



Cation Exchange: A Review

In almost all agricultural soils the surface charge is negative, meaning that they will retain positively charged ions (cations). The negatively charged soil will hold enough positively charged ions to balance the negative charge—called the cation exchange capacity (CEC). A soil with a larger negative charge can retain more positively charged ions and has a greater CEC.

Where does CEC comes from?

The cation exchange capacity is primarily determined by four soil properties:

- **Clay content (soil texture).** Since clays are usually the site of most of the cation exchange, the presence of more clay will result in a higher CEC than the same soil with less clay.
- **The type of clay (mineralogy).** The chemical conditions that were present when the clay was crystallizing determine the amount of negative charge locked in crystals (called isomorphous substitution). This negative charge is a part of the clay and does not readily change.

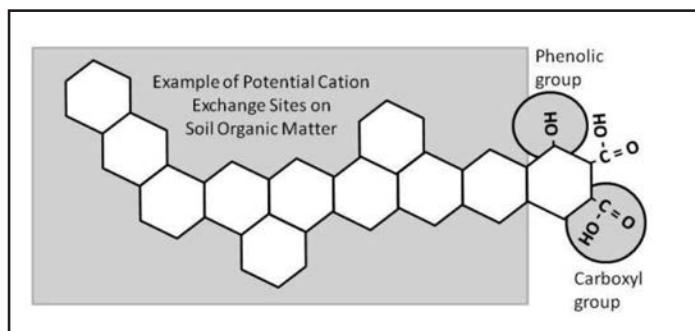


Figure 1. Up to 90% of the negative charge of humus is due to organic carboxylic and phenolic functional groups.

- **Soil organic matter.** There is no permanent charge locked in organic matter, but its CEC depends on the surrounding chemical conditions. As the soil pH increases, the hydrogen cations are stripped from the organic matter (OM) and leave a negative charge that will retain a soil cation. As the pH increases, the CEC of organic matter increases; called pH-dependent charge. (Figure 1).
- **Soil pH.** The CEC provided by organic matter is entirely determined by the soil pH. As the soil becomes more acidic, organic matter loses its ability to retain cations. (Figure 2).

Clay also has a pH-dependent charge. For some clays such as kaolinite, 50% or more the CEC can be pH dependent, while for other clays, such as montmorillonite or vermiculite, less than 10% of the CEC is affected by soil pH.

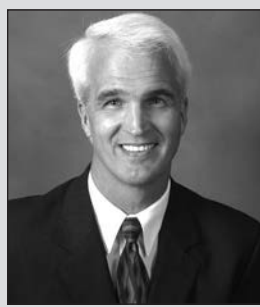
The CEC of a soil is measured in how many positively charged ions (centimoles of charge, cmol_c) will be held in a kilogram of soil. For example, if a soil contains 20 cmol_c/kg soil, it can retain 20 cmol of H^+ and exchange it with 20 cmol of another single-charged cation such as K^+ or Na^+ . This same soil can retain half as many atoms (10 cmol) of a double-charged cation such as Ca^{2+} or Mg^{2+} (20 cmol of charge). This soil can only retain 20 cmol of charged cations, regardless of what single or combination of cations might be present.

The kind and amount of clay minerals and OM influence the CEC of a soil. Most soils have a CEC between 5 and 40 cmol_c/kg , however, some can be as low as 2 cmol_c/kg or as high as 100 cmol_c/kg (Table 1).

Table 1. Range of cation exchange capacity in typical agricultural soils.

	Soil Textural Class	CEC (cmol_c/kg)
CEC is higher in soils with:	Sands (light color)	2 - 4
	Sands (dark color)	8 - 16
	Loams	10 - 15
	Silt Loams	15 - 25
	Clay & Clay Loams	20 - 50
	Organic Soils	50 - 100

Abbreviations and notes: K = potassium; Ca = calcium; Mg = magnesium; Na = sodium; H = hydrogen; Al = aluminum; Cu = copper; Fe = iron; Mn = manganese; Ni = nickel; Zn = zinc; NH_4 = ammonium



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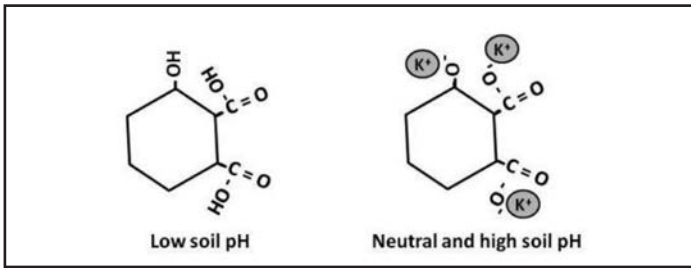


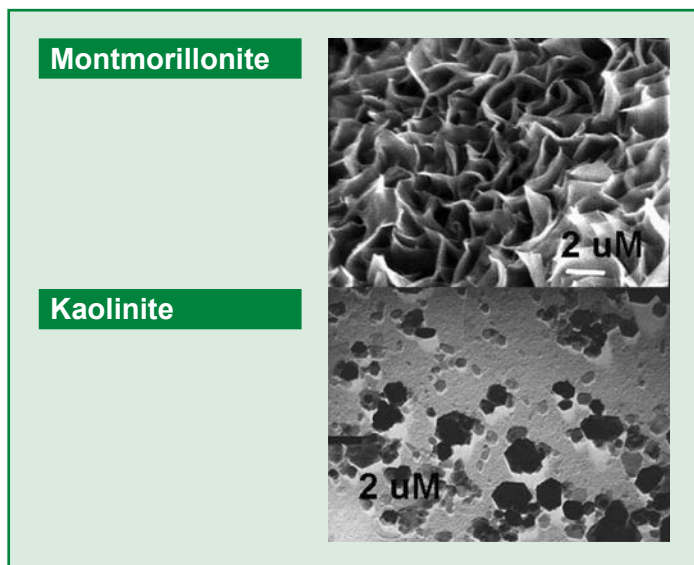
Figure 2. Some of the H⁺ ions are neutralized as the pH rises, increasing the negative charge of these organic molecules.

To understand how cation exchange works, it is helpful to understand the internal and external surfaces of clay particles. The internal layers consist of two planes of atoms on both sides of the interlayer space at the base of each tetrahedral sheet. The external surfaces are simply the outside edges of the clay. Both the internal and external surfaces generally have a negative charge and retain cations. The total surface area of different clays has a large impact on the CEC (**Figure 3**).

Of the cations held on exchange sites, only a small percentage will be dissolved in the soil water at any given time and be immediately available for plant uptake. The remaining cations held on exchange sites provide a valuable reservoir of nutrients that will be slowly released into soil solution as nutrients are acquired by plants or are leached from the soil with rainfall or excess irrigation.

Measuring the CEC of a soil is a good indicator of the nutrient holding and buffer capacity of the soil, but is not by itself sufficient for managing soil nutrients. However, knowing both the amount and chemical composition of the cations is very useful for managing soil nutrients.

Base saturation is used to describe the proportion of so-called basic cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) that are held



Electron micrographs of two clay minerals showing the difference in surface area among clay types. **Source:** Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University.

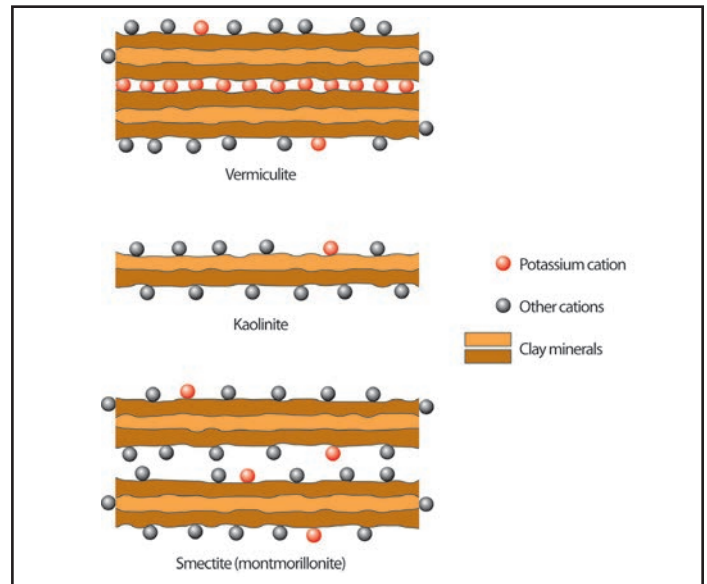


Figure 3. Cations are retained by negatively charged sites in internal sites and on the clay edges. Vermiculite clay can retain K in the interlayer with especially strong affinity (K fixation).

on the cation exchange sites. In acid soils, H⁺ and Al³⁺ become more prevalent. Other micronutrient cations (such as Mn²⁺, Zn²⁺, Cu²⁺, Fe²⁺, Fe³⁺, Ni²⁺, Co²⁺) are also found on cation exchange sites, but they only account for a very small percent of the total exchangeable cations.

Is there an ideal ratio of these cations?

There is no single ideal ratio of these cations in *all* soils. This theory of an “ideal cation proportion” was first introduced in the 1930s and 1940s. The proposed ratios were 65% Ca, 10% Mg, 5% K, and 20% H. The concept, frequently referred to as the “base cation saturation ratio” (BCSR), has been repeatedly examined for over 60 years in greenhouse, field, and laboratory research, and has consistently reported to be unfounded. Plants grown with these specific cation ratios would not have any cation nutrition problems, but there is no evidence that they will grow better or have superior cation nutrition than plants fertilized according to traditional soil testing recommendations.

While an adequate cation supply is essential for plants, there is no one ratio that must be forced in all situations (as evidenced by the productive agriculture that occurs under very diverse global soil conditions) as long as certain minimum requirements are met. Trying to achieve a single “ideal” ratio under all circumstances is unnecessary for plant growth and frequently very expensive to reach and maintain. Consider the problem posed in calcareous soils where soil Ca levels are high, but Mg and K levels are more than sufficient as well. With the BSCR approach, additional Mg and K are generally recommended to counterbalance the abundant Ca, but no crop responses are observed.

The BSCR concept has been applied in hydroponic production, but even there the *concentrations* of the cations are also important, not just their ratio. Additionally, nutrient requirements change as the plant develops and different

crops have different nutrient ratios in their vegetative and reproductive parts. Soils are commonly sampled in the 0 to 6 inch depth, while roots extend far below this depth—so where should the BCSR be measured? The notion of maintaining some H⁺ on the exchange sites was popular in the 1940s, especially in the acid soils where this concept was developed. We now understand that measurement of exchangeable H⁺ is largely a result of lab procedures and that it does not occur on most soil exchange sites, particularly in common Western soils! The BCSR system may be most useful for identifying extreme cation ratios that need special attention and correction.

Measuring Cation Exchange Capacity

Direct measurement of CEC in the laboratory is relatively expensive, so many soil testing labs estimate the total CEC instead. These estimates are made by measuring and summing the extractable basic cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) and estimating H⁺ and Al³⁺ from soil and buffer pH measurements. These estimates are generally adequate for making management decisions. If gypsum has recently been applied or an acidic extractant is used for a high pH soil that contains limestone, then erroneous measurement of exchangeable Ca²⁺ will result.

Another common technique for estimating CEC involves first saturating all the exchange sites with NH₄⁺ and then replacing the NH₄⁺ with Ca²⁺. The amount of displaced NH₄⁺ is then measured, and the CEC calculated. The CEC is also estimated by some laboratories based on the soil texture, which provides a reasonable estimate as long as the clay content and mineralogy are known.

The results from analysis of exchangeable cations are sometimes converted to units of “pounds of nutrients per acre”. This is done by accounting for the charge on the cation, the atomic weight, and using an average of 2 million pounds in the soil surface of an acre to a depth of 6 2/3 inches (**Table 2**). This information gives an estimate of the pounds of available cations, but still needs to be calibrated to crop response before it is meaningful. It reflects the quantity of exchangeable cations, not the total quantity present in the soil.

Cation exchange in soils is a familiar concept that we too often overlook. It is a fundamental soil property that allows us to manage cations in a way that promotes healthy crop growth and sustainable use of plant nutrients.

Table 2. Exchangeable cations can be converted to pounds per acre as an estimate of the total quantity of potentially available nutrients in the surface soil.

cmol _c /kg	(Equivalent weight x 20) = pounds/A*
Ca	x 400
Mg	x 243
K	x 782

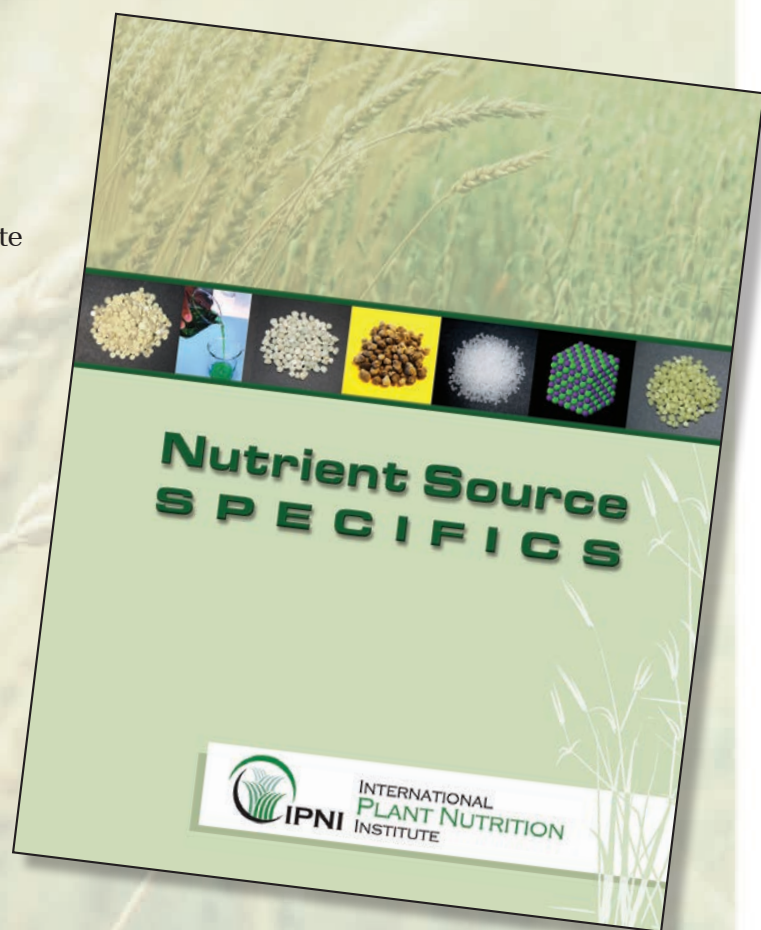
*Based on assumption of 2 million pounds of soil in the 0 to 6 2/3 inch depth in one acre)

Example: 5 cmol_c K⁺/kg would convert to 3,910 lb/A of exchangeable K⁺. This does not mean that the soil contains only 3,910 lbs of K⁺, but provides an indication of potentially exchangeable nutrient. The specific number does not give a recommendation for nutrient management until it has been calibrated with crop response.

Nutrient Source Specifics

is a series of brief, condensed, one-page fact sheets highlighting common commercial fertilizers and nutrient sources in modern agriculture. They are available as PDF files at this URL: >www.ipni.net/specifics<

1. Urea
2. Polyphosphate
3. Potassium Chloride
4. Compound Fertilizer
5. Potassium Sulfate
6. Potassium Magnesium Sulfate: Langbeinite
7. Urea-Ammonium Nitrate
8. Thiosulfate
9. Monoammonium Phosphate
10. Ammonia
11. Potassium Nitrate
12. Ammonium Sulfate
13. Sulfur
14. Triple Superphosphate
15. Nitrophosphate
16. Gypsum
17. Diammonium Phosphate
18. Calcium Carbonate (Limestone)
19. Phosphate Rock
20. Coated Fertilizer
21. Single Superphosphate
22. Ammonium Nitrate





November 2011

Nutrient Management after Drought

The southern and central Great Plains have been severely affected by drought in 2011. The states of Texas, New Mexico, Oklahoma, and parts of Kansas have seen extreme, and in some cases, record breaking drought conditions (see drought monitor map below—found at <http://droughtmonitor.unl.edu/>). In some areas crops have failed altogether, while in other areas crops will be harvested with yields that are substantially lower than average. This article covers some fundamental nutrient management considerations following drought.

Where crops failed in 2011 due to drought, farmers are asking questions on the best ways to handle their nutrient management programs for 2012. In most cases, the vast majority of the fertilizer that was applied to unharvested, failed crops should still be there in 2012—either in the soil or in the crop residue. However, farmers will need to do some soil testing to know more about the nutrient status of fields with failed corn and other crops. Farmers will also want to have some idea of the amount of nutrients present in the residue remaining in the field, and how quickly those nutrients will become available to crops.

There are a number of potential sources of nutrients other than applied fertilizers that could contribute to wheat, corn, sorghum, or soybean crops in 2012. These include:

1. Nitrate (NO_3^- -N), sulfate (SO_4^{2-} -S), and chloride (Cl⁻) in the soil profile
2. Phosphorus (P), potassium (K), and zinc (Zn) in the surface soil layer
3. Nutrients contained in crop residues

The first category consists of **mobile nutrients**, while the second category consists of **immobile nutrients**. The difference is important. Mobile nutrients are able to dissolve in soil water and can move through the soil with water,

while immobile nutrients generally stay where applied. Of the 14 essential mineral elements, the common mobile nutrients we apply as fertilizer are N, S, and Cl, and the common immobile nutrients we apply as fertilizer are P, K, and Zn.

Mobile nutrients in the soil after a failed crop

A very large portion of those mobile nutrients that were not taken up by the 2011 corn and/or wheat crops are likely still present in the top foot or two of soil. With the low rainfall in most of the southern and central Great Plains, very little of the N will have been lost. The K-State Soil Testing Lab, is already seeing higher-than-normal soil test levels for N, reflecting an accumulation of unused nitrate-N in the soil profile. Any unused S or Cl would also be present in that top foot or two of the soil profile. Most is still in the top few inches and will remain there until we receive some soaking rains.

So the first tool a farmer should think about when planning his 2012 fertilizer program is a deep profile soil test for N, S, and Cl.

Immobile nutrients in the soil after a failed crop

What about P, K, or Zn? Where these nutrients were applied to the 2011 crop, will they still be available for crops in 2012? When immobile nutrients such as P, K, and Zn are applied to the soil, they interact with different portions of the soil and are retained. Note the word “*retained*,” not “*fixed*.”

Phosphorus reacts with the clay surfaces and the iron and aluminum coatings found on soil particles and is **sorbed** to those surfaces. Sorption reactions occur in stages, and the initial stages are highly reversible. Sorbed P can be desorbed and dissolved into soil solution, replacing the P taken up by plants. This is a buffering system which maintains a small but constant quantity of available P that supplies what is required for good crop growth. This is how



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we store P in the soil and build soil test values, with little worry about P being lost. Sorbed P is the primary P fraction in soils measured by a soil test. But the soil test only reflects a fraction of the total P present in the soil. For example, most Kansas soils have an 18:1 buffer factor. If we add 18 pounds of P_2O_5 and it reacts with the soil, becoming sorbed to the clays and other minerals present, the soil test will increase 1 ppm. If we remove 18 pounds P_2O_5 through crop uptake, the soil test value will drop 1 ppm.

So how does this relate to planning for 2012? Any P applied in 2010 or 2011 for this year's crop that was not taken up was sorbed onto clays and other minerals. This creates a new equilibrium in the soil, and will increase the soil test values for P. The higher soil test values will result in a lower P fertilizer recommendation.

Potassium is a charged cation (K^+) which is attracted to, and retained on, the soil's cation exchange capacity (CEC). Like sorbed P, exchangeable K maintains a constant supply of K in the soil solution to support plant growth. Also like P, this exchangeable K can be measured by a soil test, and it is a highly buffered system. With K, every 4 to 8 pounds K_2O added will increase the soil test by 1 ppm, and every 4 to 8 pounds removed will lower the soil test by 1 ppm. The buffer factor is a function of CEC and soil minerals present. On low-CEC sandy soils this factor is closer to 4, while on high-CEC silty clay loams the value will be closer to 8. Any K applied and not taken up by the 2011 crop would have been retained on the CEC in the surface soil and remains available for 2012. And, the higher K soil test values will result in lower K fertilizer recommendations for 2012.

With Zn, a third mechanism called chelation occurs, which retains applied Zn. Soil organic matter is a strong natural chelating agent, much like some of the synthetic compounds used as fertilizer sources. Zinc sulfate added to soil slowly dissolves. A portion reacts with the organic matter and is retained in soluble, natural organic matter chelates. In fact, the vast majority of the Zn that moves to plant roots for uptake is present as a natural soil organic matter chelate. Again, this can be measured by a soil test, and there is a common buffer factor of about 10:1 with our DTPA soil test. If we add 1 pound of Zn, the DTPA soil test value will increase by about 0.1 ppm.

Testing for soil nutrients

The bottom line for soil nutrients is that any N, P, K, S, Zn, and Cl added as fertilizer and not taken up by crops is still likely there, and can be measured by soil tests. The mobile nutrients (N, S and Cl) will need to be measured using a deep profile test, while the immobile nutrients (P, K, and Zn) can be measured using a surface sample.

Measuring nutrient levels on fields after a failed crop

For those planting wheat this fall in these failed crop fields, a profile soil test for N, S,

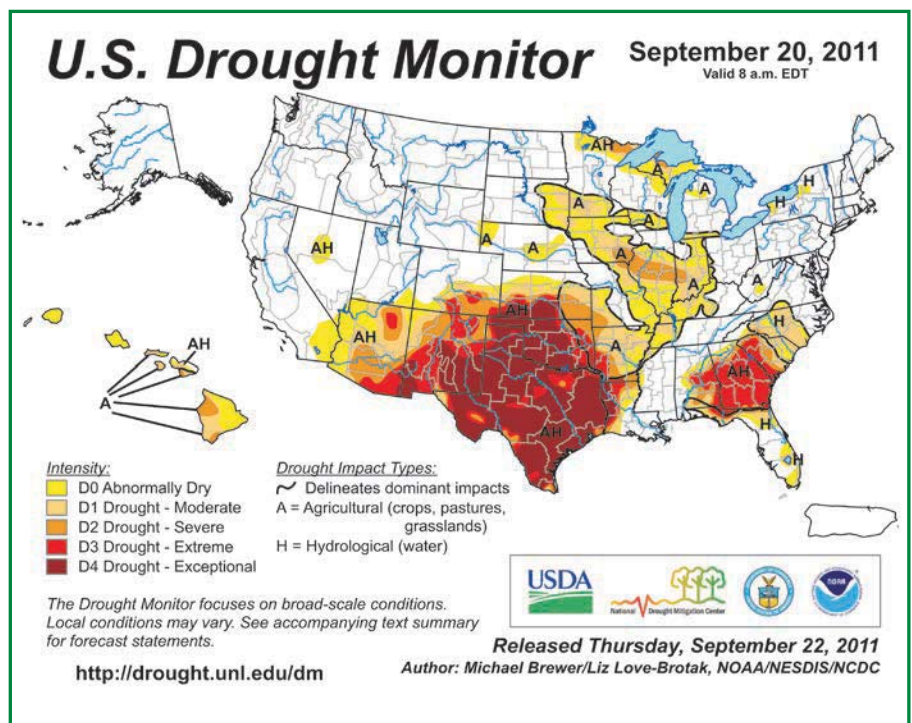
and Cl is a must. Applications of P and K should also be made based on a surface soil sample. For those planting corn or sorghum next spring, it would be best to wait until late winter or early spring to take the profile sample to get a better feel for the amount of the residual N that will be remaining in the soil. Mobile N can be moved below the root zone, especially in sandy soils if we get a wet winter.

Another potentially valuable tool to consider is the use of a crop sensor to help estimate the amount of the N being mineralized from the 2011 crop residues. Kansas has good recommendation systems for both wheat and sorghum to help interpret sensor data. The rate of mineralization will depend greatly on soil moisture and soil temperatures during March through June. A sensor-based N management system can help take some of the risk out of trying to take credit for mineralized N.

Summary

A significant amount of residual nutrients will be present in many fields where this year's crops failed. In severe situations, only a fraction of the nutrients applied were actually taken up by this year's crop. Many of the nutrients remain in the soil and can be measured using soil tests. This is especially true for the mobile nutrients such as N, S, and Cl. But to get a good estimate of the amounts present, a profile soil test to a depth of 24 inches will be required.

Many of the nutrients taken up by this year's crop will also be available, especially the K and Cl, which are not incorporated into organic compounds. However N, P, and S must be mineralized as the vegetation decays. This process will likely be faster than normal, and will increase the availability of these nutrients. But the exact rate of mineralization will depend on the weather, which is difficult to estimate. Crop sensors can help take some of the risk out of crediting these mineralized nutrients. ■





November 2011

Economist and Agronomist Agree... Pay Close Attention to Nitrogen Fertility of Winter Wheat this Season



Role of Nitrogen in Wheat Production

Nitrogen (N) performs many vital functions in the wheat plant. Wheat requires about 2.0 to 2.5 lb of available N per bushel of grain produced. Wheat forage will take up about 40 lb N/ton, assuming 2% N in the tissue. Where wheat is grazed, it takes about 1 lb of N for each 3 lb of animal gain per acre.

Shortages of N may cause reduced tillering, reduction in head size, poor grain fill, and reduced protein content. Adequate N must be available to the wheat plant at all phases of development. Thus a combination of preplant and topdress applications is desirable in many environments. Splitting N

applications generally improves use efficiency, minimizes risk to investment, and safeguards the environment. Topdress applications should be made early, prior to jointing, to maximize production efficiency. Split applications may not always be desirable, particularly in drier environments where there is low probability of N loss from the system. Therefore, all preplant (or all topdress given sufficient soil N at planting) application may be appropriate depending on specific conditions. Ultimately, timing, placement, and N source should be managed to fit the specific climatic conditions, soil type, and tillage system.



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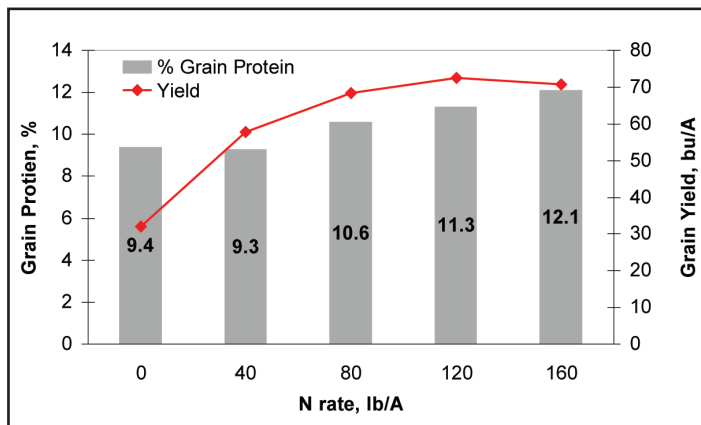


Figure 1. Relationships among N fertilizer rate, HRW wheat yield and protein content in irrigated wheat in western Kansas (*Source: Schlegel and Schafer. 1994. Kansas Fertilizer Research. p. 31-32*). Nitrogen fertilizer was broadcast as urea. Study site was Manto fine sandy loam near Garden City, KS. Data is average of 4 years (1991-1994) and 4 application timings (all fall; all Feekes 3; split fall and Feekes 3; and split fall, Feekes 3 and Feekes 8). Protein level was adjusted using 5.7 conversion from Kjeldahl N.

Among the many indicators of N deficiency in wheat is reduced grain protein content (**Figure 1**). This is of concern because the protein level of grain influences bread making qualities of wheat. As protein content goes up loaf volume increases (**Figure 2**).

Price premiums for protein have routinely been paid for hard red spring (HRS) wheat produced in the northern Great Plains, but this practice has not been so common in the HRW wheat producing areas of the central and southern Great Plains. However, the 2011-2012 wheat production year may be an exception.

Impact of Grain Protein Content on Wheat Price

The Kansas City Board of Trade (KCBT) wheat contract is based on HRW wheat value and the Minneapolis Grain Exchange (MGEX) contract is based on HRS wheat value. The Chicago Board of Trade (CBT) wheat contract is typically based on the value of soft red winter (SRW) wheat which is mostly grown in the eastern part of the U.S. Hard spring wheat has higher protein than HRW wheat, which has higher protein than SRW wheat. Since this article is mainly targeted to a hard wheat audience, SRW wheat will not be further discussed.

At this writing, the KCBT December wheat contract price is \$7.30. The MGEX December wheat contract price is \$9.26. Both HRW and HRS wheat prices are at a premium to corn prices.

In Oklahoma and the Texas Panhandle, cash wheat prices are usually higher than cash corn prices. At this writing, Oklahoma wheat prices are significantly above corn prices, except in the Panhandle. At Hooker, Oklahoma, and Keys, Kansas, the corn price is \$6.72 compared to a wheat price of \$6.66.

In the Texas Panhandle, wheat prices are mostly 10 to 15 cents above corn prices. The wheat bid is for ordinary (11%) protein wheat.

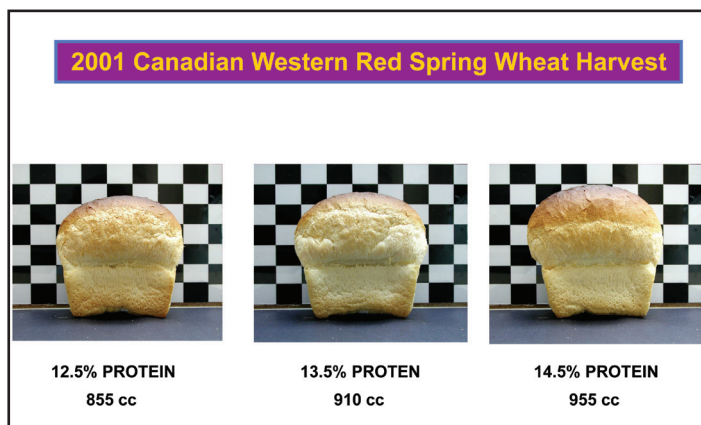


Figure 2. Impact of wheat protein content on loaf size. Higher protein content of wheat fertilized with N results in better quality bread. The lower protein wheat at left produced a more dense loaf of bread...855 cubic centimeters (cc)... while the higher protein wheat enabled the bread dough to rise more. Loaves shown are from 2001 Canadian western spring wheat harvest. *Source: Ken Preston, Grain Research Laboratory, Canadian Grain Commission, Winnipeg, Manitoba.*

The difference between wheat contract prices is most often the value of protein. For the Kansas City HRW wheat market, the basis for 11% protein is about 35 cents. The basis for 12% protein is about \$1.05; for 13% protein, it is \$1.33; and for 14% protein, it is \$1.83.

At the same time in 2010, the Kansas City basis for 11% protein was a minus 35 cents. The basis for 12% protein was 10 cents, and the basis for 13% protein wheat was 30 cents. **The current HRW winter wheat basis (for protein) is about 70 cents higher than in 2010.**

The protein premium is also prevalent in the world market. Australia's 2011 wheat harvest has just begun, and concern exists about the protein content. A report indicated that buyers are paying a \$2 premium for export wheat with 13% protein.

In most markets, 11% or higher HRW wheat protein will not be priced lower than corn and will not be used in the feed market.

Protein basis does not suggest that wheat prices will remain at current levels. World wheat stocks are above average. Protein wheat stocks are relatively tight. Wheat prices, for wheat with less than 11% protein, may decline while wheat prices for wheat with relatively high protein may maintain current levels.

The odds are that the protein premiums will remain into the 2012 U.S. winter wheat harvest. Higher protein levels should result in higher basis and higher local cash prices. Drought conditions are forecast to continue in parts of Texas and Oklahoma. Some of the drought area has sufficient moisture to establish a wheat stand. **Protein should remain an important price component at harvest.**

At the end of the day, where there is potential to make a wheat crop this season both an economist and agronomist agree that this is NOT a good season to skimp on N fertilizer applications. ■