Weld Laboratories

Understanding Soil and Your Lab Report

2018 v5.1

by Adam Crooks

About us

Weld Laboratories has served the analytical needs of the agricultural and environmental industries for nearly 40 years. Our motto has always been that chemistry is best performed by chemists.

From alfalfa and corn silage analyses to soil, manure, water, and gas/oil spill testing, Weld Labs offers a comprehensive list of analytical services to meet your needs.

Weld Labs has continuously been certified by the National Forage Testing Association (NFTA) since 1986 and holds certification in both NIRS and Wet Chemistry analyses.

FIGURE 1. SOIL FURROWS BY GORDON HATTON. CREATIVE COMMONS CC-BY-SA 2.0.

Weld Laboratories

Table of Contents

Sample Soil Report

This is an example of a soil report you may see. We will break this into sections and discuss them below.

Customer Name
Address 1
Address 2

Farmer/Grower: Growers Name
Field No.: Field #7
Requested Fertilizer Recommendation:
Crop: Corn
Yield goal: 200
Units: bu/acre

Date: 3/19/2017

Laboratory No. S17060-885

		Vs. Our Average Ag. Soil
Soil Texture	SCL	
pH	7.73	Avg
Salts, mmhos/cm	0.59	Avg
Organic Matter, %	1.8	Avg

	ppm	lbs/acre	Vs. Our Average Ag. Soil	Recommendations (add lbs. per acre)	
Nitrate-N	8.6	17	Avg	190	#N
Phosphorus	16	33	Avg	40.0	#P_2O_5
Potassium	15	30	V. Low	100	#K_2O
Calcium	3633	7266	Avg		
Sulfate-S	42	85	Avg	30.0	#S
Boron					#B
Zinc	0.0	0.1	V. Low	8.0	#Zn
Iron	12.2	24	Avg	0.0	#Fe
Manganese	1.6	3.3	Avg	2.0	#Mn
Copper	20.0	40.0	V. High	0.0	#Cu
Magnesium					#Mg

Sample Soil Report (cont)

There are four sections to a soil report, colored for clarity (see below).

The red section includes the client billing information (customer name, address 1, address 2), the published date, and an internal laboratory number which we need when you contact us about your soil. The red section also includes the farmer/grower name (sometimes a large coop or soil company will test soil for a number of different farms, this is where they track which farmer the soil belongs to). Finally, the red section includes the Field No. this is where the sample name or field name belongs (i.e. "North Pivot").

The green section is the most important section of the report. It contains a number of different tests or analyses which we performed on your soil. Each test is generally quantitative describing the amount of available nutrients in ppm, or parts per million. Converting units like ppm to lbs/acre is described in the section "Soil Calculations" below.

There is a small uncolored section at the bottom of the report where we list specialty analyses and other notes and information.

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Manganese	1.6	3.3	Avg
Copper	20.0	40.0	V. High
Magnesium			

Recommendations (add lbs. per acre)

190	#N
40.0	#P_2O_5
100	#K_2O
30.0	#S
	#B
8.0	#Zn
0.0	#Fe
2.0	#Mn
0.0	#Cu
	#Mg

Sample Soil Report (cont)

There are four sections to a soil report, we have already discussed the red and green sections.

The yellow section compares each of the soil tests or analyses to our global averages for irrigated agricultural soil (>80% corn and alfalfa). This yellow section does not change depending on which crop you are growing. Ratings include V. Low, Low, Avg, High, or V. High. This section should be used as a quick look to determine if you are "Very Low" (V. Low) or high in something that may warrant further investigation.

The blue section is everything for your fertilizer recommendation. At the top we list the requested fertilizer recommendation (Crop, Yield Goal, and Units for the yield). For this report the client wants to grow 200 bushels per acre of Corn. Below this we have the actual recommendation table. Notice it says that 190 pounds (lbs) of nitrogen must be added per acre. This 190 #N recommendation is based on the Nitrate-N ppm number in the green section (and on the same row) as well as the organic matter and yield goal. Notice when you get to iron it says "0.0 #Fe." This means that we provide a recommendation for iron but that you already have enough iron (we don't list negative numbers for excess). Boron wasn't tested, thus no recommendation. Calcium was tested, but we don't have calcium recommendations for corn.

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		Vs. Our Average Ag. Soil
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	#B
8.0	#Zn
0.0	#Fe
2.0	#Mn
0.0	#Cu
	#Mg

Understanding the Report – Soil Texture

The very first row of the green section is Soil Texture. Soil texture is important because it determines how quickly water (and also soluble nutrients) can move within the soil. The textural class is determined by how much sand, silt, and clay are present in the soil.[1] Sand, silt, and clay are chemically similar (all containing silica or silicate minerals) but drastically different in terms of particle size. Sand is all particles of diameter 0.05 to 2 mm,[A] silt is 0.002 to 0.05 mm, and clay is < 0.002 mm.[2,3] Larger particle sizes do not pack together as tightly as the smaller particles can and this allows for channels where water (and air) can flow. These channels permit proper soil respiration which is crucial throughout the life cycle of a crop. Without proper drainage the roots of almost any crop will start to rot. Conversely, sandy soils (with incredibly high drainage) require more frequent watering and fertilization as there is nothing to hold onto the water or nutrients.

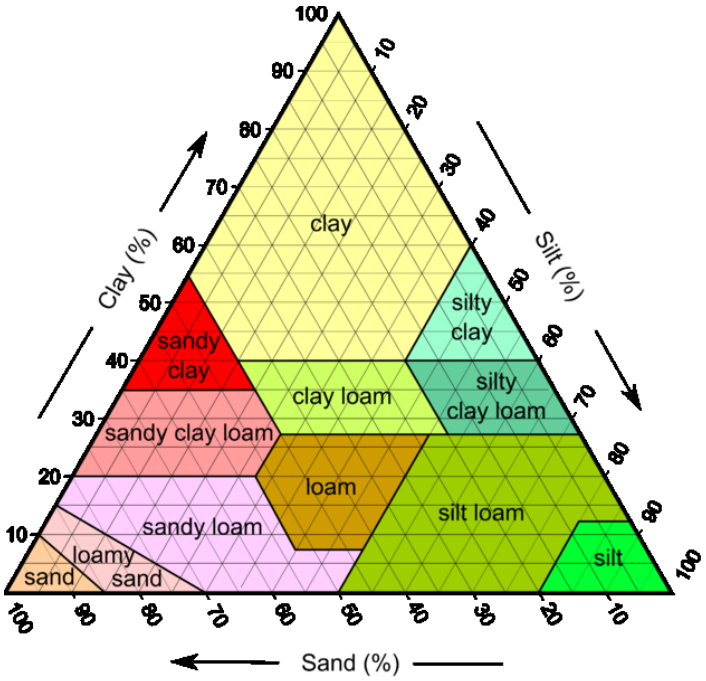

FIGURE 2. NRCS USDA SOIL TRIANGLE (REDRAWN BY MIKE NORTON). CREATIVE COMMONS CC-BY-SA 3.0.

The ideal soil texture is a mixture of sand, silt, and clay simply called "loam" colored brown in the soil triangle[B] (Figure 2).[5] When you order one of our common soil packages, a texture estimation is always included. Our texture abbreviation system is S=Sand or sandy, C = Clay, L = Loam, Silt = "Silt." The sample report above lists texture "SCL," this stands for Sandy Clay Loam. We perform this estimation by feel, but we can we perform a full soil classification for a fee. The process requires a set of screens and a hydrometer (and Stokes equations) but provides percentages for sand, silt, and clay separately.[6]

[A] When we report soil classifications we split the sand fraction into "Course Sand" and "Very Fine Sand" using sieves (or screens). The "very fine sand" is between 105 and 53 µm diameter. The "course sand" is between 2000 µm and 105 µm diameter. The USDA soil classification system splits the sand fraction into 5 categories: very fine 50-100µm, fine 100-250 µm, medium 250-500 µm, coarse 500-1000 µm, and very coarse 1000-2000 µm.[1]

[B] The original equilateral soil triangle of Davis and Bennett was more symmetrical. In 1938 the USDA changed the size limit of clay from 5µm to 2µm. The triangle has remained the same since 1951.[4]

Understanding the Report – pH

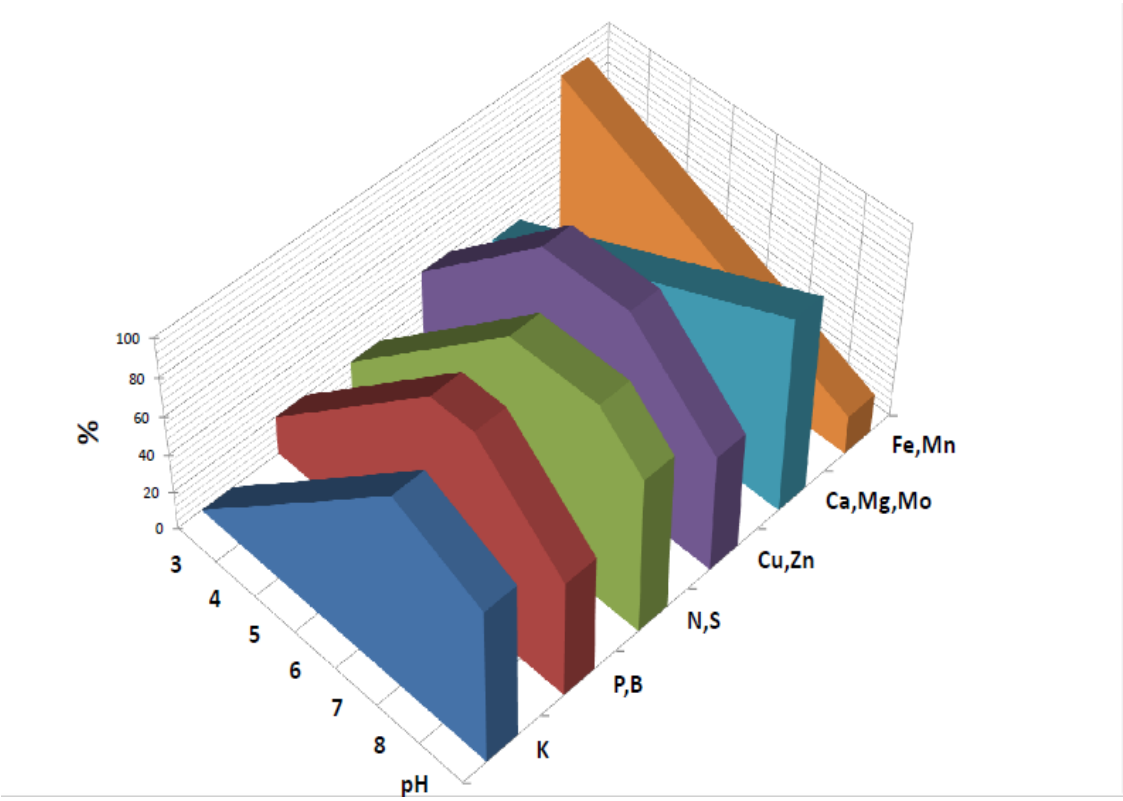

FIGURE 3. NUTRIENT AVAILABILITY VS. PH BY MOECKEL. PUBLIC DOMAIN.

There is nothing terribly special about how we measure pH. We use the industry standard: a properly calibrated pH probe on a 1:2 dilution (1 part soil, 2 parts water).[C] Remember that pH is a logarithmic scale, a pH of 6 is ten times as acidic as a pH of 7.

Soil pH is important because the availability of most plant-essential elements depend on it.[8] Nitrogen is most available at pH 6-8, whereas copper and zinc are most available at pH 5-7. Other nutrients have their own preferred ranges (see Figure 3 above). This inherent nutrient preference gives rise to specific ranges where crops grow better. Blueberries and Irish potatoes proliferate at low pH 5.0-5.5. Peanuts, rice, and watermelon do well at pH 5.5-6.5.[9] Soils in Colorado tend to be alkaline pH > 7.1 which is perfect for corn, hay, and alfalfa. Here in Colorado we rarely need to apply lime to raise pH for any crops.

Changing soil pH is generally more expensive than it is worth but can be achieved with lime[D] (to raise pH and make the soil more basic) and elemental sulfur or special fertilizers (to lower pH and make it more acidic). If you are trying to determine the

[C] This pH Method is from Soil, Plant, and Water Reference Methods for the Western Region (WSMM) S-2.10.[7] One common variation is a 1:1 dilution in $CaCl_2$ solution. Labs utilizing this method tend to be 0.3 to 0.4 pH units lower. If you require a custom dilution with $CaCl_2$ we can do this for a small added fee.
[D] Agricultural lime is pulverized limestone, $CaCO_3$.

associated cost of liming we recommend taking a few extra samples and requesting our "liming requirement" package. The liming requirement package includes "buffer pH" using the SMP buffer[E] and gives a much better estimate of how much lime it will take.

Understanding the Report – Salts

We use a standard calibrated conductivity probe (with an integrated temperature sensor and 1.0 cm path length) to measure salts on a 1:2 dilution in distilled water (method MSA Part 2 10-3.3).[8] It may seem odd to measure salt in terms of conductivity but adding salt to water makes it more conductive so this is how it has been done historically. The mmhos/cm units may seem strange but are the industry standard.[F] To convert from mmho/cm to TDS (total dissolved solids, ppm) simply multiply by 640.

If your pH is less than 8.5 and your Salts are less than 4 mmhos/cm, you can skip reading the rest of this section which details types of salt problems and remediation strategies.

Types of salt problems and remediation strategies

High concentrations of salts in soil can cause various problems with crops, but it especially affects early growth stages (germination).[10] Soils that suffer from high salt concentrations are most common in arid and semiarid regions where evaporation rates exceed precipitation rates and dissolved salts are left behind to accumulate, or in areas where irrigation changes (or addition of salty manure etc.) have caused salts to accumulate (e.g. saline seeps).[11] According to McCauley et al. there are three types of salty soils: i) saline soil, with a high concentration of soluble salts, especially Ca, Mg, and K; ii) sodic (or alkali[12]) soil where sodium is high but magnesium and calcium are not; and iii) saline-sodic soils which are essentially saline soil with elevated sodium levels as well.[11] The combination of electrical

EQUATION 1. SODIUM ADSORPTION RATIO

$$\text{S.A.R.} = \frac{Na^{+}}{\sqrt{\frac{1}{2}(Ca^{2+} + Mg^{2+})}}$$

[E] SMP stands for Shoemaker, McLean, and Pratt. Their paper "Buffer methods for determination of lime requirement of soils with appreciable amount of exchangeable aluminum" was an attempt to improve the liming requirement calculated for soils that require more than 1 ton lime/acre.

[F] The units (mmhos/cm) may seem strange at first, mho units are for conductance (1/R where R is resistance) exactly the same as Siemens. Regarding the denominator in "mmhos/cm" remember that while resistors are measured in ohms, they can be shaped differently and made from materials of different resistivity $\rho = R * (A/L)$, A = cross-sectional area (cm^2), L = material length (cm) (the units for resistivity are thus ohm-cm). What we actually measure isn't conductance, it is conductivity ($1/\rho$) measured in S/cm or mho/cm. The extra "m" in "mmho/cm" is because we measure much smaller (1/1000th to be exact) amounts of conductivity milli mho's/cm.

conductivity (EC), sodium adsorption ratio (SAR), and pH allow us to classify a soil (see Table 1).

TABLE 1. CLASSIFYING SALINE/SODIC SOIL.

	EC (mmhos/cm)	SAR	pH
Normal Soil	< 4	< 12	< 8.5
Saline	> 4	< 12	< 8.5
Sodic	< 4	> 12	> 8.5
Saline-Sodic	> 4	> 12	< 8.5

Generally agricultural soils will be classified as "normal." In fact, we don't generally run an SAR in our routine packages. If your EC exceeds 4 or your pH is > 8.5 we highly recommend running an SAR to determine which type of saline/sodic soil you have. Saline soils can exhibit a white crust on the surface of the soil.[13] Saline soils also cause osmotic stress in the plant where there is less water available to it and the plant must use extra energy to get at the water. Symptoms look like drought stress (wilting, leaf burn, growth problems, plant death). Sodic soils have high amounts of Na^+ in the cation exchange capacity (CEC) exchange sites (where there are typically other cations like Ca^{2+}, Mg^{2+}) and a pH above 8.5. Sodic soils cause the soil colloid to disperse (and clog soil pores), thus reducing air and water permeability in the soil.[13] According to McCauley et al. this low permeability and infiltration can cause ponding and crusting when dry.[13] The general result is reduced or inhibited seedling emergence.[13]

Reclaiming saline soil starts with excess water and changing crops (to barley, or some other salt tolerant crop).[12] Often it is worth investigating drainage of the soil, and sources of irrigation water as well (we have an irrigation water quality package for this). To reclaim sodic or saline-sodic soil you typically need to: i) add gypsum or calcium carbonate to help replace sodium at the exchange sites; ii) apply excess water to push the sodium deeper into the soil; and iii) change crops to something salt tolerant.[12]

Understanding the Report – OM (Organic Matter)

Organic matter (OM) is essential in productive soil, it is a storehouse of nutrients, contributes to the cation exchange capacity (CEC), and also contributes to soil drainage and structure.[12,14] Soils rich with organic matter typically have a darker appearance with visible remnants of straw or root systems (Figure 4). Organic matter in soil is commonly determined by two methods: 1) loss-on-ignition (LOI) at 450°C (MSA 29-4.3.2.4), and 2) the Walkley-Black method (MSA 29-3.5.2).[8] We use the colorimetric Walkley-Black variant specified by Sims and Haby[15] (method MSA 29-3.5.2)[8] unless there is too much organic matter or obvious interference (at which point we switch to LOI).

Organic matter is a reservoir for C, N, and to a much lesser degree P, Fe, S, and many other micronutrients. As previously mentioned adding organic matter can increase soil aggregation which increases water permeability and improves the structure of the soil.[12] In general, rapid decomposition of OM in soil is a good sign for both soil structure and microbiological health. Healthy soil has a dark color, and an earthy odor.

Coarse soils generally have less OM than finer soils (with high clay content).[12]

FIGURE 4. SOIL RICH IN ORGANIC MATTER. BY WPSOPO. CREATIVE COMMONS CC-BY-SA 3.0.

It is important to note that organic matter is not required for high producing soils when fertilizer is applied but high OM reduces the fertilizer required. Adding organic matter to soil is generally accomplished in three ways: i) by plowing-in a cover crop (i.e. clover, sweet peas, sometimes even alfalfa); ii) by adding high OM manure or compost; and iii) by adding peatmoss, dry leaves, or sawdust with extra nitrogen. Extra N compensates for over-stimulating soil microorganisms which happens when material is added with C:N ratios over 30.[12] What is the ideal OM? If you have too much OM you can leach nutrients similar to over-fertilization. Farmers generally shoot for 3% OM while gardeners try to stay around 5-6%.[16]

Understanding ppm Available Nutrients

Parts per million (ppm) *nutrient-name* can be understood as "the number of milligrams of available *nutrient-name* per kilogram (2.2 lbs) of dry soil." (Also lbs/acre = ppm*2 for a 6" soil depth). The word available is underlined because in all soil analyses listed below "ppm" in the green section of the soil report we measure nutrients available to the plants, not total nutrients.[G] Available nutrients are determined by using specific extracting solutions for each family of nutrients to mimic plant removal from the soil.

[G] Total nutrients can be determined but generally this isn't helpful for agriculture and is a little more expensive as we have to digest the material first.

Available Nitrate-N

Why Nitrate-N? Measuring nitrate is the best way to determine how much available nitrogen is in your soil.[H] Why do we care so much about nitrogen? Nitrogen is a primary macronutrient.[I] Nitrogen is also a mobile nutrient, meaning that with over application it can leach from the soil into surrounding waters.[J] (States have added laws concerning nutrient pollution and it is becoming important to understand mobility).

We analyze available Nitrate-N with the industry standard method.[K] Upon request, we can also test "Organic-N" via kjeldahl digestion for a small added fee.[D]

Plants need nitrogen for cell components, proteins, and DNA among other things. Plant life as we know it wouldn't exist without nitrogen.

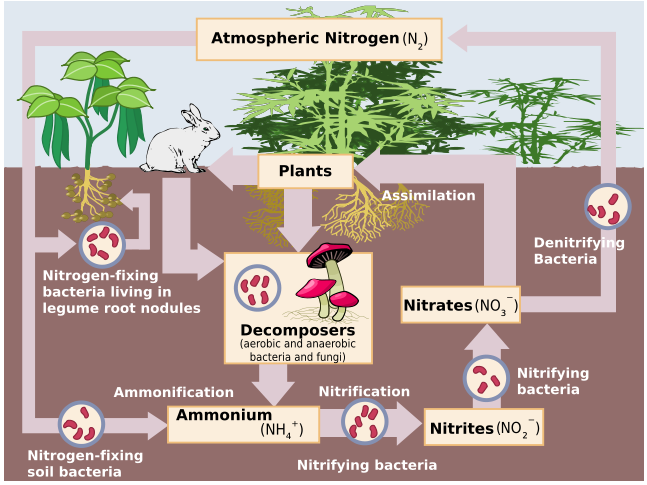

FIGURE 5. NITROGEN CYCLE BY JOHANN DRÉO. CREATIVE COMMONS CC-BY-SA 3.0.

[H] A common question is "how do I convert from Nitrate-N to plain old nitrate (NO_3^-)?" The answer is: multiply your Nitrate-N by 4.43 to get Nitrate-Nitrate. There are other forms of nitrogen that could be present (ammonia, bound organic-N) but they are usually smaller than Nitrate-N because they are slowly generated by soil bacteria (Figure 4). We can test for soil ammonia or "Organic-N" (total hydrolyzable N via TKN, MSA 32-2.2.4[8]) for a small added fee. Plants can readily utilize nitrate and ammonia forms of nitrogen but other forms need to be mineralized or converted to nitrate by bacteria and decomposers.

[I] Plants need macronutrients in larger amounts for optimal growth when compared with micronutrients. (Plants won't grow without macronutrients). The list of macronutrients includes C,H,O (structural); N, P, K (primary nutrients); Ca, Mg, S (secondary nutrients). Micronutrients are trace elements used sparingly by most plants and include: Fe, B, Cu, Cl, Mn, Mo, Zn, Co, and Ni.[17]

[J] Nutrient mobility depends on a number of factors including soil moisture and CEC (cation exchange capacity) but general patterns emerge… Some nutrients are considered to be completely immobile, these include: P, Mg, NH_4^+, Cu, Fe, and Zn. Some nutrients are considered to be partially or slightly mobile: K, Ca, Mo, Co, and Ni. Finally, some nutrients are simply "mobile" including: NO_3, B, S, Mn, and Cl^-.[17]

[K] We extract the soil in 2M KCl solution, 5 grams nitrogen is weighed out and 25 ml of extracting solution is added and shaken for half an hour (method WSMM S-3.10).[7] We use the colorimetric method with copperized cadmium reduction (MSA 33-8.3, WSMM S-3.10).[7,8] Extraction solutions are considered stable for 24 hours. Samples are run on an autosampler which utilizes a 5-point calibration curve.

Legumes have developed root nodules containing symbiotic rhizobia bacteria (Figure 5) which help fix atmospheric nitrogen (N_2) and reduce required fertilizer. With deficient nitrogen crops exhibit specific symptoms (i.e. corn will yellow at the center of the leaf along the vein). Each crop also exhibits specific symptoms of nitrogen excess (i.e. corn will have extremely dark green leaves and grow so quickly that the stem cannot support the ears… an effect called "lodging"). Be sure to avoid the first number (N-P-K)[18] when buying fertilizer if you already have too much N.

Available Phosphorus (P)

Phosphorus is a primary macronutrient found in every living cell.[12] It is required for cellular respiration and metabolism of starch, protein, and fat. Available[L] phosphorus is present as phosphates (PO_4^{3-}) of differing forms.[M] Due to the solubility problems of many of these forms, organic-bound phosphorus can be especially important.

Organic-bound phosphorus is decomposed by soil microbes and once decomposed becomes plant available as unbound phosphates or hydrogen phosphates.[N] The importance of organic

FIGURE 6. GRAPE LEAF PURPLING DUE TO INSUFFICIENT P. ORIGINAL PHOTO BY KAREN. CREATIVE COMMONS CC-BY-2.0.

[L] The concentration of total phosphorus in soil varies from about 0.02 to 0.4% but most of this is not available to the plant.[12]

[M] These differing forms include: i) Complexes with calcium and magnesium; ii) organic combinations like phytic acid (present in the organic matter fraction); iii) adsorbed ions on the surface of clay particles; and iv) compounds with iron and aluminum.[12] Phosphorus availability depends on the solubility of the four types of phosphate complexes. Figure 2, from the pH section above, attempts to provide a simple diagram of P availability vs. pH… but it is a bit oversimplified. Each of the four complexes above has its own solubility. Iron and Aluminum complexes are not plant-available and become important below pH 5. Starting around pH 6.3 and extending to about pH 7.6 phosphates can be found ionically bound (plant available) to clay particles. Extending into the alkaline range starting at about pH 7 calcium phosphates (or similar forms) predominate. Aeration has been cited to increase availability (or reduce reversion to insoluble forms) due to carbon dioxide.[12]

[N] Fuller and Dean grew wheat and soybeans with radiolabeled phosphorus, then tilled them into the soil and grew ryegrass. As much as half of the phosphorus in the ryegrass came from the organic remnants of the wheat and soybeans.[12,19] The organic-bound phosphorus even did well against superphosphate applied in equal amounts (the organic-bound species was determined to be about 70% as effective as fertilizer).[12,19]

matter for phosphorus should not be underestimated at any soil pH. (We can test for organic-bound phosphorus for an added fee,[O] our available P doesn't include it).

We test for available phosphorus using the "Olsen Bicarbonate" procedure[20] (MSA 2nd 24-5.4[8], also see WSMM[7]).[P] This requires a 1:20 extraction in 0.5 molar $NaHCO_3$ solution at pH 8.5 (skake time 30 min).[20] We read the phosphate complexes absorbance at 880 nm.[Q] We have a full soil laboratory and can also run many other phosphorus methods (i.e. Bray) for a small fee.

Adding phosphorus can hasten maturity and deepen roots of almost every crop grown in low phosphorus soil. Even in soil that tests sufficient for P many farmers apply about 20 lbs/acre "starter P" to develop a good root on the crop. Different crops (especially those grown in low-P soil) respond well to banding application[21] of phosphorus.

Phosphorus assimilation is tied to soil fungi[R] and magnesium, but most irrigated soils have plenty of magnesium. If plant tissue appears deficient in P (Figure 6) but your soil has plenty of P, request a soil Mg test.[S] Symptoms of P deficiency include: i) dark green leaves which bronze and then turn purple or develop dark brown spots; ii) small, spindly plants that seem brittle or fragile; and iii) delayed maturity, sometimes with shriveled seeds.[12] Conversely, to remediate soil which has excessive P, plant beans, cowpeas, or some other legume as a cover crop and use it as green manure. Be sure to avoid the middle number (N-P-K)[18] when buying fertilizer if you already have too much P.

[O] Our procedure to test for organic-bound phosphorus comes from Methods of Soil Analysis (MSA 2nd 24-3.3) and requires a comparison of 1N H_2SO_4 extractions before and after heating to 550°C.

[P] Olsen postulated that the best phosphate extraction solution for high calcium soils (like those in CO, WY, NE, and other states west of the Mississippi) would require displacing the phosphate on the soil colloid with HCO_3^- or CO_3^{2-} while diminishing the activity of calcium. Olsen designed his method on western soils in northern Colorado (specifically around Fort Collins).

[Q] This is a pH dependent color development (the familiar ammonium molybdate /antimony potassium tartrate method reduced in ascorbic acid). We monitor absorbance at 880 nm and plot samples against a 5 point calibration curve.

[R] Up to 90% of plant species exhibit Mycorrhizae or "fungus root" where Mycorrhizal fungi grow symbiotically with plant root systems.[22] Some types penetrate root cells while others do not but in both types plant absorption of phosphorus (P) and zinc (Zn) generally increases. Some plants have also shown increased production of plant growth hormones such as cytokinins and gibberellins.[22]

[S] Magnesium deficiency can also show as white or light stripes down the leaves.

Available Potassium (K)

Potassium (K) is a *slightly mobile* primary macronutrient important for plant leaves, stems, and roots. In leaves, K is utilized in opening and closing of stoma, and adding K can thus increase the efficiency of CO_2 assimilation during photosynthesis.[12] In stems, it helps maintain osmotic balance and keep the plant cells turgid. In roots, it increases growth and improves drought resistance.[23] Potassium enhances translocation of sugar and starch and helps plants produce grain high in starch.[23] If phosphorus is found in excess, having enough available[T] potassium can help prevent a rapid, unhealthy rate of maturity that could lead to lodging.[12]

We extract available potassium (K) with the industry standard 1.0 molar ammonium acetate adjusted to pH 7.0 with ammonium hydroxide or acetic acid. We extract K at a 1:5 ratio, shaking it for 5 minutes. We analyze K quantitatively with a flame atomic emission spectrophotometer in an air-acetylene flame. This procedure is from Methods of Soil Analysis (extraction MSA 13-3.5.2[8] 1:5, analysis MSA 13-3.3.3[8]).

FIGURE 7, POTASSIUM DEFICIENT TOMATO LEAF. BY GOLDLOCKI. CREATIVE COMMONS CC-BY-SA 3.0.

Our fertilizer recommendations default to "broadcast" application, "banding" application can reduce the total potash (K_2O) required but placement of the band is critical to not inhibit seedling emergence.

In many plants potassium deficiency is typically shown by yellowing and drying (or "firing") around the edges of the older, lower leaves (Figure 7, by Goldlacki[24]).[12] In alfalfa whitish spots begin to appear when potassium is deficient.[25] Excess K can hinder Ca, and especially Mg absorption by the plants. If this happens in cool season grasses that ruminants are grazing on, "grass tetany" or "milk fever" can result. If you already have excess K, avoid fertilizer with the third number in the N-P-K fertilizer system.[18]

[T] Total potassium in soil can exceed 2%, most of this is tied up in mineral silicates that are not plant-available. Some types of clay (e.g. Illite clays) trap potassium in layers that aren't plant available even when wet.[23] (Most clay will release K once wet so Illite is an exception, not the rule). The common index for K is "available potassium" which is the sum of water-soluble K and NH_4OAc exchangeable K. We can provide the water-soluble K number for an added fee.

Available Calcium (Ca)

Calcium rarely limits plant growth because there is so much of it in the soil. Colorado soils typically contain more than 3000 ppm available Ca. In fact, we don't even provide calcium fertilizer recommendations for most crops grown in Colorado. Calcium is however still important for all plants. Legumes and tomatoes can contain a lot (more than 2%) of calcium in their foliage, whereas grasses and cereals typically contain 0.2% to 0.5%.[26]

What is the function of calcium? Calcium is an integral part of plant cell walls where it plays an important role, linking acidic pectin residues within them.[27] Calcium can also bind to phospholipids in the lipid-bilayer of plasma membranes to provide stability.[27] Finally, calcium assists plants with ion transport and protects against other ions (e.g. Cu^{2+}) which may be present in toxic amounts.[26]

Available calcium (Ca) is extracted in pH 7.0, 1.0 M ammonium acetate, similar to potassium. It is extracted at a 1:5 ratio by shaking for 5 minutes. Ca is quantitated with a flame atomic emission spectrophotometer. This procedure is from Methods of Soil Analysis (MSA 14-3.3, 14-4).[8]

Calcium uptake is passive and happens in the xylem (root to shoot). Some people believe that there is a perfect Ca/Mg ratio for each crop but research has shown that these margins can vary quite a bit (1:2 to at least 1:8 Mg:Ca with no deficiencies) without affecting yield for agronomic crops.[28] Calcium is mobile only in the xylem, not the phloem so deficiencies appear with new growth exclusively. Rates of calcium uptake are related to transpiration. Generally deficiencies appear in acidic soil and the best correction is liming the soil. One common example of deficiency is blossom-end rot in tomatoes (Figure 8)[29]. Deficiency of calcium has also presented with poor root development, leaf necrosis, leaf curling, and fruit cracking.[27]

FIGURE 8, CALCIUM DEFICIENCY IN TOMATO, KNOWN AS "BLOSSOM-END ROT" BY A13EAN. CREATIVE COMMONS CC-BY-SA 3.0.

Excess calcium cannot be washed from the soil because of the strong clay-Ca^{2+} interaction (Ca is the predominant cation on the soil colloid).[28] We have never seen a case of calcium in such high excess that it affects yields (when other nutrients are not lacking and soil pH is not the problem).

Available Sulfate-S (S)

Sulfur is an important mobile secondary macronutrient that is frequently required in amounts similar to phosphorus.[30] Sulfur exists in many different forms including some reduced forms[U] but most of the sulfur in plants is taken up by roots as inorganic sulfate (SO_4^{2-}) using xylem transport processes (transpiration).[30] In the alkaline soils of Colorado, only inorganic sulfate is directly available for plant transpiration.[V] In soils with large amounts of organic matter much of the sulfur can be bound in it. According to the USDA NRCS as each 1% of organic matter[W] in the topsoil decomposes it releases 10 to 20 pounds of nitrogen, 1 to 2 pounds of phosphorus, and 0.4 to 0.8 pounds of sulfur per acre.[32]

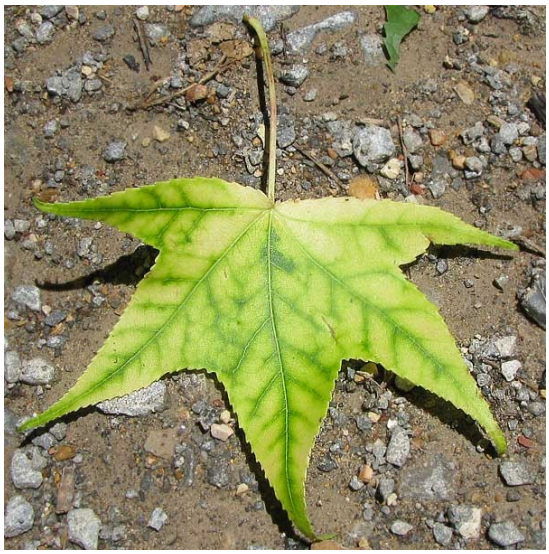

FIGURE 9. SWEETGUM LEAF SHOWING INTERVEINAL CHLOROSIS. BY JIM CONRAD. PUBLIC DOMAIN.

The organic forms[X] of S are particularly important because in humid, semi-humid, and even some semi-arid regions more than 95% of the total sulfur is bound in the organic

[U] The forms of sulfur include inorganic sulfate, sulfide, polysulfide, thiosulfate, tetrathionate, sulfite, elemental sulfur, and organic-bound S.[8] The soil report is listed as Sulfate-S to convert to Sulfate multiply by 3. Atmospheric SO_2 can also be harvested when present, but this process only happens if soil S is insufficient.[30]

[V] Sulfates can adsorb to soil colloid below pH 6.5; this adsorption is greater in soils with aluminum and iron oxides present in large amounts. This adsorbed sulfur is also considered plant-available but is negligible in Colorado. In non-calcareous soil of temperate regions inorganic sulfate generally represents < 5% of the total S.[31]

[W] The USDA NRCS also mentions that soil organic matter (bulk density 1.2 g/cm³) holds 90% of its weight in water making it especially important for no-till and dryland farmers.

[X] How do reduced sulfur forms arise? As an example, soil could be treated with elemental sulfur. When this happens soil microbes first convert much of it to tetrathionate and thiosulfate.[8] The plant still can't utilize these reduced forms of sulfur until it has been oxidized to sulfate. For this reason, oxidizing microbes from the following genera become important: *thiobacillus*, *pseudomona*, and *arthrobacter*.[30] These microbes process the reduced forms of sulfur into sulfate (thus mineralizing the sulfur). Conversely, soil microbes can also convert sulfate into organic-bound sulfur. Soil S can be constantly cycled between organic and inorganic forms.[30]

matter.[8] The fastest and cheapest way to analyze this fraction is to get a "total sulfur" test[Y] and subtract the plant-available sulfate-S from a traditional soil report (this assumes that 100% of all other reduced forms can be treated as "organic-bound S").

The soil report sulfate-S number reports free inorganic, as well as adsorbed forms of sulfur, both generally considered to be plant-available. This plant-available index is only available because we have chosen the correct extracting solution.[Z] Our sulfate-S method is room temperature extraction of 5g soil in 0.01M $Ca(H_2PO_4)_2$ followed by turbidimetric determination at 420nm (MSA 28-5[8], specifically WSMM S-11.10[7]). Considerable seasonal fluctuation of soluble sulfates is expected because of changes in mineralization rates of organic-bound S, uptake by plants, and leaching.[8] The easiest way to counteract seasonal variation is to submit extra samples. If you suspect sulfur deficiency, look for reduced plant growth and chlorosis of younger leaves (Figure 9 by Jim Conrad[33]).[7] This deficiency impairs plant metabolism and begins with interveinal yellowing that gradually spreads over the whole leaf area.[30] Tissue samples can be submitted to confirm visual suspicion. Sulfur toxicity is *extremely* rare. Ward found general depression of growth and fruit production in cucumbers at 480 ppm added sulfate-S.[34] They spotted necrotic spots on leaves. Jordan and Reisenauer believe that sulfate toxicity in arid regions is probably due to limited uptake of calcium in these plants.[35]

Available Boron (B)

Various extraction techniques have been used to determine plant-available[AA] boron in soil. The most common methods are water and hot water extraction. We use the hot water extraction (WSMM S-7.10)[7], curcumin analysis (MSA 25-3)[8].[BB]

[Y] To get at total sulfur you either have to oxidize it to sulfate or reduce it to sulfide. It is generally easier to oxidize it to sulfate. This procedure can be accomplished with sodium carbonate fusion or by dry ashing at 550°C in the presence of sodium carbonate (and sometimes Ag_2O). We prefer this "dry ashing" method (MSA 2nd 28-2.2.3).

[Z] Choosing your Sulfate-S extracting solution is especially important because you want to desorb an adsorbed anion on the soil colloid. The strength of the extracting anion varies with coordination ability according to the series: hydroxyls > phosphates > sulfates = acetates > nitrates = chlorides.[8] The most attractive solution becomes the one of Fox (1964) 0.01M $Ca(H_2PO_4)_2$. If soluble sulfate is required (as opposed to available Sulfate) we can extract in 0.15% $CaCl_2$ (extraction is as-received because drying increases the extracted sulfates by ~20%)[8] for a small fee.

[AA] Total boron is present in the crust of the earth at about 7 to 80 µg/g.[8] It can be analyzed via Na_2CO_3 fusion at 900°C. Diana et al. have used a peroxide digest to determine organic-bound B fractions.[36] Even these fractions are not considered immediately available to plants.

Boron is important to various parts of plants. It is essential for cell walls in particular, symptoms of B deficiency include: i) reduced growth of shoots and roots (apical meristems); ii) brittle leaves and stems due to an inhibition of cell wall synthesis or structural integrity; iii) necrosis of terminal buds; iv) abortion of fruit or flower; and v) inability to regulate pore size of the cell wall (resulting in too-thick and rigid cell walls).[37]

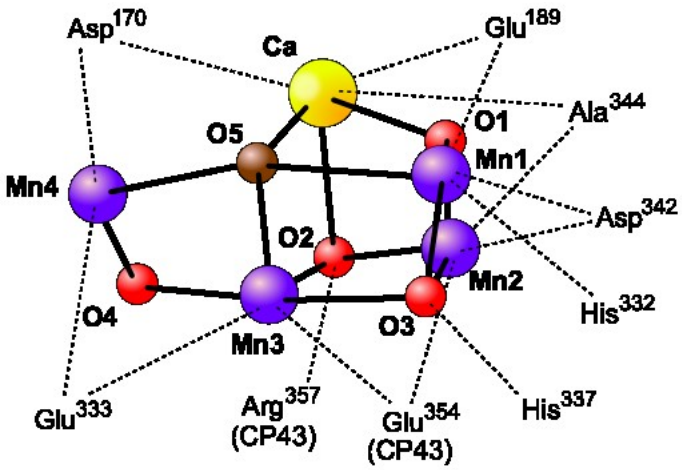

FIGURE 10. MANGANESE CLUSTER IN PHOTOSYSTEM (II). BY YIKRAZUL. CREATIVE COMMONS CC-BY-SA 3.0.

Boron deficiency can also hamper reproductive tissues in plants. In seeds this B deficiency results in poor quality and premature flowering or fruit drop. Seed or fruit yield increases of over 100% have been seen in fruit trees and almonds with added foliar boron.[37] In pollen tubes B helps form cell walls by mobilizing materials from the golgi bodies and endoplasmic reticulum. Pollen tubes grown in deficient boron often burst or develop swollen tube tips.[37]

Boron also plays important roles in: i) general plant metabolism,[CC] ii) nitrogen metabolism,[DD] and iii) the plasma membrane.[EE]

[BB] We determine how much boron is present in the extract colorimetrically with a reaction involving curcumin (MSA 25-3).[8] The process starts with 0.04g circumin and 5g oxalic acid in 100ml of 95% ethanol. We then take a 0.5 ml aliquot of either sample or a standard containing 0.1 to 2 µg B/ml and add 2 ml of this circumin-oxalic acid reagent at bring to dryness slowly at 55-65°C. After drying, 95% ethanol is added and the new rosocyanin complex is carefully dissolved. Absorbance is typically read at 540nm.

[CC] The efficiency of photosystem II (Figure 10 by Yikrazul, based on computational paper by Knapp et al.)[38,39] is reduced in conditions of deficient B.[37] The ascorbate/glutathione cycle (which detoxifies hydrogen peroxide, a typical waste product of metabolism) seems to exhibit B dependency because ascorbate and glutathione levels are reduced in deficient B (it could therefore play a role in alleviating oxidative stress).[37]

[DD] B is also implicated in nitrogen metabolism; in B deficient soil, plant nitrate (NO_3) levels increase as a consequence of reduced nitrate reductase activity.[37] Brown et al. claim that in some species of peas and soybeans boron levels can reduce nitrogenase activity; some attribute this to the role B plays in protecting nitrogenase from oxygen-related damage.[37]

[EE] Boron also plays a role in the plasma membrane. According to Brown et al. B deficiency has been shown to disrupt or change: i) membrane transport processes; ii) structure and composition of the membrane; and iii) activity of membrane-localized proteins.[37] Transport of B can be both active (in deficient soil) and

Boron is considered a mobile nutrient and fertilization should proceed with the same cautions applied for nitrogen.[17] Crop sensitivity to excess boron varies quite a bit but toxicity can start as low as 0.9 ppm. This toxic excess can sometimes be visually confirmed by signs of mottling of the tips and edges of older leaves.[40] Most farmers that test low for boron (< 0.3 ppm) will apply 1 lb/acre and test for boron 2-3 years later (unless they are growing a something boron intensive like apples).

Available Zinc (Zn)

The total concentration of zinc in soil is 10-300 mg/kg (average 50 mg/kg) depending on the parent rock the soil was weathered from as well as other properties of the soil.[41] Of this only a small percentage is available to plants. About half the soil of the world is considered to be deficient in available zinc.[42] The factors affecting soil availability include: soil texture, microbial activity, soil moisture, soil temperature, other trace elements, and phosphorus.[41] We simulate soil zinc availability by using the industry standard DTPA[FF] extraction (method MSA 19-3.3,[8] WSMM S-6.10).[7] We read zinc using flame atomic absorption using a five point calibration curve.

FIGURE 11. ZINC DEFICIENT CORN IN FOREGROUND. HEALTHY IN BACKGROUND. BY ALANDMANSON. CREATIVE COMMONS CC-BY-SA 4.0.

Zinc is an immobile micronutrient. This is the first micronutrient discussed so it merits further explanation. For a crop like corn, macronutrients like nitrogen (N) are typically taken up in hundreds of pounds per acre (~200 lbs/ac). Micronutrients are required in much smaller amounts; crops almost always take up less than 0.5 lbs of zinc per acre.[44]

Zinc is taken up in the divalent (Zn^{2+}) form. After zinc is transported[GG] from the soil to the plant it is utilized in various enzymes and biological processes.[HH] Zinc deficiency in

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passive (when plenty of soil boron is available). Active transport requires channel proteins which must exist because they are supported by mercuric chloride inhibition studies.[37]

[FF] DTPA = Diethylenetriaminepentaacetic acid. Adjusted to pH 7.3 with hydrochloric acid. The DTPA method was developed by Norvell and Lindsay (1978)[43] on Colorado soils and was chosen because it simultaneously complexed Fe, Mn, Zn, and Cu with decent stability constants.

[GG] Plants have adapted some incredible transport processes for metals. For instance, in deficient conditions graminaceous plants' cells release phytosiderophores to chelate metals which can then be incorporated into

plants reduces i) growth (grain yields more than dry matter),[42] ii) tolerance to stress, and iii) chlorophyll synthesis.[41] In cases of acute zinc deficiency, chlorosis of leaves, stunted growth, and small leaves can be observed.[41] Severe deficiency causes a bilateral yellowing or bleaching along the midrib (chlorosis) in upper (younger regions) of corn (Figure 11).[46]

When high levels (>200 lbs P_2O_5/acre)[47] of phosphorus (P) are available or applied to corn, wheat, soybeans, and other crops on calcareous soil, a Zn deficiency can manifest itself.[48] The full mechanism is not yet understood.[II]

When fertilizing with zinc it is important to note the difference between broadcast and band application (band application can reduce the requirement to ~ 1/5 the broadcast requirement but position of the band is critical). Applying excess zinc can be bad for certain crops (eg. cereal crops)[47] that are sensitive. Plant sensitivity varies, but one study of root and shoot growth for common wheat demonstrates markedly reduced growth at leaf tissue tests above 300 mg/kg.[49]

Available Iron (Fe)

Iron exists in the soil in both the Fe(II) and Fe(III) oxidation states.[JJ] The most important role for iron in plant growth is in oxidation-reduction reactions which occur during cellular respiration.[12] Iron is also required for formation of chlorophyll in leaves.

The behavior of iron in soil is governed by pH and oxidizing or reducing conditions present in the soil.[50] Acidic or reducing soil conditions promote mobilization and solubility of Fe minerals.[50] In the absence of acidic soil conditions… how does the iron reach the

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the plant via specialized transport proteins. For further details please see Sharma et al.[41] and references therein.

[HH] These enzymes and biological processes include carbonic anhydrase, hydrogenase, RNA polymerase,[41] and the synthesis of cytochrome.[45] These enzymes are important for photosynthesis, carbohydrate metabolism, maintaining the integrity of cellular membranes, protein synthesis, genetic transcription, and pollen formation.[45]

[II] Hafeez et al.[45] explain that "four possible causes have been considered responsible: i) a P-Zn interaction in soil reducing uptake, ii) a slower rate of translocation of Zn from root to shoot, iii) simple dilution effect, and iv) metabolic disorder related to the imbalance." (Note that the dominant hypothesis of the 1970's, a $Zn_3(PO_4)_2(s)$ complex, is not considered to be the problem anymore).[45]

[JJ] The total iron present in cultivated soil is typically 20-40 g/kg, most of which is present as crystalline iron oxides or hydroxides (goethite and hematite) which aren't readily plant-available.[50]

plants? One way is waiting for the soil microbes to get it first.[KK] These complexes are important forms of iron storage for both plant acquisition pathways below (even though they are not expressly mentioned).

How is iron acquired by plants? Dicots (and non-graminaceous monocots) use a reduction-based iron uptake mechanism.[LL] In contrast monocots use a chelation strategy.[MM]

Our tests for plant-available iron depend on the DTPA extraction.[NN] We extract our soil in DTPA (MSA 19-3.3[8]) and test according to method WSMM S-6.10[7] (we use 5g soil).

FIGURE 12. CHLOROSIS IN SOYBEANS. BY ALANDMASON. CREATIVE COMMONS CC-BY-SA 4.0.

Iron is one of the most important micronutrients and deficiency is a frequent problem in calcareous soils above pH 7. Plants deficient in iron turn bright yellow in color, a disease called chlorosis (Figure 12 displays typical interveinal chlorosis in soybeans). It is important to know that iron deficiencies are can be present even when plenty of "total iron" is in the soil. Above soil pH 7.8 or 8.0 if there is zone of calcium carbonate[OO] accumulation within 12 inches of the surface iron will probably be deficient.[12] Iron

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[KK] The principal means by which soil microbes obtain iron in deficient soil is through the synthesis and release of iron binding molecules called siderophores.[50] The iron-siderophore complexes are easily transported into the microbe cell through special transport proteins.

[LL] First iron(III) is reduced to iron(II) (by iron chelate reductase) then the iron(II) is brought into the plant across the root cell membrane (by metal transporter proteins).[50] During this process additional protons are released acidifying the rhizosphere and enhancing iron(III) chelate reductase activity. Alfalfa is resistant to iron deficiency because it releases phenolic chelators that enhance the rhizosphere as well.[51]

[MM] Monocots use phytosiderophores which chelate iron (III) and are then brought directly into the plant by specific transport proteins.[50] As monocots; rice, corn, and wheat utilize a chelation strategy in low iron soil.[41] For further information see the excellent review papers by Sharma et al.[41] and Colombo et al.[50]

[NN] Lindsay and Norvell determined that DTPA is the most useful solution for simultaneous determination of Cu, Fe, Mn, and Zn. This solution has been used successfully for Colorado soils since 1978. The extractant is designed to avoid excessive dissolution of $CaCO_3$ with the release of occluded Fe (which is why there is some calcium in the solution).

[OO] Large amounts of bicarbonate can also reduce iron uptake by plants.[12]

deficiencies can also appear if the water table is high or the soil is poorly aerated. Treating iron chlorosis begins with (1) picking resistant crops, (2) trees and shrubs can be sprayed with iron sulfate (1% solution), (3) soil around large trees and shrubs can be injected with iron salts, (4) soil treatment with chelated iron for general crops.[12]

Although rare, excess iron can also be toxic.[8] There is an exchangeable iron test where an ammonium acetate extraction is performed. If the soil is well aerated, and at slightly alkaline pH, the exchangeable iron should little to none.[8] In acidic or water-logged soil there may be lots of exchangeable iron present.[8] This test is not useful on normal Colorado soil (and not part of our normal soil packages) but we can run it for a small fee.

Available Manganese (Mn)

Manganese is a mobile micronutrient. Mn is the twelfth most abundant element in the earth's crust. Total Mn in soil ranges from 20 ppm to over 3000 ppm[8] with an average of 650 ppm.[52] Levels of plant available Mn[PP] also exhibit a wide range.[8] Various plant enzymes[QQ] are activated by Mn and it can affect processes such as plant respiration, disease resistance, nitrogen regulation, amino acid synthesis, hormone levels in the plant, and synthesis of lignin.[52]

We test Mn availability in soil by extracting with DTPA (method MSA 18-3.4[8], 5g sample, analysis follows WSMM S-6.10[7]). Toxicity testing is recommended if your DTPA Mn test is very high (your soil pH is probably < 5.5 where Mn toxicity is common). The extractable Mn test (MSA 18-3.2[8]) is our standard for toxicity testing. The soil is extracted at a 1:5 ratio by shaking on a reciprocal shaker in 1 N ammonium acetate solution.

[PP] Mn has seven stable oxidation states: +1,+2, +3, +4, +5, +6, and +7… but on the surface of the earth only Mn(II), Mn(III) and Mn(IV) are found.[8] Mn(III) rapidly disproportionates in solution which means that Mn(II) and Mn(IV) are the main species of interest (Mn is generally absorbed in its divalent form). By 1931 copper, iron, zinc, manganese, and boron were all determined to be essential for plant growth and the "Golden Age" of plant nutrition began.[52] According to Reisenauer Mn differs from the other micronutrients in that it can accumulate in plants to more than 50x what they need.[52]

[QQ] Mn is required for specific proteins that i) release oxygen from chloroplast in photosystem II (Figure 9); ii) breakdown superoxide radicals in the superoxide dismutase of peroxisomes and mitochondria; and iii) regulate nitrogen in the urea cycle (arginase in mitochondria).[52]

Plants Mn requirements are met at 20-40 mg/kg (tissue concentration) and toxicity is reached at 400-2000 mg/kg (quite a bit of variance between plant species).[52] Deficiency symptoms appear first in the youngest leaves. Where Mn is low, plants will show a breakdown of chlorophyll and leaf tissue between the veins. Iron deficiency gives a bright yellow color but manganese is more yellow-brown (Figure 13).[12] Plants have a number of mechanisms to help harvest Mn from the soil.[RR] The most sensitive crops to Mn deficiency are oats, wheat, soybeans, spinach, sugarbeets, and various fruits.[52] Mn toxicity presents as crinkled leaves and chlorosis[12] in younger plant tissue and dark brown speckles in older plant tissue.[52] Poor drainage (and low soil oxygen) and low soil calcium can contribute to toxicity problems in soil.[52]

FIGURE 13. MN DEFICIENCY IN CABBAGE LEAF. BY ALANDMANSON. CREATIVE COMMONS CC-BY-SA-4.0.

Manganese is often deficient in pH neutral to slightly alkaline soils. Slight deficiency doesn't seem to affect yield of fruits but severe deficiency can cause death of trees and greatly reduced yields in other crops.[12] Foliar sprays and soil treatments are both used.[SS] $MnSO_4$ is by far the most common Mn fertilizer because chelated Mn is displaced[TT] by other cations in soil solution.[52]

[RR] According to Graham and Quirk, in the late nineteenth century Adeny (1894) discovered that microbes could reduce Mn;[52] later Beijerinck (1913) demonstrated that they could also oxidize Mn (Bertrand noted that this oxidation can happen at some distance from the organism, indicating an active diffusible exudate).[52] According to Ghiorse, Mn oxidizing bacteria include *Arthrobacter*, *Bacillus*, *Pseudomonas*, *Hyphomicrobium*, *Corynebacterium*, *Proteus*, *Flavobacterium*, *Enterobacter*, and *Citrobacter*.[52] Mn reducing bacteria include primarily *Bacillus*, but other common soil bacteria (e.g., members of the genera *Pseudomonas*, *Clostridium*, *Micrococcus*, *Arthrobacter*, and *Acinetobacter*) have also been studied.[52]

[SS] Sprays are typically 1 to 5 pounds of $MnSO_4$ per 100 gallons of water. Crops get 50 to 100 lbs per acre, Trees get 200 lbs/ac.[12] MnO, $MnCO_3$, $MnCl_2$, chelated Mn, fritted glass with prescribed Mn release rates, and MnO_2 have been used as sources of Mn in fertilizer.

[TT] Clarkson reported that fertilizing with Mn-EDTA chelates has been shown to provide less Mn than free Mn(II) (studies with radiolabelled ^{14}C found the Mn absorbed 50 times as much as the EDTA suggesting that

Banded application of $MnSO_4$ is more effective than broadcast because the Mn^{2+} isn't exposed to as many reactive sites[uu] in the soil (sites where the Mn is bound in forms which are not exchangeable or quickly oxidized by soil microbes).[52]

Available Copper (Cu)

Copper is a immobile[vv] micronutrient. The average concentration of total copper in the crust of the earth is 68 ppm.[56] The total copper content of soil ranges from 2 to 250 ppm.[57] Most of this total copper is not considered plant-available (in Colorado the average agricultural DTPA-extractable Cu is 1.8 ppm). Copper is important for photosynthetic electron transport, oxidative stress responses, mitochondrial respiration, cell wall metabolism, hormone signaling, nitrogen metabolism, flowering, and it is also needed in various enzymes and proteins.[53,58]

We analyze copper by extracting with DTPA (method MSA 19-3.3[8], 5g sample, analysis follows WSMM S-6.10[7]). The most common soil amendment for deficient soil is copper sulfate.[12]

The average concentration of copper in plant tissue is 10 ppm.[58] Among world agricultural crops: wheat, barley, and oats are the most sensitive to copper deficiency (Jung et al.).[53] It is always wise to get a soil copper test if you are growing these crops or higher demand crops like beets, spinach, tomatoes, small grains, and sunflowers. If your soil pH is over 7.4 it is generally a good idea to get copper tested as well (copper availability decreases

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the chelate is broken down at the cell surface). Clarkson also mentions that translocation of labeled Mn is faster in soil infected with bacteria from the rhizosphere than in sterile soil. He also performed an experiment on iron-starved barley (starved for 17 days) and then tracked xylem uptake of labeled ^{54}Mn and ^{59}Fe, both Mn and Fe flux is increased (in the first few hours) in the stressed plant.[52] Socha and Guerinot report that "the majority of transporters implicated in Mn translocation have broad specificity for several divalent cations including Fe, Zn, Cu, Cd, Ca, Co(cobalt), and Ni(nickel)."[53] Their specific list of gene transporter families involved includes: NRAMP, YSL, ZIP ZRT/IRT1, CAX, CCX, CDF/MTP, P-type ATPases, and the vascular iron transporter.[53]

[uu] According to Reuter et al. the basic idea here is that the Mn is concentrated in a zone where soil conditions retain Mn solubility (acidic pH due to other acidic macronutrients applied in the band like ammonium sulfate, ammonium nitrate, or monocalcium phosphate).[52] Norvell noted that Mn mobility (in acidic soils) increased when chloride salts were applied in the band (probably due to the coupling of the oxidation of chloride to the reduction of Mn-oxides).[52]

[vv] According to Jones and Belling, no leaching of copper occurred after applying 4.4 lbs of copper on sand even during heavy rainfall.[54] Copper availability and extractability decrease over time[54] via an "aging" or fixation process. This process depends on three properties: Occlusion within organic matter, diffusion in soil pores (dominant at low pH), and precipitation/nucleation.[55] At soil pH>6 precipitation ($Cu^{2+} \rightarrow Cu(OH)^{+} + H^{+}$) predominates (although the contribution from organic matter cannot be neglected).[55]

above pH ~7). Copper deficiency is most frequent on very sandy soils or peat/muck soils with very high organic matter.[12] When copper is not present deficiency symptoms appear in younger leaves and reproductive tissues. If your soil DTPA-Cu test is < 0.6 ppm it will likely respond[WW] to copper for wheat and other sensitive crops.[7] Symptoms can look like chlorosis, wilting, drooping (twist or be malformed[58]), and reduced growth.

Plants have adapted methods[XX] of maintaining the proper copper concentration inside and outside of their cells… but occasionally imbalances happen. The properties of copper as a redox-active transition metal essential for plant growth also make it toxic in excess.[58] When copper is in excess, redox cycling between Cu(II) and Cu(I) can catalyze the production of hydroxyl radicals. These hydroxyl radicals can then damage DNA, oxidize lipids, change fatty acid composition of thylakoid membranes, damage proteins, and induce general oxidative stress in the plant.[58] This damage can manifest as necrosis, chlorosis (Figure 14), and inhibited root growth.[58] There are especially high risks for toxicity if copper has been applied as a fungicide (some manures can also be quite high in copper).

FIGURE 14. CHLOROSIS IN RASPBERRY. BY JERZY OPIOLA. CC-BY-SA 4.0.

[WW] Below 10^{-14} molar, deficiency symptoms generally arise in nutrient media.

[XX] Genetics of copper transport have been developing rapidly in the last twenty years. Plants have been shown to up-regulate CTR/COPT Cu-transporter (trans-membrane transporter) gene expression during copper deficiency; the shoots essentially request more copper from roots genetically.[58] Yruela goes on to discuss P-Type ATPases (designed as CPx-ATPase, PAA1, PAA2, HMA1-8), which are utilized in: i) transporting copper to chloroplast; ii) ethylene signaling (signal is typically used for plant-pathogen interaction or abiotic stress); and iii) antioxidant enzyme activity.[58] Note that these P-Type ATPases typically transport Cu(I), where for other metals they transport the divalent species. There is a family of Cu-chaperones (CCH, COX17, CCS), cytosolic metal receptor proteins, that play important roles in homeostasis.[58] There is also a family of N-ramp transporters of divalent metals that are implicated in copper transport.[58] For additional information on copper transport the reader is directed to Yruela's paper[58] and references therein.

Solvent and Method Table

Test	Solvent	Method
pH	1:2 Water	WSMM S-2.10
Salts	1:2 Water	MSA 10-3.3, WSSM S-2.40 (by mass not scoop volume)
Organic Matter	Aqueous	Colorimetric Walkley-Black method (MSA 29-3.5.2) variant specified by Sims and Haby
NO_3-N	2M KCl	Copperized cadmium reduction (MSA 33-8.3, WSMM S-3.10)
P	0.5M $NaHCO_3$	MSA 24-5.4 (Olsen Bicarbonate)
K	1M $NH_4CH_3CO_2$	Extraction MSA 13-3.5.2 1:5, Analysis MSA 13-3.3.3 Alternatively, WSMM S-5.10 (we use 5g sample)
Ca	1M $NH_4CH_3CO_2$	MSA 14-3.3, 14-4 or WSMM S-5.10 (we use 5g sample)
S	0.08M $Ca(H_2PO_4)_2$	WSSM S-11.10
B	Hot Water (0.02 M $CaCl_2$)	Hot water extraction WSSM S-7.10, Curcumin analysis MSA 25-3
Zn	DTPA solution	WSMM S-6.10
Fe	DTPA solution	WSMM S-6.10
Mn	DTPA solution	WSMM S-6.10
Cu	DTPA solution	WSMM S-6.10

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