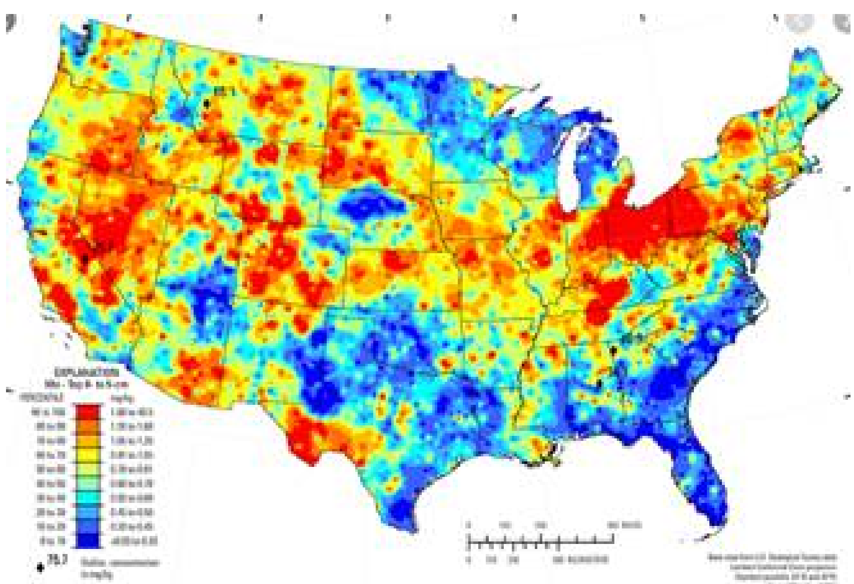
Sodium Molybdate's Agricultural Applications

By Jonathan Goodstein, M.S. Student, Carnegie Mellon, Department of Chemistry, 2020

When you think of elements that are important to plants, you might come up with nitrogen, phosphorus, and potassium (NPK), the three main nutrients critical to plant growth. For decades, agronomists have touted the importance of these elements, with the addition of secondary nutrients calcium, magnesium, and sulfur. However, there are 8 critical micronutrients which all plants absolutely require. Some, like zinc and iron, are relatively abundant in the soil, but the others are less plentiful and therefore overlooked, especially molybdenum. Molybdenum is a particularly important micronutrient for plants, and it's rarely found in sufficient amounts in soil, meaning many plants don't get enough of it.

Molybdenum is not a very common element, but it is required for life in every plant and animal. Being the rarest life-sustaining element means it's hard for animals and plants to get enough Molybdenum without supplements. The naturally occurring deficiency of molybdenum makes it the single most important micronutrient because it acts as the primary limiting factor to growth. The amount of molybdenum will closely determine how slow or fast many processes occur, especially the creation and transformation of some cellular substances. This means that when plants don't have enough molybdenum, biological processes will slow down, limiting both the plant's growth rate and harvest production.



The importance of molybdenum in agriculture shows up in both the soil and the plants themselves. First, molybdenum is important in soil due to bacteria that perform a process called nitrogen fixation. This process takes nitrogen gas from the air (N_2) and converts it to ammonia (NH_3) or ammonium cations (NH_4^+), both of which plants can use. Plants need to pull this fixated nitrogen from the ground because the airborne N_2 is so stable it requires massive amounts of excess energy, (which plants don't have,) to break it down. The bacteria perform nitrogen fixation using an enzyme called molybdenum nitrogenase, which, as the name suggests, contains molybdenum. To give the bacteria enough molybdenum for this enzyme to be at optimal concentrations, upwards of 3ppm molybdate in the soil is generally needed, with cruciforms and legumes requiring higher amounts. Applying sodium molybdate to the soil, not only leverages a plant's ability to uptake more nitrogen and grow faster, it also reduces fertilizer requirements, which further reduces production cost. But this is not the only benefit plants and farmers can get from molybdenum.

All plants have four unique enzymes that require molybdenum, and these enzymes are critical to plant function. Each of these enzymes have many different parts, but they all contain a particularly important chemical known as the molybdenum cofactor. The molybdenum cofactor is the part of the enzyme that contains molybdenum, and it varies slightly depending on which enzyme it is connected to. It is also the reactive site of each enzyme. In each of the four cases, the enzymes cannot form without the presence of the molybdenum cofactor, meaning molybdenum is required in a plant for the enzymes to exist within it. The importance of molybdenum becomes even clearer when the functions of these enzymes are described.

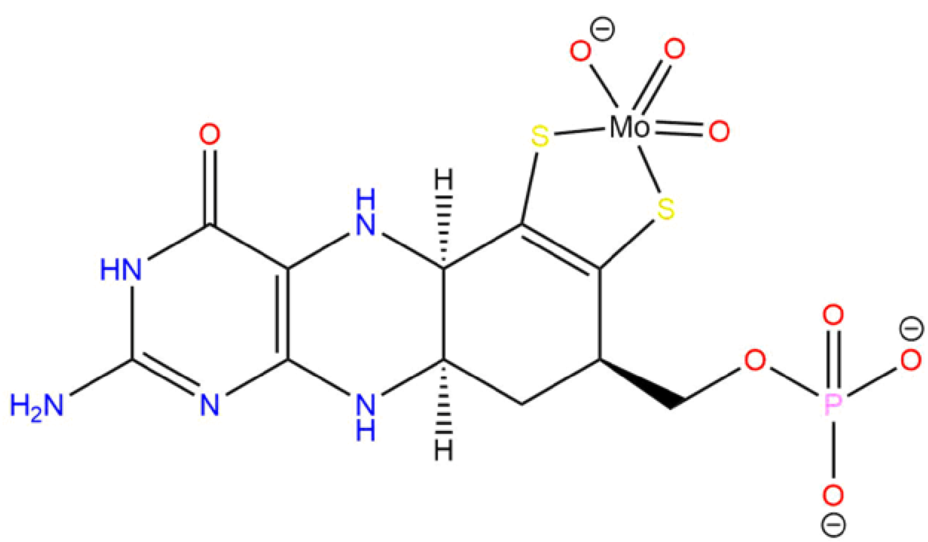


Figure 1: Standard Form of Molybdenum Cofactor

The first key enzyme is called nitrate reductase, and it reduces any nitrates (NO_3^-) in the plant into nitrites (NO_2^-). This is important because most nitrogen in fertilizer is applied as nitrates (ammonium nitrate, for example), but plants are only able to use this after converting it to nitrite. To do this, they employ the nitrate reductase enzyme, which they can't make without sufficient molybdenum present. The concentration of nitrate reductase depends directly on the amount of molybdenum in the plant. Additional molybdenum leads to an increase of this enzyme, which in turn causes faster conversion of nitrates into nitrites. Without the enzyme, nitrate levels get too high and the nitrates react with other chemicals in the plant. This will directly harm or even kill the plant.

The second key enzyme is called sulfite oxidase, and it oxidizes sulfites (SO_3^{2-}), which are toxic to plants, into sulfates (SO_4^{2-}), which are extremely useful. Despite the toxicity, sulfite can get into plants through sulfur dioxide in the atmosphere, which is a common pollutant. However, once they are turned into sulfates, they can allow for development of critical sulfur-containing substances, including protein components like cysteine. Without the molybdenum, there would be an absence of this enzyme, resulting in the toxic sulfites accumulating in the plant and creating significant harm to it.

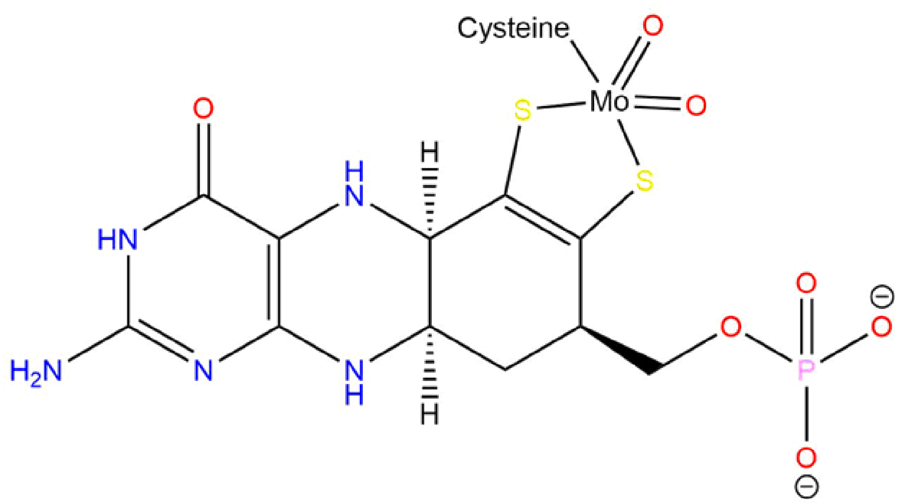


Figure 2: Molybdenum Cofactor Structure for Sulfite Oxidase and Nitrate Reductase

The third critical enzyme is called aldehyde oxidase, and it produces two important hormones called ABA (abscisic acid, $C_{15}H_{20}O_4$) and IAA (indole-3-acetic acid, $C_{10}H_9NO_2$). ABA is a stress response hormone that helps return the plant to a healthier state. IAA is most present in younger plants, as it stimulates growth processes. High IAA concentrations lead to greater leaf area and more sugars to nourish the plant. Without enough molybdenum, there would be restricted ABA or IAA, which causes wilting or plant mortality.

The fourth enzyme, xanthine oxidase, is still relatively mysterious, and the functional activity is being investigated.

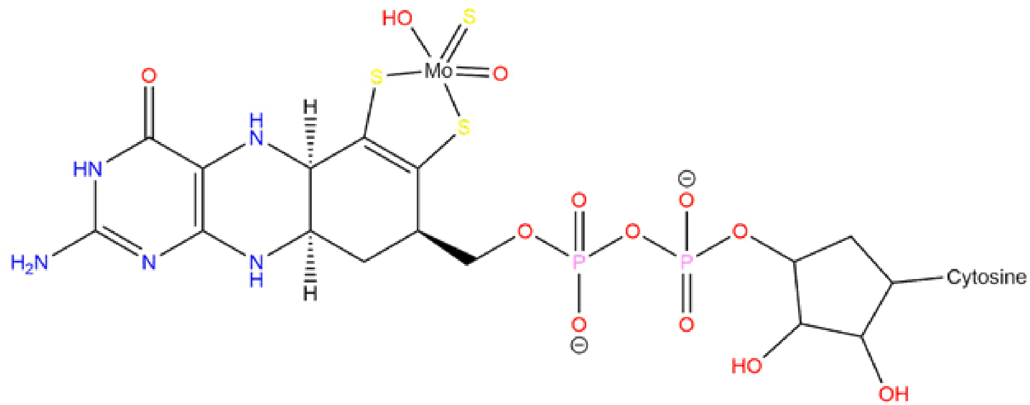


Figure 3: Molybdenum Cofactor Structure for Aldehyde Oxidase and Xanthine Oxidase

There are a vast number of studies, spanning several decades, that show sodium molybdate is a key requirement for plants. While there is general agreement that application of sodium molybdate is helpful for almost all plants, quantifiable benefits have been shown in the following specific crops:

- Legumes (Soy, Peas, Alfalfa, etc.)

- Muskmelon (including honeydew and cantaloupes)
- Wheat
- Barley
- Potatoes
- Mustard
- Corn
- Oats
- Grapes
- Tomatoes
- Berries (Pomegranates, Blueberries, Strawberries, etc.)
- Citrus
- Nuts
- Carrots

- Cruciforms (Broccoli, Cabbage, Kale, Radish, etc.)

Overall, most studies of these plants showed that 3-10 ppm foliar application of sodium molybdate is effective in making plants grow faster and produce more harvest. They also showed that 75 g/ha spray of sodium molybdate on soil is helpful when the soil is deficient in molybdenum. In numerous studies, the molybdenum had more benefits besides faster growth and better production: plants contained more micronutrients and fewer nitrates. Plants also display increased root or tuber size, and improved NPK levels.

Despite being a trace metal, molybdenum is critical for plant function. Many studies show that molybdenum helps plants grow faster, producing a greater harvest, and potentially reducing farming cost by encouraging nutrient production. Without the molybdenum, plants won't make the enzymes they need, which could hurt or kill them. In these applications, liquid solutions of sodium molybdate is the preferred choice when considering molybdenum-containing chemicals to apply.

To provide plants required molybdenum, sodium molybdate is the top choice for many reasons. Molybdate (MoO_4^{2-}) is the main way molybdenum naturally occurs in soil – not dimolybdate ($Mo_2O_7^{2-}$), heptamolybdate ($Mo_7O_{26}^{6-}$), molybdenum sulfide (MoS_2), or molybdenum trioxide (MoO_3). Also, as long as soil pH is greater than 4, Sodium Molybdate will remain in soil quite well. However, higher levels of molybdate will be needed when there are significant amounts of oxides, clay, or limestone in the soil. Another advantage of sodium molybdate is that it can be applied to either foliage or the soil directly, and it can be used as a solid or in solution. Sodium molybdate is extremely water-soluble – in the North Metal & Chemical Co. lab, we have dissolved nearly 2 pounds of it per quart of water, but ammonium dimolybdate is difficult to dissolve in water. In addition, U.S. molybdate manufacturers sell sodium molybdate as a dihydrate solid, an anhydrous solid, and as a solution, providing the options that will best serve your needs.

[ASIDE: NITROGEN FIXATION]

Nitrogen-fixing bacteria convert nitrogen gas from the atmosphere into ammonia, which is much more usable. The key enzyme in this process is called molybdenum nitrogenase, and it uses molybdenum in a very different manner than plants. Rather than using a variation of the molybdenum cofactor, it instead uses a molecule known as the iron-molybdenum cofactor, which has a separate and much more complicated structure featuring large proportions of iron and sulfur. Nitrogen binds to the cofactor at one of the iron atoms and undergoes a several-step process to be converted into ammonia. While the reaction site is not located directly at the molybdenum atom, the element is still required for the enzyme to form. This is one more important biochemical process in which molybdenum is particularly critical for optimal plant growth.

Works Cited:

Molybdenum Trafficking for Nitrogen Fixation. Jose A. Hernandez, Simon J. George, and Luis M. Rubio. *Biochemistry* **2009** *48* (41), 9711-9721. DOI: 10.1021/bi901217p

Cell Biology of Molybdenum in Plants. Ralf R. Mendel. *Plant and Cell Reports* **2011** *30* (10), 1787-1797. DOI: 10.1007/s00299-011-1100-4

Molybdenum Effects on Muskmelon (Cucumbis melon) Seedlings. Sheri McLane. Iowa State University, 2018

Effect of Soil Applications of Sodium Molybdate on the Quality of Potatoes: Polyphenol Oxidase Activity, Enzymatic Discoloration, Phenols, and Ascorbic Acid. Cyrus B. Munshi and Nell I. Mondy. *Journal of Agricultural and Food Chemistry* **1988** *36* (5), 919-922. DOI: 10.1021/jf00083a008

Molybdate in Rhizobial Seed-Coat Formulations Improves the Production and Nodulation of Alfalfa. Jiqiong Zhou, Bo Deng, Yingjun Zhang, Adam B. Cobb, and Zhao Zhang. *PLoS ONE* **2017** *12* (1), doi:10.1371/journal.pone.0170179

Potato Tubers Contamination With Nitrate Under the Influence of Nitrogen Fertilizers and Spray With Molybdenum and Salicylic Acid. Ahmed S. Elrys, Ahmed I. E. Abdo, and El-Sayed M. Desoky. *Environmental Science and Pollution Research,* **2018** *25*, 7076-7089. DOI: 10.1007/s11356-017-1075-y.

Predicting Molybdenum Toxicity to Higher Plants: Influence of Soil Properties. S. P. McGrath, C. Mico, R. Curdy, and F. J. Zhao. *Environmental Pollution* **2010** *158* (10), 3095-3102. DOI: 10.1016/j.envpol.2010.06.027.

Metabolic Changes in Mustard Plants Associated with Molybdenum Deficiency. C. Chatterjee, N. Nautiyal, S. C. Agarwala. *New Phytologist* **1985** *100* (4). DOI: 10.1111/j.1469-8137.1985.tb02797.x.

The Role of Molybdenum in Agricultural Plant Production. Brent N. Kaiser, Kate L. Gridly, Joanne N. Brady, Thomas Phillips, Stephen D. Tyerman. *The Annals of Botany* **2005** *96* (5), 745-754. DOI: 10.1093/aob/mci226.

Mineral Nutrient Deficiencies and Nutrient Interactions in Pomegranate. R. A. Marathe, A. A. Murkute, and K. Dhinesh Babu. *National Academy of Science Letters* **2016** *39,* 407-410. DOI: 10.1007/s40009-016-0487-4.