methods, 517 – 550. D.L. Sparks et al. (Eds.). Soil Science Society of America, Inc. Madison, Wisconsin, 1996

Hargrove, W.L. 1986. The solubility of aluminum-organic matter and its implication in plant uptake of aluminum. Soil Sci. 142: 179-181.

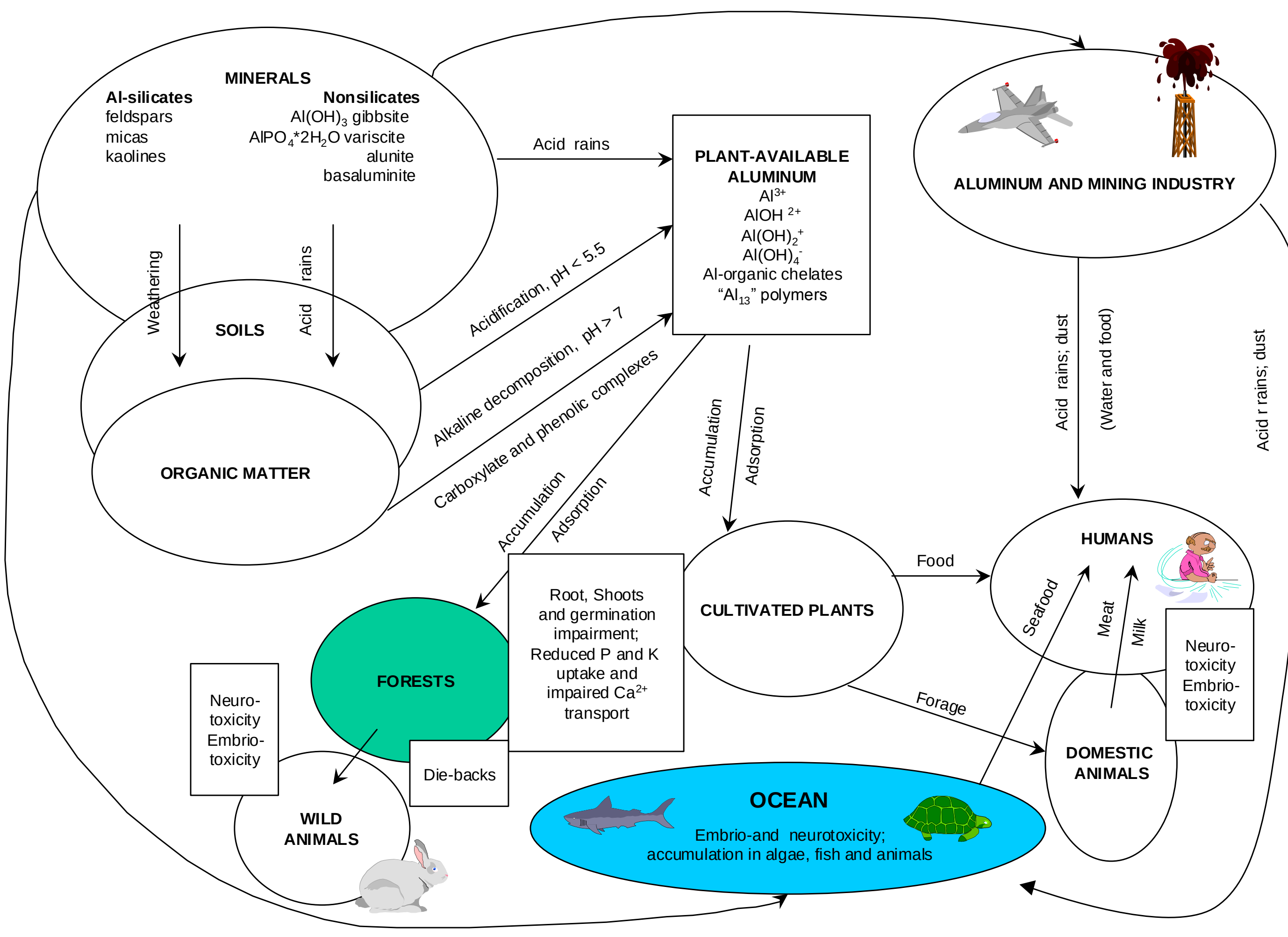
Lewis, T.E. (Editor). 1989. Environmental chemistry and toxicity of aluminum. 1989, Lewis Publishers, Inc., 344 P.

Sparling, D.W. and Lowe, T.P. 1996. Environmental hazards of aluminum to plants, invertebrates, fish and wildlife. Rev. Environ. Contam. Toxicol., 145: 1-127.

Strid, H. 1996. Aluminum toxicity effects on growth and on uptake and distribution of some mineral nutrients in two cultivars of spring wheat.

Authors: Olga Kachurina and Alan O'Dell

ALUMINUM CYCLE



SODIUM

Status:	Micronutrient required only by some plants.
Form taken up by plant:	Na^+
Mobility in plant:	Relatively mobile.
Deficiency symptoms:	In C4 plants - chlorosis in leaves and necrosis in the leaf margins and tips; lower chlorophyll a/b ratios and lowered photosystem II activity
Plant most susceptible to deficiencies:	Some desert and salt-marsh species and C4 species, succulents; Australian *Atriplex* species.
Toxicity symptoms:	Causes decrease in growth and yield, yellowing and withering of the plants; Na salts retards germination amount of Na-containing substance needed to kill the plant: NaCl -1.8%, NaBr - 1.2%, $NaNO_3$ - 1.7%, Na_2SO_4 - 0.8%, Na_2PO_4 - 1.5%, Na_2CO_3 - 1.1%.
Adverse effects on plants:	Pronounced under low concentrations of other components of soil solution; at high concentrations impedes water uptake by plants; may enter the plant in preference to K ions depriving the plant of an essential nutrient and inhibiting some enzymes; decreases absorption of Ca^{++}, Mg^{++}, and K^+ in some plants; impairs cell membrane.
Role of nutrient in plant growth:	Readily taken up by plant; function is similar to that of potassium - activator for a wide variety of important enzymes; activates ATPase (membrane transport); is involved in osmosis balance; facilitates absorption of N, P, K in some plants due to enhancing permeability of cells to salts (in sugar beets, carrots), favors the accumulation of fructose, promotes conversion of fructose to glucose, increases sucrose content in some plants, reduces the motility of stomatal openings; uptake of Na when K is sufficient can improve vigor and color of foliage, increase disease resistance, and decrease wilting in

hot dry weather in celery, mangel, sugar beet, Swiss chard, table beet, turnip, barley, carrot, cotton, flax, oat, pea, tomato, vetch, wheat; in C4 plants Na is needed for transporting CO_2 to the cells where it is reduced to carbohydrates; activates membrane translocator system.

Role of Na for microbes: Inhibits initiation of glycolysis, inhibits intracellular enzymes, activates few extracellular enzymes; specifically required by blue green algae, Aerobacter species (activates fermentative enzymes); actively required by halobacteria and halococci; required by nitrogen fixing microorganisms.

Concentrations in plants: 0.0013-3.51% of dry matter, 0.016 - 16.78 % in ash; halophytes are very rich in Na; buckwheat, corn and sunflower have unusually low content of Na;

Origin in soils and plants: 1) parent material: silicate minerals- alkali feldspars (albite, microcline), hornblende, tourmaline, sodium sulfate minerals - thenardite (Na_2SO_4), aphthitalite - $(Na,K)_2SO_4$, glauberite ($Na_2SO_4.CaSO_4$), hanksite ($9Na_2SO_4.2Na_2CO_3.KCl$); 2)ocean spray, 3) salts precipitated via rain, 4) ground water, 4) loess , 5) brines (for 1 barrel of crude oil 10 barrels of brine produced).

Concentration in atmosphere: 1500-5500μg/m^3

Concentration in biosphere: 1.65 mol/hectare (average composition of living matter).

Concentration in seawater: 10500 ppm

Concentration in lithosphere: 750-7500 mg/kg dry matter

Accumulations of Na in soil: Accumulates under restricted internal drainage, or shallow water table and high evaporation when Na^+ can move upwards and accumulate at or near soil surface.

Behavior in soil: At low concentrations, Na can deteriorate soil structure by dispersing clays and organic colloids (dispersive soils are easily erodible); causes increase in the hardness and relative impermeability of the B horizon and a decrease in thickness of the humus-enriched A horizon; in form of chloride, increases the osmotic pressure of soil water and lowers the availability of water to plants; Na-affected soils release substantially smaller percentage of the total nitrogen than the other soils; Na reduces evaporation and increases the water- holding power of the soil, through an exchange of bases it is capable of rendering certain relatively insoluble nutritive salts more available to plants; high pH caused by high concentration of Na^+ leads to reduced availability of some micronutrients and contribute to aluminum and boron toxicity, Co and Mo become more soluble in alkaline soils.

Forms in soils: Most Na exists as soluble salts of NaCl, Na_2SO_4 (white alkali), Na_2CO_3.

Interactions with other nutrients: Substitutes potassium in case of a deficiency in potassium in some species; Na prevents Al toxicity (where Ca content is decreased); prevents poisonous effect of excess K, NH_4, Mg, Ca, Cu; high concentrations of Na strengthens Cl-toxicity in some plants Na stimulates absorption of N and P by plants, in others inhibits uptake of Ca, Mg, K; in saline soils Na ions compete with the uptake of K^+; $CaSO_4$ and elemental S help in leaching Na^+ out.

Fertilizer sources: Sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), sodium chloride (NaCl).

Pesticides sources: Fungicide - sodium omadine; herbicide - $NaClO_3$ (sodium chlorate).

References:

Bibliography of the literature on sodium and iodine in relation to plant and animal nutrition. 1948. 1 ed., v.1.

Cairns, R.R., R.A. Milne, and W.E. Bowser. 1962. A nutritional disorder in barley seedlings grown on Alkali solonetz soil. Canadian Journal of Soil Science, 42, no.1:1-6.

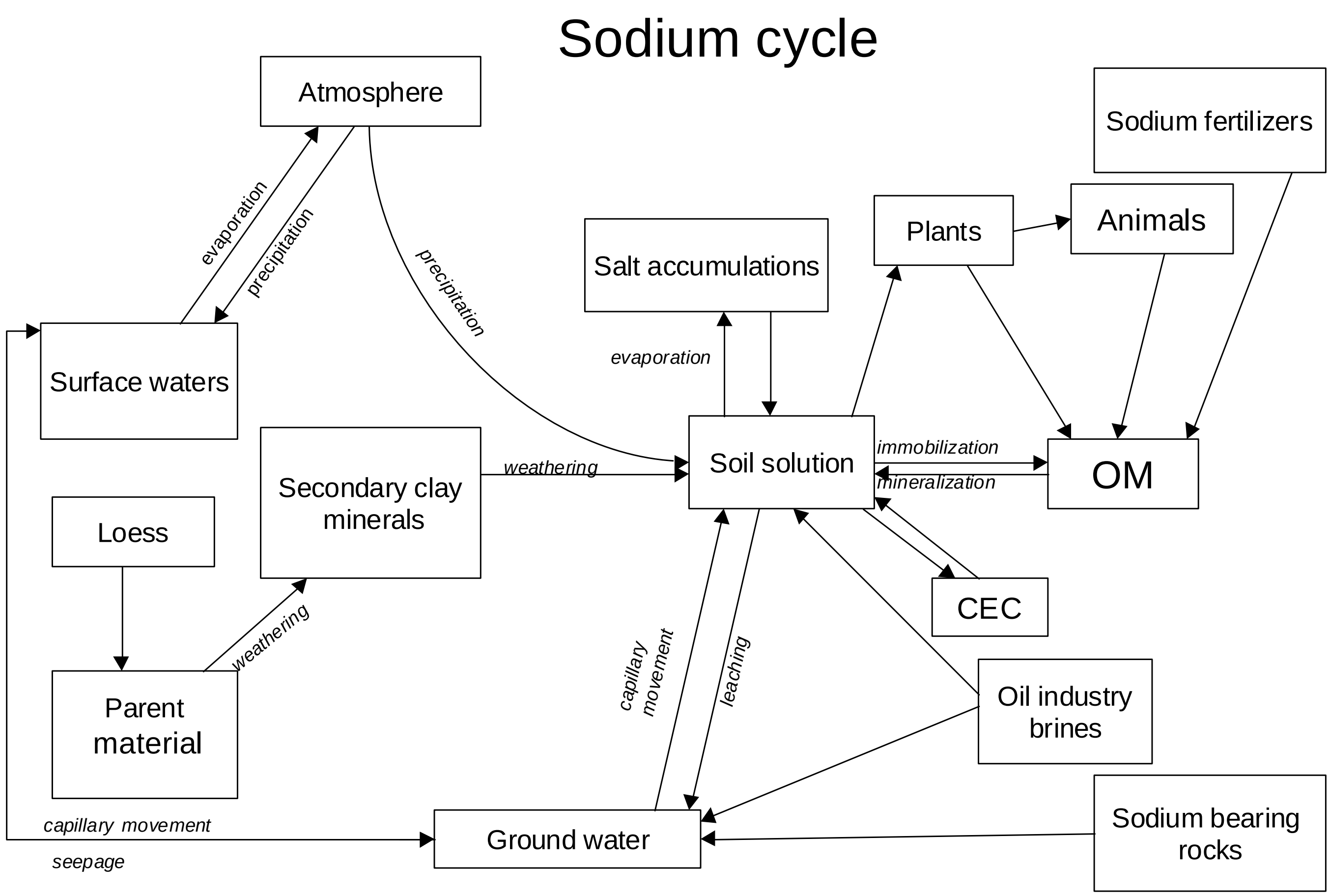
Curtis, H.1983. Biology. Worth Publishers, Inc. New York.

Harmer, P.M., and Benne E.J. 1945. Sodium as a crop nutrient. Soil Science, 60:137-148

Harrison, P.M., and K.L. Hoare. 1980. Metals in biochemistry. Chapman and Hall. London and New York.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford University Press. New York, Oxford.
Metal ions in Biological systems. 1984. Ed. by H. Sigel. Marcel Dekker, Inc.New York and Basel. vv.18, 20, 24.
Osterhout, W. J. V. 1908. The value of sodium to plants by reason of its protective action. Berkeley, The University Press.
Peil, K.L. 1968. Studies on natural microbial populations... Master of Science Thesis. Oklahoma State University.
Pipkin, H.R. 1969. Uptake and redistribution of calcium and sodium in the tomato plant. Master of Science Thesis. Oklahoma State University.
Plant physiology. 1963. Ed. by Steward, F.C. Academic Press, Inc. San Diego, New York, Boston, London, Sydney, Tokyo, Toronto.
Salisbury, F.B., and Ross, C.W. 1992. Plant physiology, 4th ed. Wadsworth Inc., California.
Wells, R.C. 1923. Sodium sulfate: its sources and uses. Washington, Government printing office.

Author: Elena Jigoulina



VANADIUM

Form taken up by the plant:	V_2O_5
Mobility in soil:	No/Yes (Becomes mobile at pH 5.0 with redox potential of –100 and at pH 8.0 with redox potential of –330),
Deficiency symptoms:	None
Effect of other nutrients on uptake:	Ni, Mn, and Cu inhibit uptake and Mo enhances the uptake of V.
Role of nutrient in plant growth:	Still unknown
Role of Vanadium in microbe growth:	Part of vanadium nitrogenase in many Azotobacter species
Concentration in plants:	1 ppm
Abundance on earth:	~300 ppm
Effect of pH:	pH of normal soils have no effect. However, pH < 3.0 or >8.5 increases solubility.
Oxidation states:	+5 to -1
Soluble species:	VO^{2+}, $H_2VO_4^-$, and $HV_2O_5^-$
Interaction with other species:	O, N, P, C, Si, and B

References:

Clark, R.J.H. 1968. The Chemistry of Titanium and Vanadium. Elsevier Publishing Company, New York, NY.

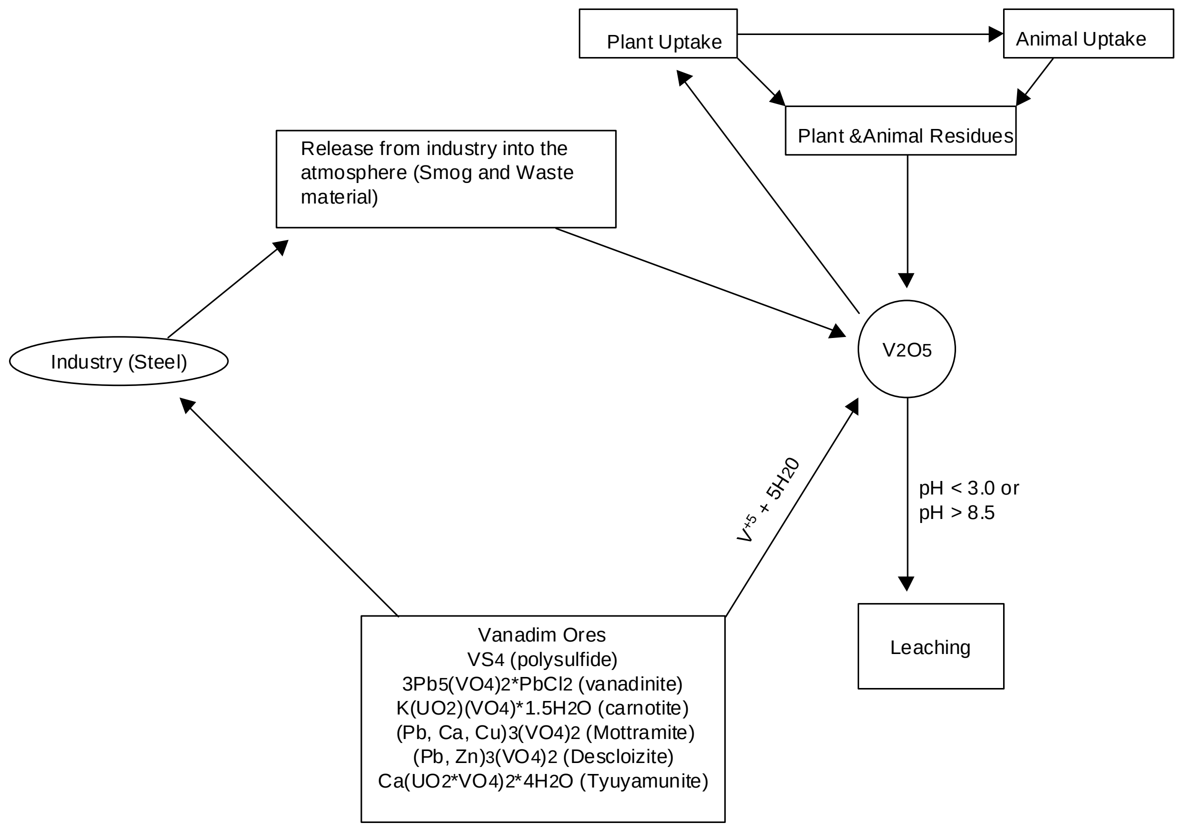
Fargasova A. and E. Beinrohr 1998. Metal-Metal Interactions in Accumulation. pp 1305-1317 in Chemosphere Vol. 36 No.6. Elsevier Science Ltd, Great Britain.

Hudson T.G. 1964. Vanadium Toxicology and Biological Significance. Elsevier Publishing Company, New York.

Lai Y.D. and J.C. Liu 1997. Leaching Behaviors of Ni and V From Spent Catalyst. Pp 213-224 in Journal of Hazardous Materials Vol. 53. Elsevier Science B.V.

Yates M.G., E.M. De Souza and J.H. Kahindi 1997. Oxygen, Hydrogen, and Nitrogen Fixation in Azotobacter. pp 863-869 in Soil Biology and Biochemistry Vol. 29 No. 5/6, Elsevier Science Ltd. Great Britain.

Author: Bryam M. Howell



OXYGEN

Form taken up by plants:	O_2, Diatomic oxygen
Mobility in the soil:	Yes
Mobility in the plant:	Yes
Deficiency symptoms:	Oxygen is essential for respiration, and low concentrations will stunt root growth; microbial oxidation will be slowed
Role of the nutrient in plant:	Respiration in roots; Redox e- acceptor
Concentration in plant:	Depends on conditions
Concentration in soil:	Depends on conditions
Effect of pH on availability:	None
Interaction with other nutrients:	Nitrogen (denitrification); Effects other elements oxidation states
Fertilizer sources:	None

References:

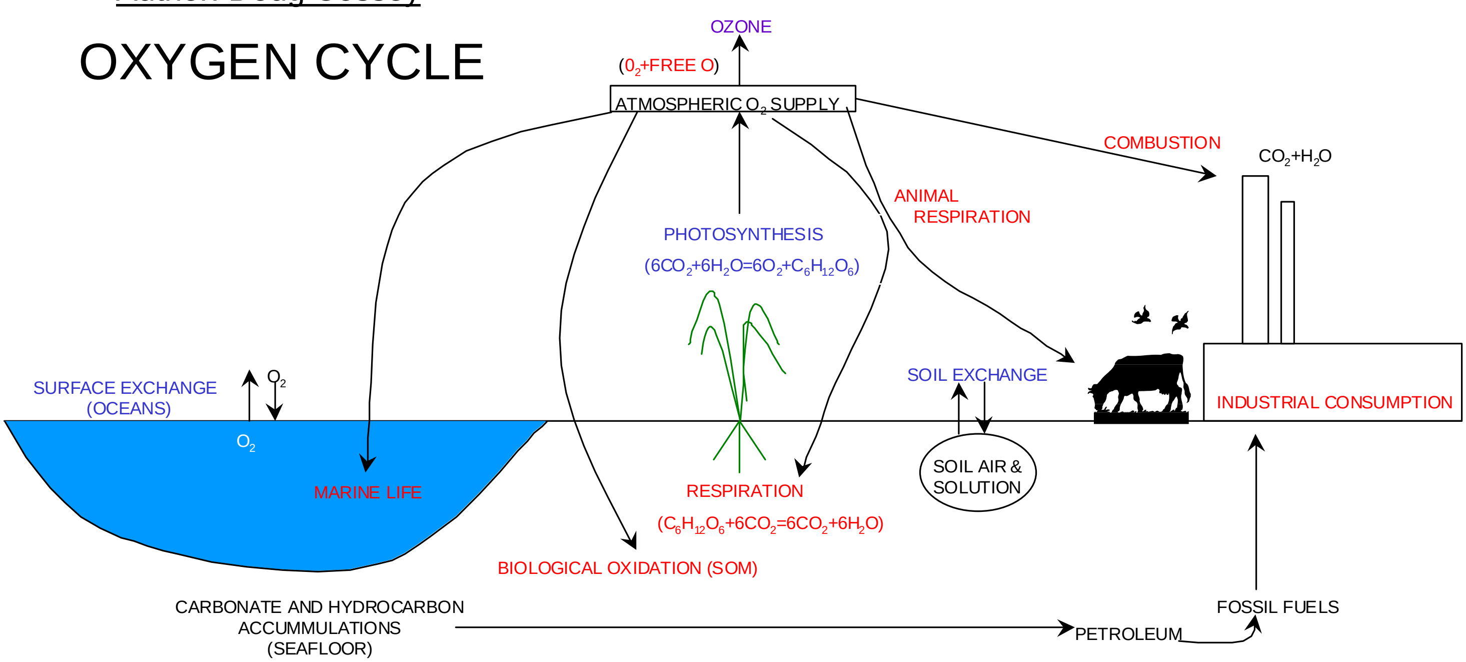
Linsdsay, W.L. 1979. Chemical Equlibria in Soils. John Wiley & Sons, NY.

Raun, W.R., G.V. Johnson, R.L. Westerman. 1998. Soil-Plant Nutrient Cycling and Environmental Quality. Agron 5813 Class Book.

Tisdale, S.L., W.L. Nelson, J.D. Beaton, J.L. Havlin. 1985. Soil Fertility and Fertilizers 5th edition. Macmillan Publishing Co. NY.

http://www.geo.perdue.edu/~geos191/lect7/oxygen.html

Author: Doug Cossey



SILICON

Form taken up by plant: $Si(OH)_4$ - monosilicic acid

Mobility in soil: No/Yes

Mobility in plant: Forms concrete particles built of silica ($Si(OH)_4 . nH_2O$) and opaline ($SiO_n(OH)_{4-2n}$). Silica may complex with cell wall polymers. Monosilicic acid is mobile in xylem sap.

Deficiency symptoms: Deficiency results in greater susceptibility to biophage-related diseases, lower tolerance, in some cases, of drought, salinity, and toxicity by minerals, including aluminum and manganese, and higher level of lodging in cereal stems (with possible decrease in yield)

Role of nutrient in plant growth: Silica particles provide resistance to mechanical compression, strength to cell walls and air canals; they also decrease relative share of biomass consumed by biophages.

Plants can be divided into four groups, according to Si uptake/influx mechanism:

1. Passive
2. Active
3. Exclusive
4. Active uptake/active exclusion depending on concentration in environmental solution

Concentration in plants: (SiO_2 fraction of the dry weight):

1. High (0.1 - 0.15) - wetland grasses
2. Intermediate (0.01 - 0.03) - dry land grasses
3. Low (<0.01) - dicotyledones

Concentration in soils: 1 to 40 mg/l Si in soil solution

Effect of pH on availability: [$Si(OH)_4$] mobility increases as pH decreases

Concentration in groundwater: 3.5 to 28 mg/l Si

Concentration in freshwater: 0.5 to 44 mg/l Si

Concentration in sea water: 1 to 7 mg/l Si (bulk), 0.0001 to 0.2 (surface)

Fertilizer sources: Metallurgy wastes

"As yet there is no evidence that Si has any role in [higher] plant biochemical processes but is present at low levels in many leaf cell types." [6] p. 470.

References:

Silicon and Siliceous Structures in Biological Systems. Edited by Tracy L. Sipson and Benjamin E. Volcani. Springer-Verlag, pp. 16-17, 387, 410.

Silicon Biochemistry. Ciba Foundation Symposium 121. John Wiley & Sons, 1986, pp. 17, 28-29, 90-93.

J. A. Raven. The transport and function of silicon in plants (review). In "Biological Reviews of the Cambridge Philosophical Society," v. 58 (May 1983), pp. 179-207.

J. J. R. Frausto da Silva, R. J. P. Williams. The biological Chemistry of the Elements. Clarendon Press, Oxford, 1991, p. 468.

H. F. Mayland, J. L. Wright, R. E. Sojka. Silicon Accumulation and Water Uptake by Wheat. In "Plant and Soil," v. 137 no. 2 (Nov. 1991), pp. 191-199.

M. J. Hodson, A. G. Sangster. Observations on the distribution of mineral elements in the leaf of wheat (Triticum aestivum L.), with particular reference to silicon. In "Annals of botany," v. 62 (November 1988), pp. 463-471.

J. G. Menzies, D. L. Ehret, P. A. Bowen. Surprising Benefits of Silicon. In "American Vegetable Grower," v. 40 (March 1992), pp. 82-84.

V. Matichenkov, E. Bocharnikova. Total Migration and Transformation of Silicon in Biochemical Subsystems. Modern Antropogenic Influence on the Global Change of Si Cycle. In "GAIM Science Conference Abstracts." (http://gaim.unh.edu/abstracts.html)

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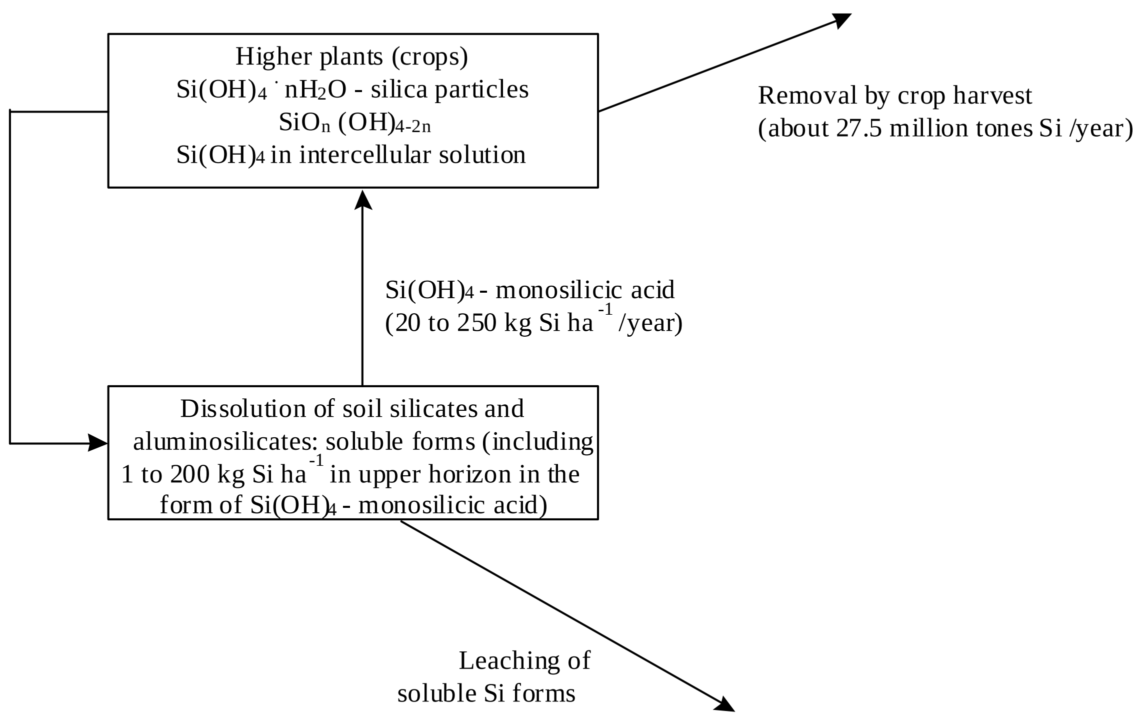


13. EXAMPLE EXAMS

First Hour Exam, February 16, 1996

Name:__________________________

T F The optimum pH range for rapid decomposition of various organic wastes and crop residues is 6.5 to 8.5.

T F Lignin content can be a reliable indicator for predicting residue decomposition rates

T F Cellulose generally accounts for the largest proportion of fresh organic material (corn stalks, wheat stubble)

T F As the pH increases from urea hydrolysis, negative charges become available for NH_4^+ adsorption

T F Urea hydrolysis consumes H^+

T F Nitrogen fertilizers increase soil acidity when used in cropping systems.

T F Lignin is insoluble in hot water but can be soluble in at high pH.

T F Nitrification is synonymous with oxidation

T F In general, denitrification is only found on soils where pH<6.0

T F Ammonia volatilization is greatest when soil pH > 7.0

T F CH_3COOH is a weak electrolyte.

T F $NH_4^+ \leftrightarrow NH_3 + H^+$, pKa = 9.3

T F If the hydrogen buffering capacity of a soil were known to be high, gaseous losses of N as ammonia should be less when urea is applied.

T F Soil organic matter levels are generally low in calcareous soils

T F Autotrophs obtain their energy from sunlight or by the oxidation of inorganic compounds and their carbon by the assimilation of CO_2

T F As NH_3 is lost by volatilization, NH_4^+ ions dissociate to NH_3 and H^+ to maintain equilibrium in the soil solution. The net result is that volatilization tends to decrease pH and reduce the volatilization rate.

T F Two moles of H+ are consumed for each mole of urea hydrolyzed

ORGANIC MATTER:

1. Using the figures below, calculate the total kg N/ha/yr that would be mineralized from the organic matter fraction of the soil. Use only the 0-15 cm layer. From your answer, how much additional N fertilizer (kg/ha) would you recommend if a farmer had a 7000 kg/ha wheat yield goal?

a. Bulk density: 1.5 g/cm3
b. Soil organic matter: 2%
c. N in organic matter: 2%
d. Percent N mineralized/yr 2%
e. 1 kg N needed for every 30 kg wheat

2. Which of the following management practices would lead to increased soil organic matter levels?

    a. N fertilization
    b. N fertilization at rates greater than needed for maximum yield
    c. N P and K fertilization at recommended rates
    d. Use of high lignin crop in rotation
    e. Zero or minimum tillage
    f. Application of manure
    g. Application of polyester 'Husker' red waste

3. A formerly very important person (GB) was standing two steps away from an imposter (SW). As fate would have it, GB was denitrified and SW was oxidized two times. During a terrible storm GB was struck by a bolt of lightning, however, SW escaped but was carried far away in the winds and the clouds and later deposited in a dried up desert soil where he remained until the end of time.

    a. GB was originally NO_3 and SW was NH_4
    b. GB and SW were both NO_3
    c. GB and SW were both NH_4
    d. GB was R-NH_2 and SW was NH_4

4. In Wallace's paper, it was stated that there is considerable concern over the annual global increase in CO_2 in the atmosphere. They also stated that

    a. annual global increases are around 1.5 ppm
    b. annual global increases are around 15 ppm
    c. the world pool of soil organic matter carbon is 3000 GT

d. the world pool of soil organic matter is 3000 GT

NITROGEN:

1. End products in the Nitrogen cycle include
   a. $R\text{-}NH_2$
   b. NH_3
   c. NH_4+
   d. NO_3-
   e. N_2
   f. N_2O
   g. NO_2-
   h. NH_4OH

2.

Nitrogen Source	Chemical Formula	% N
Ammonium nitrate	______________	___
Urea	______________	___
Anhydrous ammonia	______________	___
Ammonium sulfate	______________	___
Ammonium phosphate	______________	___

3. Work by Bidwell noted that to convert NO_3^- to NH_3, a total of ____ electrons must be added per molecule. The intermediate compounds of nitrogen that were proposed followed which order

   a. NO_3^-, NO_2, $N_2O_2^=$, NH_2OH, NH_3
   b. NO_3^-, N_2O, $N_2O_2^=$, NH_2OH, NH_4
   c. NO_3^-, N_2O, $N_2O_2^=$, NH_2OH, NH_3
   d. NO_3^-, NO_2^-, N_2O, NH_2, NH_3

4. Some of the problems associated with estimating plant gaseous N loss have included the following. Indicate whether each problem will lead to overestimation (O) of plant N loss, no change or stationary (S) or an underestimation (U) of plant N loss (circle the correct option, O, S or U)

O S U Volatile N losses from plants occur continuously over the full growing season and only become detectable from aboveground plant tissue when the rates of loss exceed the rates of uptake by roots.

O S U The maximum N content of the crop at an intermediate growth stage was underestimated and total plant N accumulated at maturity was overestimated.

O S U If the mechanism existed for plant roots to lose N to the soil and this took place continuously over time without accounting for differences in soil organic and inorganic N.

5. Work by Francis et al., 1993 suggested that fertilizer N losses between anthesis and maturity from the aboveground biomass of corn plants had a range of

   a. 10 to 20%
   b. 10 to 40%
   c. 20 to 50%
   d. 30 to 80%

T F The denitrifying bacteria responsible for reduction of nitrate to gaseous forms of nitrogen are facultative anaerobes that have the ability to use both oxygen and nitrate (or nitrite) as hydrogen acceptors.

T F Denitrification in soils under anaerobic conditions is controlled largely by the supply of readily decomposable organic matter.

T F Analysis of soils for mineralizable carbon or water-soluble organic carbon provides a good index of their capacity for denitrification of nitrate.

T F The resultant pH from urea hydrolysis in most soils ranges between 7 and 9

T F Soils are buffered against both a decrease and increase in pH to some degree.

T F When urea is applied to the soil surface, NH_3 volatilization losses will not be economically serious unless the soil surface pH is above 7.5

T F Microbial reduction could mean denitrification

T F Microbial oxidation could mean aminization and/or nitrification

6. Define soil-plant inorganic nitrogen buffering and describe the buffering mechanisms which explain this concept.

UREA: (15 points)

1. What is "Hydrogen ion buffering capacity" in soils? Why is this important when considering urea hydrolysis?

2. Ammonia volatilization from applied urea is approaching 80% in a regional crop production project in west Africa. Researchers in the area do not know what is happening, but they do know they have a problem as crops are continually N deficient, even though they applied the recommended rate. Chose 3 'tools' (all come in an unlimited supply) from the Dr's bag below that you will take with you to solve their problem. Soils in the area have 1-2% organic matter, low CEC, the climate is tropical and people are <u>hungry</u>.

   a. NSERVE
   b. Urease inhibitor
   c. Manure
   d. Ammonium nitrate
   e. Exchange resin (H+ supply)
   f. Tillage equipment for incorporation of urea

3. During hydrolysis, H^+ is consumed and pH increases. List three materials that could be applied with urea (H^+ supply) that could decrease the initial rise in pH as a result of urea hydrolysis.

NITROGEN USE EFFICIENCY:

1. Work by Wuest and Cassman, 1992 demonstrated that to achieve acceptable grain protein levels for bread wheat, N should be supplied ___________ to improve N uptake during grain fill.
   a. <u>late in the season</u>
   b. <u>early in the season</u>
   c. <u>at anthesis</u>

2. Using the numbers in the following table, calculate N uptake and fertilizer recovery using the 'difference method.'

Applied N kg/ha	Grain Yield kg/ha	N content %	N uptake kg/ha	Fertilizer Recovery %
0	1000	1.9	_______	__________
50	1300	2.2	_______	__________
100	2000	2.3	_______	__________
150	2000	2.4	_______	__________

3. Fertilizer N recovery generally

   a. decreases with increasing applied N
   b. decreases with decreasing applied N
   c. increases with increasing applied N
   d. increases with decreasing applied N

4. Westerman and Kurtz, 1973 discussed the 'priming effect. What was this?

5. Fill in the blank:

Element	**mobil in soil**	**mobil in plant**	**form taken up by plants**
N	_________	__________	____________
P	_________	__________	____________
K	_________	__________	____________
S	_________	__________	____________
Ca	_________	__________	____________
Fe	_________	__________	____________
Mg	_________	__________	____________

BONUS:(5 points)

Outline the countries of Peru, Niger and Pakistan.

0

Agronomy 5813
Second Hour Exam, April 3, 1996

Name:________________________

T F Micronutrient deficiencies are found on only a small percentage of the worlds arable land.

T F Cl, B, Mo, Fe, Mn, Zn, and Cu are present in soils in small amounts excluding Fe.

T F Boron deficiencies are generally found in fine textured soils.

T F Boron is the least mobile in the plant of all essential elements

T F Mo deficiencies should look like N deficiencies since Mo interferes with N metabolism

T F Fe is the most commonly deficient element of the micronutrients with Zn being the second most common

T F Absorption is adhesion in an extremely thin layer of molecules to the surfaces of solid bodies or liquids with which they are in contact.

T F For most minerals the strength of cation adsorption or lyotropic series is $Al^{+++}>Ca^{++}>Mg^{++}>K^{+}=NH4^{+}>Na^{+}$

T F Fox et al., 1964 found that $Ca(H_2PO_4)_2$ was found to be a better extractant for sulfur than KH_2PO4

T F Applied P can induce S deficiencies in acid soils

T F Liebig and Dr. Johnson roomed together in college

T F The sufficiency concept is based on Mitscherlich's equation dy/cx =(A-y)c

T F What we know as 'Bray's Mobility Concept' was initially developed for mobile nutrients

T F Grass tetany generally occurs when forage contains K/(Ca+Zn) > 2.2

T F $^{15}N^{14}N$ is naturally present in the atmosphere at approximately 0.366% while the remaining $^{14}N^{14}N$ is 99.634%

Exchange:

1. Exchangeable acidity is comprised of
    a. H ions obtained from the hydrolysis of exchangeable, trivalent Al
    b. Hydrolysis of partially hydrolyzed and nonexchangeable Al
    c. Weakly acidic groups, mostly on organic matter
    d. Exchangeable H+

2. a. Explain the difference between using an unbuffered salt to measure the CEC at the soils normal pH and the use of buffered salt solutions.

b. Will a buffered ammonium acetate solution over or underestimate CEC when used on an acid soil? Why?

3. In 1977, Polemio and Rhoades developed a new CEC procedure. What kind of soil was this procedure developed for, and what made it different from conventional CEC.

4. Kamprath discussed anion exchange capacity. His work stated that
    a. Adsorption of anions to + charged sites could take place in hydrous oxide minerals which were amphoteric
    b. The order of adsorption strength was $H_2PO_4 > NO_3 > SO_4 > Cl$
    c. Generally more significant on soils with pH < 6.0
    d. Anion exchange is negatively correlated with Base Saturation
    e. Increased P in solution decreased SO_4 adsorbed by the soil

Theoretical Applications in Soil Fertility

1. The sufficiency concept adheres to which of the following

a. Amount extracted from the soil is inversely proportional to yield increases from added nutrients
b. Calibrations exist for the changing levels of available nutrients with fertilizer additions and yield response
c. Concept assumes little if any effect of the level of availability of one ion on that of another
d. Recognizes that an addition of the most limiting element may cause more efficient utilization of a less limiting element

2. Why is the Sufficiency Concept not used for mobile nutrients?

3. A soil fertility experiment was conducted for three consecutive years in fields X, Y and Z which were sub-divisions of a uniform loam soil. Yields for the treatments applied are listed below. (Rates of fertilizers were adequate, but not in excess). Fill in the missing data by applying the appropriate concept(s).

		Yield, kg/ha	
Treatment	Field (X)	Field (Y)	Field (Z)
NP	5200	____	6000
NPK	6000	8000	____
NK	5800	____	____
PK	5000	4000	5000
N	____	____	____

% sufficiency K = _____
% sufficiency P = _____

4. When Bray originally modified the Mitscherlich equation, it was largely because Mitscherlich considered c to be a constant. Bray demonstrated that c and c1 varied with

a. crop
b. planting density/pattern
c. nutrient applied (source)
d. method of placement
e. rainfall
f. temperature

5. Using the following limits, what ranges would % H saturation potentially have based on the modified work of Graham, 1959?
Ca:65-85
Mg: 6-12
K: 2-5

a. H: ___ - ____

Explain your answer.

6. Fried and Dean developed what is now known as the 'A value.' What is this and how is it calculated.

7. What did Liebig's law of the minimum state?

8. In the Olson et al., (1982) paper, they found no differences in yield when following the different soil-test laboratory recommendations. How did they suggest that the soil test be changed?

9. Anderson and Nelson 1975 referring to linear-plateau models recommended that
   a. more rates need to be placed in the plateau phase of the response pattern
   b. more rates need to be placed in the sloping phase of the response pattern
   c. several treatment levels need to be concentrated near the vicinity of the anticipated optimum

Micronutrients:

1. What is a chelate? Give an example.

2. Given the following information, fill in each blank

	Log_{10} K
$Fe(OH)_3 \longrightarrow Fe^{+++} + 3(OH^-)$	-39.4
$Fe^{+++} + L \longrightarrow FeL$	12.2
$3(OH) + 3H^+ \longrightarrow 3H_2O$	42
$Fe(OH)_3 + L + 3H^+ \longrightarrow FeL$	___
$Fe(OH)_3 + L + 3H^+ \longrightarrow FeL$	___

If the soil pH is 6 and the concentration of citrate is 10^{-7} , calculate the concentration of FeL

How does this compare to what you might observe for Fe at a pH of 7.0 if the concentration of Fe3+ in the soil solution was governed only by the solubility of Fe(OH)3

Radioisotopes

1. Alpha radiation is/has
   a. particulate source of radiation
   b. the nucleus of the He atom
   c. a charge of +2
   d. high specific ionization
   e. low penetration

2. Gamma radiation is characterized as
   a. not having a mass
   b. having high penetration
   c. electromagnetic radiation with the speed of light
   d. not having a charge

3. When measuring ^{15}N using a mass spectrometer which of the following would be true?
   a. the ratio of ion currents (R) includes detection for $^{14}N^{14}N$, $^{15}N^{14}N$ and $^{15}N^{15}N$
   b. N_2 gas is generated via dry combustion of the sample and delivered in set volumes to the mass-spec.
   c. ^{15}N is an extremely safe isotope of N since it is stable, although somewhat radioactive

4. Discuss the differences between enriched, depleted and atom excess ^{15}N

5. What will the activity of 5 mC ^{32}P in 5 ml be in 36 days? (show all calculations)

6. How much ^{32}P would you put into a system to assure 500 cpm after 60 days using an instrument with a 20% counting efficiency and 10% P utilization efficiency.

Soil Testing/Critical Levels

1. Rank the following methods in terms of how conservative or liberal they are when used for assessing critical levels (1 most conservative, 5 liberal)

____ Cate-Nelson
____ Linear-Plateau
____ Mitscherlich
____ Quadratic
____ Square Root

2. Provide a legitimate equation for each method below which would be representative of response data that increased and then leveled off. Be careful to use the appropriate + or - values associated with each coefficient.

1. Quadratic____

2. Linear-Plateau____________________________________

3. Square Root______________________________________

4. Bray modified Mitscherlich ____________________________

BONUS:(5 points)

Outline the countries of Colombia, Japan, Togo, Burma and Libya.

0

Agronomy 5813
Final Exam, April 29, 1996

Name:____________________________

T / F (1 point each)
Multiple choice (3 points each)
Fill in the blank (1 point each)
Essay/Problems (points listed by question)

<u>NITROGEN</u>

T F The best time to take a soil sample for NO_3-N in Oklahoma was demonstrated to be December (work by Ascencio), but we currently use August-September.

T F Most of the N being mineralized in soil comes from the fraction of the soil organic matter that is easily decomposed, therefore, mild alkaline or acid chemical solutions should make good extractants

T F $^{15}N^{14}N$ is naturally present in the atmosphere at approximately 0.366% while the remaining $^{14}N^{14}N$ is 99.634%

T F NH_4+ <---> NH_3 + H+, pKa = 7.3

T F Urea hydrolysis produces H which drives pH up

T F The major transport form of N to the developing endosperm is glutamine which is also the major product formed in roots absorbing NO_3^-

1. Researchers at ISU recently discounted Soil-Plant Inorganic N Buffering as nothing more than a fertilizer industry sham. They presented work which showed that N-use efficiencies never exceeded 70% and that all unaccounted N was lost due to NO_3-N leaching. Using a detailed description of Soil-Plant Inorganic N Buffering, explain why it would be impossible for **<u>all</u>** unaccounted N to be lost via leaching **(10 points)**

2. Ammonia volatilization is influenced by

- a. urease activity
- b. temperature
- c. CEC
- d. H ion buffering
- e. soil water content
- f. N source and rate
- g. crop residues
- h. method of application
- I. hydrolytic enzymes

3.

Nitrogen Source	Chemical Formula	% N
Ammonium nitrate	______________	___
Urea ______________	___	
Anhydrous ammonia	______________	___
Ammonium sulfate	______________	___
Ammonium phosphate	______________	___

4. Which of the following stable isotopes are used in soil/plant research

a. ^{14}N
b. ^{18}O
c. ^{13}C
d. ^{3}H
e. ^{90}Sr
f. ^{13}N

5. To the best of your ability, provide a complete diagram of the Nitrogen cycle and all associated components discussed in class and listed on the cycle returned to you this past week **(20 points).**

6. When urea fertilizer is broadcast on the surface of high pH soils, ammonia volatilization can take place. Provide the two chemical reactions which ultimately lead to ammonia volatilization **(5 points)**

a.

b.

SPECTRAL RADIANCE

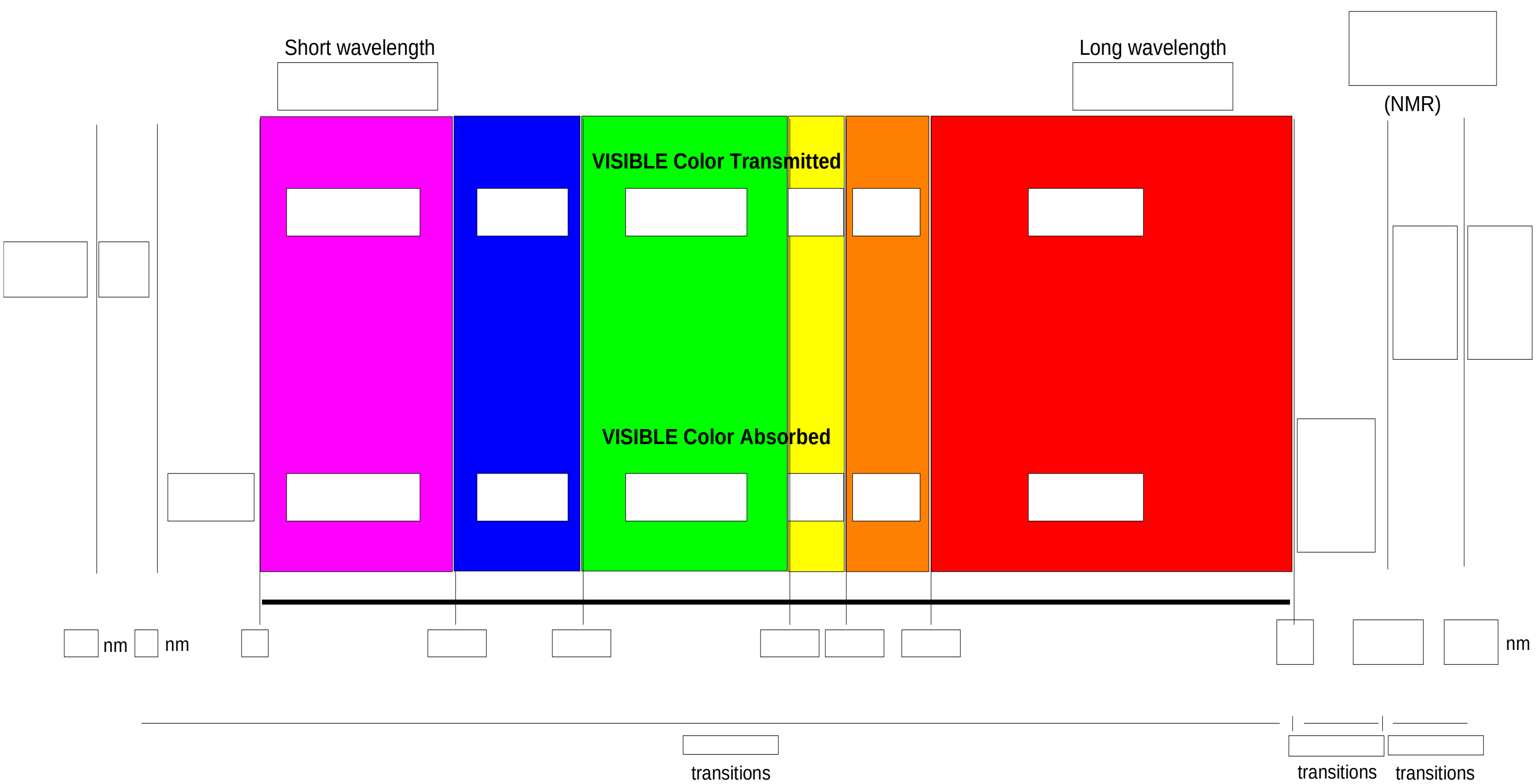
T F Spectral radiance measurements can be used to detect plant N deficiencies, but they cannot be used to detect soil N supply or potential mineralization.

T F The shorter the wavelength, the greater the frequency and the greater the energy

T F Energy of a single photon is proportional to its frequency or inversely proportional to its wavelength

T F At 780, 1500 and 2150 nm, the vibrational energy of R-NH_2 groups can be detected.

1. In the figure below, fill in all blanks as per our discussions in class (15 points)



2. Electromagnetic radiation possesses a certain amount of energy. The energy of a unit of radiation called the ___________ is related to the ___________ by

E = __ *__ = __*__/__

where E = _________
h = _________
v = _________
c = _________
λ = _________

EXCHANGE

T F Sandy soils with small amounts of clay and organic matter are poorly buffered and require only small amounts of lime to change soil pH

T F Base saturation (Ca+Mg+K+Na)/CEC in meq/100 g or cmol/kg is generally considered to be an indicator of weathering

T F Hydrogen ion buffering assumes that a soils total acidity is comprised of exchangeable acidity + nonexchangeable titratable acidity

1. Exchangeable acidity is comprised of
   a. H ions obtained from the hydrolysis of exchangeable, trivalent Al
   b. Hydrolysis of partially hydrolyzed and nonexchangeable Al
   c. Weakly acidic groups, mostly on organic matter
   d. Exchangeable H^+

2. Explain the difference between using an unbuffered salt to measure the CEC at the soils normal pH and the use of buffered salt solutions (5 points)

3. Why is soil pH such a valuable tool? Briefly indicate what relationships you know to exist with soil pH and why each is so important (10 points)

4. Echangeable acidity includes
    a. H ions obtained from the hydrolysis of exchangeable NH_4
    b. Hydrolysis of partially hydrolyzed and nonexchangeable NH_4
    c. Weakly basic groups, mostly on organic matter
    d. Exchangeable H

5. With time Anion Exchange is expected to become more important in soils. Explain. (5 points)

MICRONUTRIENTS

T	F	Boron moves up the xylem but does not move back down the phloem
T	F	Molybdenum deficiencies can look like N deficiencies since N metabolism is affected
T	F	Fe concentrations in soils generally range from 1 to 5 % or 1000 to 5000 ppm
T	F	Mn toxicity's can be corrected by liming acid soils

1. Which of the following micronutrients are present in the soil in relatively small amounts

a. Cl b. B c. Mo d. Fe e. Mn f. Zn g. Cu h. Ca

2. Given the following information, calculate the following

	$\log_{10} K$
$Fe(OH)_3 \longrightarrow Fe^{+++} + 3(OH^-)$	-39.4
$Fe^{+++} + L \longrightarrow FeL$	12.2
$3(OH) + 3H^+ \longrightarrow 3H_2O$	42
$Fe(OH)_3 + L + 3H^+ \longrightarrow FeL$	_____

If the soil pH is 8 and the concentration of citrate is 10^{-5} , calculate the concentration of FeL **(10 points).**

RADIOISOTOPES

T F When depleted forms of ^{15}N are used in crop production experiments, the rates to be applied must be higher and their utility in terms of time is decreased

T F All gamma emitting isotopes also emit some particulate form of radiation

T F The greater the energy of radiation the higher its penetrating power

1. When measuring ^{15}N using a mass spectrometer which of the following would be true?
   a. The ratio of ion currents (R) includes detection for $^{14}N^{14}N$, $^{15}N^{14}N$ and $^{15}N^{15}N$
   b. N_2 gas is generated via dry combustion of the sample and delivered in set volumes to the mass-spec.
   c. ^{15}N is an extremely safe isotope of N since it is stable, although somewhat radioactive

2. Discuss the differences between enriched, depleted and atom excess ^{15}N. When should enriched materials be used and when should depleted materials be used? (5 points)

3. How much ^{32}P would you put into a system to assure 1000 cpm after 90 days using an instrument with a 30% counting efficiency and 10% P utilization efficiency. Formulas needed are; $A = Ao\ e^{-\lambda t}$, 2.22×10^9 cpm/mC, 1 mC ^{32}P weighs 3.2×10^{-9} g, $\lambda = 0.693/t_{½}$, half life of ^{32}P = 14.3 days, 1 mC = 3.7×10^7 dps (10 points)

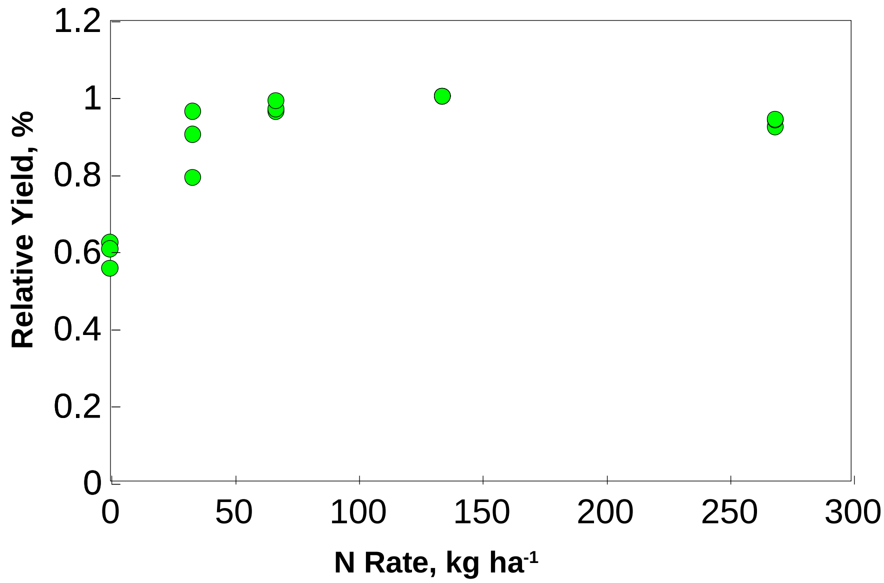
BIOMETRICAL APPLICATIONS

T F Stability analysis can be used to interpret treatment by genotype interactions

T F SED stands for standard error of the difference between two equally replicated means and is computed as √2*MSE/n

T F In an experiment with 10 treatments, the power (ß) of the test can be doubled by increasing the number of replications from 2 to 4.

1. We used the NLIN Procedure in SAS to develop linear-plateau models which would be used to detect critical levels. Using the data in the graph below, provide a range of values and steps that would predict the intercept, slope, joint and plateau (combined this must be less than 100 iterations)



PROC NLIN; DATA = ONE BEST = 2;
PARMS B0 = ____ to ____ by ___ B1 = ____ to ____ by ____ NJOINT = ____ to ____ by ____;
IF NRATE < NJOINT THEN DO;
MODEL YIELD = ___ + ___*____;
DER.B0=______;
DER.B1=______;
DER.NJOINT=______;
END;

How many iterations are there in your program? ________

From your work on page 7, provide a reasonable estimate for each of the following parameters
a. slope ________________
b. intercept______________
c. joint _________________
d. plateau______________

SOIL TESTING/CRITICAL LEVELS

T F Liebig stated that the yield was directly proportional to the amount of the deficient nutrient present and the crop content of the nutrient

T F The sufficiency concept and Bray's mobility concept are consistent with one another

T F The Base Cation Saturation Ratio concept that was developed by Bear in 1945 was extremely effective in determining nutrient deficiencies for high OM soils in temperate climates.

T F The sufficiency concept is based on Mitscherlich's equation dy/cx =(A-y)c

T F What we know as 'Bray's Mobility Concept' was initially developed for mobile nutrients

T F Grass tetany generally occurs when forage contains K/(Ca+Mg) > 2.2

1. When Bray originally modified the Mitscherlich equation, it was largely because Mitscherlich considered c to be a constant. Bray demonstrated that c and c1 varied with

a. crop
b. planting density/pattern
c. nutrient applied (source)
d. method of placement
e. rainfall
f. temperature

2. Define all components of Bray's modified Mitscherlich equation. What was this used for? (5 points)

3. Explain why sufficiency cannot be used for mobile nutrients (5 points)

4. Using Bray's modified Mitscherlich's growth function, calculate the percent sufficiency, c, and c1 values for the following data. (Soil test value for P = 18; N, K and all other nutrients adequate but not present in excess) (10 points)

kg P/ha	Yield, kg/ha	% Sufficiency
0	2000	____
25	4000	____
50	5700	____
75	6000	____

c = _____
c1= _____

ORGANIC MATTER

T F Cellulose and common crude protein forms decompose more rapidly than the other forms of organic matter found in soils

T F The five major groups of microorganisms include Bacteria, Actinomycetes, Fungi, Algae and Protozoa

T F Blue-green algae are also classified as cyanobacteria, they are considered to be photoautotrophs and can fix atmospheric N non-symbiotically.

T F Lignin contents are more reliable than C:N ratios for predicting residue decomposition

1. A soil is known to have a bulk density of 1.47, has 2% organic matter, organic C:N ratio of 10:1, and is known to mineralize approximately 3% of the total N each year. Organic C comprises up 48% of the total organic matter. Using the 0-15 cm layer, determine the kg of N which will be mineralized. (10 points)

2. Identify the major components of soil organic matter, and the general composition of each form (soil in northern Oklahoma or Southern Kansas)

Form	Formula	Composition, %
1.______________	___________	________________
2.______________	___________	________________
3.______________	___________	________________
4.______________	___________	________________
5.______________	___________	________________

BONUS:(5 points)

Outline the countries of Vietnam, Portugal, Ireland, El Salvador and Pakistan.

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Quizes Spring 1996

January 12, 1996
Quiz #1

1. Present annual additions of CO_2 to the atmosphere are estimated to be

    a. 3 GT and 2 GT remain in the atmosphere
    b. 5 GT and 3 GT remain in the atmosphere
    c. 3 GT and 3 GT remain in the atmosphere

2. Doubling the rates of CO2 in the atmosphere can
    a. double the rate of photosynthesis of C-3 type plants
    b. double the rate of photosynthesis of C-4 type plants
    c. triple the rate of photosynthesis in C-3 type plants

3. If the CO2 concentration in the atmosphere is greatly increased, one of the consequences could be that
    a. soils containing CaO would be become unproductive
    b. soils containing $CaCO_3$ would experience more dissolution and pH would drop thus increasing aluminum toxicities
    c. soils containing $CaCO_3$ would experience more dissolution and pH would increase and Fe deficiencies would increase

---

January 26, 1996
Quiz #2

1. To the best of your abilities, provide a diagram of the nitrogen cycle

---

January 29, 1996
Quiz #3

1. Work by Ferguson et al. (1984) defined Hydrogen Ion Buffering. Provide your definition.

2. Ferguson et al. (1984) noted that the resultant pH from urea hydrolysis in most soils would range from;
a. 7 to 9
b. 7 to 10
c. 7.5 to 9.5

3. When urea is applied to the soil surface, NH_3 volatilization probably will not be economically serious unless the soil surface pH

a. is greater than 7.5, or if urease activity is high independent of pH
b. is greater than 7.5 independent of urease activity
c. is greater than 7.5

4. Define Soil-plant inorganic N Buffering

January 31, 1996
Quiz #4

1. To the best of your abilities, provide a diagram of the nitrogen cycle

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February 7, 1996
Quiz #5

1. Moll et al., 1982 conducted nitrogen use efficiency experiments on
a. wheat
b. corn
c. alfalfa
d. all of the above

2. The work by Moll et al., 1982 discussed 'efficiency of use' which was calculated as
a. grain weight/nitrogen supply
b. total nitrogen removed/nitrogen supply
c. grain yield/grain N
d. grain N/total N uptake.

To the best of your abilities, provide a diagram of the nitrogen cycle

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February 23, 1996
Quiz #6

1. Define

a. ^{15}N natural abundance
b. ^{15}N atom excess
c. ^{15}N enrichment
d. ^{15}N depleted

2. When should depleted ^{15}N materials be used in field experiments and what advantages do they have.

3. When should enriched ^{15}N materials be used in field experiments and what advantages do they have.

March 13, 1996
Quiz #7

1. In Dr. Solie's lecture he stated that both biomass and total N uptake could be measured using spectral radiance measurments. Circle the correct wavelength at which red, near infrared and green spectral radiance measurements were taken.

Red	NIR	Green
550	440	200
671	1000	350
780	780	550

2. Automated spectral radiance measurements that are being collected at OSU are closely related to previous work using

a. nitrate selective ion electrodes
b. chlorophyll meters
c. inductive coupled argon plasma

3. Dr. Solie discussed field element size. What was this, why is it important and what has the work at OSU found concerning 'field element size?'

March 15, 1996
Quiz #8

1. Define Liebig's law of the minimum as per Bray's paper.

2. Describe Bray's root system sorption zone and the root surface sorption zone.

3. Bray discussed why c (log (A-y) = log A - cb) from Mitscherlich was constant. Which of the following were reasons why c should not be constant.

a. not all nutrient forms follow a % sufficiency concept
b. demonstrating constancy of c for an immobile nutrient is impossible if a mobile nutrient is deficient
c. changing the kind of plant should change c (different rooting patterns)
d. planting pattern should vary the competition for a nutrient.
e. method of placement (fertility pattern) should vary the value of c

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April 15, 1996
Quiz #9

1. Dr. Touby Kurtz noted that in Dr. Bray's 1948 paper, 'Requirements for a Successful Soil Test', there were several major requirements

a. The extracting solution should remove as quantitatively as practical the soil form(s) of the nutrient important to plant growth
b. The amount removed should be measured with reasonable accuracy and speed
c. There must be a useable relation between the amounts extracted and the growth and response of the crop to the nutrient in fertilizer rate trials under various conditions.

2. Work by Blackmer et al., 1996 indicated that
a. reflected radiation from a corn canopy at 550 nm could be used to predict grain yield.
b. the ratio of light reflectance between 550 and 600 nm to light reflectance between 800 and 900 nm also provided sensitive detection of N stress
c. measurement of spectral radiance near 2500nm was useful in identifying R-NH2 groups in plants

3. Name the three transitions which can take place in molecules when exposed to high and low energy wavelengths.

April 22, 1996
Quiz #10

1. Work by Nye et al., (1961) found that
a. Saturation of Al on the exchange complex interfered with Fe uptake and resulted in decreased concentration of Cl in soil solution
b. Because of the strong sorption of K competing with Al in concentrated solution, KCl should be an effective displacing agent for exchangeable Al
c. It is possible to displace all of the exchangeable Al in soils with dilute solutions of Ca, K or Na salts

2. Work by Bray and others noted that
a. It is possible to displace exchangeable Al with excess K applications on soils low in K and with a high pH, thus causing Ca deficiencies.
b. it is possible to displace exchangeable Al with excess K applications on soils high in K and a low soil pH, which can lead to Fe toxicity.
c. it is possible to displace exchangeable Al with excess K applications on soils high in K and a low soil pH, and that this can then lead to P deficiencies due to the precipitation of Al-P forms.

3. Circle the optimum pH for plant uptake of the following species.

a. NO_3	3-5	5-6	4.5-6	6-7
b. NH_4	3-5	5-6	4.5-6	6-7
c. H_2PO_4	4-5	5-6	6-7	7-8

4. Work by Olson and Dreier, 1956 documented the synergistic effect of applying N and P on nutrient uptake which would later become known as
a. complex NP ratio
b. rhizosphere pH phenomenon
c. dual placement
d. complementary band

Concentration to mass/unit volume

1728 in3/ft3
Pb (g/cm3)

Pb NO3-N

g		0.0022045 lb		28316.736 cm3		21780 ft3		453.542g		0.000001g		0.002204623 lb		ug		lb N
--	*	---------------	*	-------------------	*	-----------	*	----------	*	-----------	*	---------------	*	-----	=	------
cm3		g		ft3		1 ac(0-6")		lb		ug		g		g		ac (0-6")

Pb NO3-N

g		1 g		1 kg		100000000 cm2		2.54cm*6		ug		kg N
--	*	---------------	*	------------------	*	------------------	*	-----------	*	-----	=	---------
cm3		1000000 ug		1000 g		ha (0-6 in deep)		1 in (0-6")		g		ha (0-6 in deep)

Pb * NO3-N * 1.3597254 = lb NO3-N /ac (0-6")
Pb * NO3-N * 2.7194508 = lb NO3-N /ac (1-12")

Pb * NO3-N * 1.524 = kg NO3-N/ha (0-6")
Pb * NO3-N * 3.048 = kg NO3-N/ha (0-12")

How to calculate porosity of a soil, knowing bulk density (ρ_b) and assuming a particle density (ρ_b) of 2.65 g/cm^3.

Porosity is given by 1 - V_s/V_t, , but we know that $\rho_b = M_s/V_t$ and $\rho_s = M_s/V_s$ so:
$M_s=\rho_b * V_t$ and $M_s=\rho_s * V_s$ since both equations are equal we can say that

$\rho b * V_t = \rho_s * V_s$ now dividing both terms of the equation by $\rho_s * V_t$ we get that
$\rho_b/\rho_s = V_s/V_t$

Therefore porosity can be obtained as follows:
$f = 1 - \rho_b/\rho_s$ so if a soil has a bulk density of 1.50 and assuming a particle density (ρ_b) of 2.65 g/cm^3, porosity of that soil will be = 1 - 0.56= 0.44

Depth cm	cm Deep	PB	Pb/Ps=Vs/Vt	Porosity= 1-Vs/Vt	Pore vol. per depth		wet	dry	%mois	cm of water	
0 to 15	15.00	**1.49**	**0.56226415**	**0.437735849**	6.566037736		1.046333	0.908667	0.151504	0.994781	
15 to 30	15.00	**1.57**	**0.59245283**	**0.40754717**	6.113207547		1.104167	0.935167	0.180716	1.104757	
30 to45	15.00	**1.53**	**0.57735849**	**0.422641509**	6.339622642		1.059	0.896833	0.180821	1.146339	
45 to 60	15.00	**1.75**	**0.66037736**	**0.339622642**	5.094339623		1.209667	0.975667	0.239836	1.221806	
60 to 90	30.00	**1.48**	**0.55849057**	**0.441509434**	13.24528302		0.788	0.6795	0.159676	2.114957	
90 to 120	30.00	**1.39**	**0.5245283**	**0.475471698**	14.26415094		0.758167	0.673333	0.12599	1.797142	
120 to 150	30.00	**1.44**	**0.54339623**	**0.456603774**	13.69811321		0.7255	0.650333	0.115582	1.583252	
150 to 180	30.00	**1.68**	**0.63396226**	**0.366037736**	10.98113208		0.666833	0.595333	0.120101	1.318843	
				%							
										11.28188	
					76.30188679						

Assumming a Particle density of PS=2.65g/cm^3

Depth*porosity

14. STATISTICAL APPLICATIONS

Reliability

Estimated probabilities (reliabilities) of treatment (any treatment where a direct comparison can be made with a check) response compared to a check for the sample of treatment differences (years or locations) can be determined as defined by Eskridge and Mumm (1992) where: RNi = P(Z > - ydi/sdi) such that Z is a standard normal random variable and ydi and sdi are estimates of the sample mean difference and standard deviation, respectively. A modified reliability estimate (economic reliability, REi) can be calculated by subtracting the costs (in yield units) of the fertilizer and its application from the mean difference for the ith treatment (di) against the treatment check as: REi = P(Z > -(ydi - ci)/ sdi) where ci represents the equivalent yield necessary to pay for the fertilizer and its application for a given price ratio. These values are then substituted in the equation to calculate reliability for normally distributed differences. The recalculated reliability represents the normal probability that a treatment will outperform the treatment check in a quantity superior to ci, therefore, providing an estimate of the economic feasibility of the practice as well as allowing direct comparisons of net benefits among calculated reliabilities for a given price ratio.

Yld Difference		Cost of N in bu/ac			Yld Dif (using cost)		
10		5.69			4.31		21 cents/lb N
6		5.69			0.31		N applied at a rate of 80 lb/ac
2		5.69			-3.69		wheat price = $2.95/bu
10		5.69			4.31		cost = $16.8 (to apply N)
-2		5.69			-7.69		need 16.8/2.95 = 5.69 bu increase to pay
-3		5.69			-8.69		for the N
5		5.69			-0.69		
7		5.69			1.31		
6		5.69			0.31		
4		5.69			-1.69		
4.5	c=average(d5:d14)				-1.19		
2	c=COUNTIF(d5:d14,"<0")				5		
0.8	c=ABS(d17-10)/10				0.5		
4.428443	c=STDEV(d5:d14)				4.428443		
1.016158	c=d16/d19				-0.268717		
0.845223	c=NORMSDIST(d20)			REi	0.394074		

Surface Response Model

linear and quadratic relationships of x and y with z and a linear interaction term.

Z = x x2 y y2 xy

```
libname lib2 'c:\temp';
data one;
input x y z;
filename grafout 'c:\temp\surf.gsf';
goptions nodisplay gsfmode=replace device=hpljs2
   GSFNAME=GRAFOUT gwait=15 fby=xswiss hby = 1.75 gouttype=dependent;
title f=xswiss 'Surface Model';
proc rsreg data = one out = two;
   model z = x y /predict;
proc g3grid data = two out = three;
   grid x*y=z/spline;
proc g3d data = three gout=new;
   plot x*y=z;
run;
```

Procedure for Determining Differences in Population Means

```
data one; input sample time $ ph P oc k;
cards;
1       A       6.17    21.47  0.924  150
2       A       6.27    18.69  0.939  139
3       B       6.16    21.20  1.042  142
4       B       5.65    41.74  1.054  144
proc ttest;
classes time;
var ph p k oc;
run;
```

Randomized Complete Block Randomization

```
Title ' RCBD 3 reps, 13 treatments';
proc plan seed = 37275;
factors blocks = 3 ordered trts = 13;
run;
```

Program to output Transposed Data

```
data one;
Input yr trt yield;
Cards;
88      1       1000
88      2       2000
88      3       2400
89      1       4000
89      2       3200
89      3       3500
data two; set one;
proc sort; by trt yr;
proc transpose data = two out = three prefix = y ;
id yr;
var yield;
by trt;
proc print;
run;
```

Contrast Program for Unequal Spacing

```
proc iml;
dens={0 100 600 1200}; **
p=orpol(dens);
t=nrow(p);
do i=1 to t;
  pr=abs(p[,i]);
  pr[rank(abs(p[,i]))]=abs(p[,i]);
  do j=t to 1 by -1;
    if pr[j] > 1.e-10 then scale=pr[j];
    if abs(p[j,i]) < 1.e-10 then p[j,i]=0;
  end;
  p[,i]=p[,i]/scale;
end;
print p;
run;
```

The only thing that needs to be changed is the trt values.

Output

Trt	P	lin	quad	cubic
0	1	-3.8	19.416667	-11
100	1	-3	1	14.4
600	1	1	-40.66667	-4.4
1200	1	5.8	20.25	1

Test of Differences in Slope and Intercept Components from Two Independent Regressions

```
data one;
input exp x y;
if exp = 1 then intc_dif = 0;
if exp = 2 then intc_dif = 1;
slop_dif = intc_dif*x;
cards;
1       3.31878  45.8971
1       3.31716  45.24701
1       3.31162  42.59693
2       3.26607  54.4
2       3.32216  40.7
2       3.31122  55.7
data two; set one;
proc sort; by exp;
proc reg;
model y = x intc_dif slop_dif;
run;
proc reg;
by rep;
model y = x;
run;
```

Linear-Plateau Program

```
data one;
  input rep trt x  y;
cards;
proc nlin data = one best = 3;
parms b0=200 to 400 by 20 b1=-12 to -5 by 1 njoint=5 to 30 by 2;
        if x<njoint then do;
        model y = b0 + b1*x;
        der.b0=1;
        der.b1=x;
        der.njoint=0;
end;
        else do;
        model y=b0+b1*njoint;
        der.b0=1;
        der.b1=njoint;
        der.njoint=b1;
end;
        file print;
        if _obs_ =1 and _model_ =0 then do;
```

```
        plateau = b0 + b1*njoint;
        put plateau=;
end;
        plateau=b0+b1*njoint;
        id plateau;
        output out = new p = pry parms=b0 b1 njoint sse=sse;
run;
proc plot;
        plot y*x='+' pry*x='*'/overlay;
run;
proc means noprint;
        var y sse b0 b1 njoint plateau;
        output out = new2 n = tdf
        mean = y sse b0 b1 njoint plateau
        css=csst;
data new3; set new2;
        intercpt=b0; slope=b1; joint=njoint;
        rsq=(csst-sse)/csst;
        edf=tdf-3;
        ssr=csst-sse;
        msr=ssr/2;
        mse=sse/edf;
        f=msr/mse;
        probf=1-(probf(f,2,edf));
keep intercpt slope joint plateau rsq f probf;
proc print;
run;
```

Linear-Linear Program

```
data one;
  input rep trt x  y;
cards;
proc nlin data = one best = 2;
parms b0=50 to 100 by 10 b1=-0.5 to -0.1 by 0.01 joint=10 to 50 by 10
        b2 = -.5 to .1 by 0.05;
        if x<joint then do;
        model y = b0 + b1*x;
        der.b0=1;
        der.b1=x;
        der.joint=0;
        der.b2=0;
end;
        else do;
        model y=b0+(b1-b2)*joint+b2*x;
        der.b0=1;
```

```
        der.b1=joint;
        der.joint=b1-b2;
        der.b2=x-joint;
end;
        file print;
        if _obs_ =1 and _model_ =0 then do;
        joinlev = b0 + b1*joint;
        put joinlev=;
end;
        joinlev=b0+b1*joint;
        id joinlev;
        output out = new p = pry parms=b0 b1 joint b2 sse=sse;
run;
        proc plot;
        plot y*x='+' pry*x='*'/overlay;
run;
        proc means noprint;
        var y sse b0 b1 joint b2 joinlev;
        output out = new2 n = tdf
        mean = y sse b0 b1 joint b2 joinlev
        css=csst;
data new3; set new2;
        intercpt=b0; slope=b1; joint=joint; slope2=b2; jresp=joinlev;
        rsq=(csst-sse)/csst;
        edf=tdf-4;
        ssr=csst-sse;
        msrg=ssr/3;
        mse=sse/edf;
        f=msrg/mse;
        probf=1-(probf(f,2,edf));
        keep intercpt slope joint slope2 joinlev rsq msrg mse edf f probf;
        proc print;
run;
```

Experiment: Influence of Nitrogen Rate and Mowing Height on Sensor Based Detection of Nutrient Stress

Treatment	N rate lb N/1000 ft^2/month	Mowing Height inches
1	0	0.5
2	0.5	0.5
3	1.0	0.5
4	1.5	0.5
5	0	1.5
6	0.5	1.5
7	1.0	1.5
8	1.5	1.5

Replications: 4
Experimental design: CRD

CRD Source of variation	df	**CRD** Source of variation	df	**RCBD** Source of variation	df
Total (4*8)-1	31	Total (4*8)-1	31	Total (4*8)-1	31
				block	3
height	1	treatment	7	treatment	7
nrate	3				
nrate*height	3				
error	24	error	24	error	21

```
proc glm;
classes height nrate;
model yield = nrate height nrate*height;
contrast 'Nrate_lin' nrate        -3 -1 1 3;
contrast 'Nrate_quad' nrate    1 -1 -1 1;
contrast 'Nrate_cub' nrate      -1 3 -3 1;

contrast 'height*nrate_lin' height*nrate  -3 -1 1 3 3 1 -1 -3;
contrast 'height*nrate_quad' height*nrate 1 -1 -1 1 -1 1 1 -1;

means nrate height nrate*height;
run;
```

height							
0.5				1.5			

nrate

0	0.5	1.0	1.5	0	0.5	1.0	1.5

height							
0.5				1.5			
1				**-1**			

nrate **(linear)**

0	0.5	1.0	1.5	0	0.5	1.0	1.5
-3	**-1**	**1**	**3**	**-3**	**-1**	**1**	**3**

interaction coefficients (height*nrate_lin)

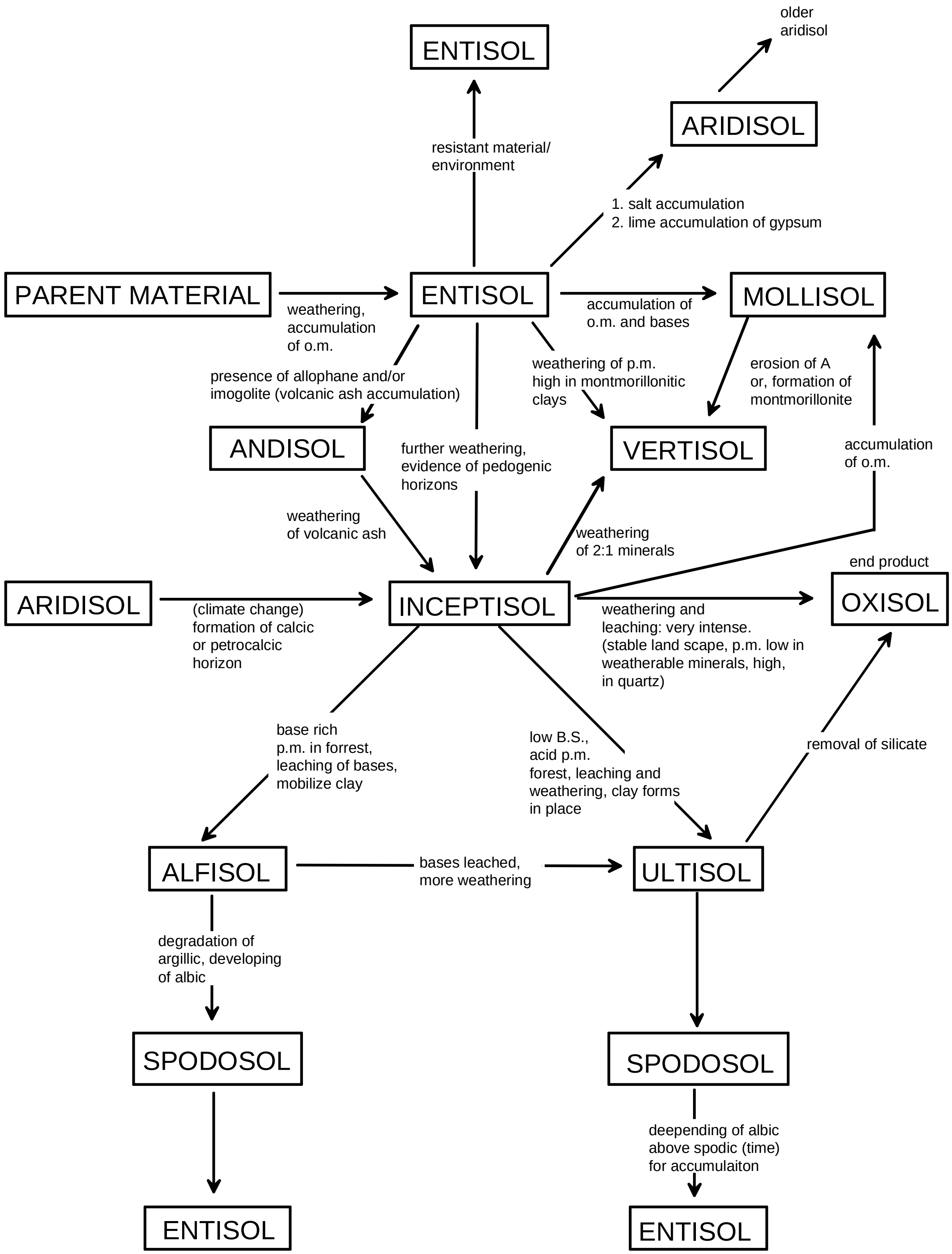
-3	**-1**	**1**	**3**	**3**	**1**	**-1**	**-3**

Method for Determining Significant Differences in Joints From
Two Independent Linear-Plateau Models
**** If the confidence intervals about the joint estimates overlap, there are no significant differences ****

t-joint = Joint 1 - Joint 2
____
Sqrt(variance1 + variance2)

where variance1 and variance 2 are determined by squaring the Asymptotic std. errors about each joint estimate

		Grain Yield			Soil Accumulation	
		Stillwater 222, 1988	Stillwater 222, 1993		Stillwater 222, 1988	Stillwater 222, 1993
Joint		56.089	55.87		102.028	104.13
Asymtotic std. error		8.6632	8.2856		5.84154	4.6067
variance (Asym. std error)2		75.051	68.6512		34.1236	21.2217
dfe		13	9		13	10
t-calc		0.01827			0.28255	
	TDIST	0.9857		TDIST	0.78197	


ENTISOL
older
aridisol
ARIDISOL
resistant material/
environment
1. salt accumulation
2. lime accumulation of gypsum
PARENT MATERIAL
weathering,
accumulation
of o.m.
ENTISOL
accumulation of
o.m. and bases
MOLLISOL
presence of allophane and/or
imogolite (volcanic ash accumulation)
weathering of p.m.
high in montmorillonitic
clays
erosion of A
or, formation of
montmorillonite
ANDISOL
further weathering,
evidence of pedogenic
horizons
VERTISOL
accumulation
of o.m.
weathering
of volcanic ash
weathering
of 2:1 minerals
end product
ARIDISOL
(climate change)
formation of calcic
or petrocalcic
horizon
INCEPTISOL
weathering and
leaching: very intense.
(stable land scape, p.m. low in
weatherable minerals, high,
in quartz)
OXISOL
base rich
p.m. in forrest,
leaching of bases,
mobilize clay
low B.S.,
acid p.m.
forest, leaching and
weathering, clay forms
in place
removal of silicate
ALFISOL
bases leached,
more weathering
ULTISOL
degradation of
argillic, developing
of albic
SPODOSOL
SPODOSOL
deepending of albic
above spodic (time)
for accumulaiton
ENTISOL
ENTISOL

If we could shrink the Earth's population to a village of precisely 100 people. With all existing human ratios remaining the same, it would look like this:

There would be 57 Asians, 21 Europeans, 14 from the Western Hemisphere (North and South) and 8 Africans.

- 51 would be female; 49 would be male.
- 70 would be nonwhite; 30 white.
- 70 would be non-christian; 30 christian.
- 50% of the entire world's wealth would be in the hands of only 6 people
- and all 6 would be citizens of the United States.
- 80 would live in substandardized housing.
- 70 would be unable to read.
- 50 would suffer from malnutrition.
- 1 would be near death; 1 would be near birth.
- Only 1 would have a college education.
- No one would own a computer.

When one considers our world from such an incredibly compressed perspective, the need for both tolerance and understanding becomes glaringly apparent.

Convert the following to kg N/ha

2 mM solution of N provided as NH_4NO_3
200 ml of solution applied per day for 35 days
applied to pots having a surface area of 15 cm

area = pi*r^2 = 0.01766m^2

$$\frac{\text{kg N}}{\text{ha}} = \frac{0.002\ \text{M}}{\text{L}} \quad \frac{14\ \text{g N}}{\text{mole N}} \quad \frac{1\ \text{kg}}{1000\ \text{g}} \quad \frac{10000\text{m}^2}{\text{ha}} \quad \frac{7\ \text{L}}{0.01766\text{m}^2}$$

= 111 kg N/ha

Syllabus
Course: **Plant and Soil Sciences 5813**
Course Title: **Soil-Plant Nutrient Cycling and Environmental Quality**

Instructor: William R. Raun (044 North Ag. Hall)
Tel: 744-6418
FAX: 744-5269
email bill.raun@okstate.edu

Objectives:
1). To study the relationships between soil nutrient supply and plant response, and to understand associated theoretical applications with macro and micronutrients.
2). Evaluation of applied techniques for determining fertilizer response using soil test indices and yield goals. Theoretical understanding of non-destructive soil tests using spectral radiance measurements.
3). Comprehensive review of the nitrogen cycle. Class development of nutrient cycles for P, K, S, Ca, Fe, Mg, B, Mn, Cl, Cu, Zn and Mo. Comprehensive study of nutrient interactions and tracer/recovery techniques in agricultural sciences.

Attendance: mandatory
Text: none required
Course Outline:

Week	**Exam/Activity**
January 10-14	
January 17-21	
January 24-28	
Jan 31- Feb 4	First Hour Exam
February 7-11	
Feburary 14-18	
February 21-25	
Feb 28 – Mar 3	
March 6 - 10	Second Hour Exam
March 13-17	Spring Break
March 20-24	
March 27-31	
April 3-7	
April 10-14	Nutrient Cycle DUE
April 17-21	
April 24-28	
May 1-5	Final Exam, Friday May 5, 2000 10:30-12:20

Added projects/class activities subject to change

Grading Procedures		**Grading Procedures:**
2, 1 hour exams	200	A 85-100%
Quizes	100	B 70-84%
Assignments	200	C 60-70%
Nutrient Cycle	50	D <60%
Final Exam	200	
Total	750	

References

Bohn, H., B.L. McNeal and G.A. O'Conner. 1979. Soil Chemistry. J. Wiley & Sons.

Dowdy, R.H., J.A. Ryan, V.V. Volk and D.E. Baker (ed). 1981. Chemistry in the Soil Environment. Am. Soc. of Agron. Special Publication No. 40. Madison, WI.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York, NY.

Mortvedt, J.J., P.M. Giordano and W.L. Lindsay (ed.) 1972. Micronutrients in Agriculture. Soil Science Society of America, Inc., Madison, WI.

Page, A.L. (ed.). 1982. Methods of Soil Analysis. Part 2. 2nd ed. Agronomy 9. Madison, WI.

Peck, T.R., J.T. Cope, Jr. and D.A. Whitney (ed.) 1977. Soil Testing: correlating and interpreting the analytical results. Am. Soc. of Agron. Special Publication No. 29., Madison, WI.

Sanchez, P.A. 1976. Properties and Management of Soils in the Tropics. John Wiley & Sons, Inc., New York, NY.

Tisdale, Samuel L., Werner L. Nelson, James D. Beaton and John L. Havlin. 1993. Soil fertility and fertilizers. 5th ed. Macmillan Pub. Co. New York, NY.

Westerman, R.L. (ed.). 1990. Soil testing and plant analysis. 3rd ed. Soil Sci. Soc. Am. book series; no. 3. Madison, WI.