Chemical concepts in HLB mitigation programs

By Arnold Schumann

uring the past 10 years, the Florida citrus industry has experienced unprecedented losses of grove acres and fruit yields due to citrus greening disease or huanglongbing (HLB). The recommended HLB management methods designed to limit its spread throughout the state relied on early detection and removal of infected trees, and the suppression and isolation of the associated Asian citrus psyllid (ACP) vector. These standard procedures failed to curb the spread of HLB for multiple reasons, most notably due to the already endemic ACP

population in Florida at the time HLB was discovered,

and the existence of less well-managed, dooryard citrus trees and abandoned groves throughout the commercial citrus-producing regions acting as a conduit for uncontrolled disease spread.

Because many HLB-associated symptoms visible on affected tree canopies are linked to real nutrient deficiencies triggered by the disease, growers, vendors and scientists developed enhanced nutrition programs to slow the rate of tree and yield decline. Various combinations of fertilizer products and systemic acquired resistance (SAR) inducing chemicals are routinely mixed as "cocktails" and applied together with pesticides as foliar sprays using ground equipment and sometimes aerial sprays. Enhanced soil fertilization programs were developed to further bolster tree health, particularly to slow the decline of root systems associated with HLB.

Although nutrition is not a cure for HLB, it remains the most useful, practical defense in mature groves against the incurable citrus disease, albeit at a considerable, additional annual expense. Some of the important chemical principles and guidelines for optimizing the use of fertilizers and other chemicals to manage HLB are discussed in this article.

SPRAY-TANK MIXTURES

The cost of applying agrochemicals in citrus groves is sufficiently high to warrant as much tank mixing and co-application of different products as possible without compromising product integrity and efficacy. Grove maintenance sprays routinely combine insecticides, fungicides/bactericides, adjuvants, petroleum oils and nutritional fertilizer products in high-volume, groundapplication equipment.

Reasons for using spray-tank mixtures include:

- 1) Efficiency and synergy
 - Improved leaf deposition, penetration of spray components
 - Multiple pest/disease control (e.g., psyllid and leaf miner) is often needed at a given time.
 - Integrated pest management with nutrients, SAR, pesticides and fungicides
- 2) Economics
- Reduced fuel, equipment maintenance and labor costs due to fewer spray trips
- 3) Environmental and grove impacts
 - Water (spray carrier) savings through less tanks sprayed
 - Fewer spray trips are required through the grove, and consequently reduced traffic impacts on soil and groundcover vegetation.
 - Energy savings and reduced carbon footprint due to improved fuel economy

Potential problems resulting from the use of mixtures in spray tanks can adversely affect delivery of the active ingredients to the trees and result in low product efficacy. Problems caused by mixing products may include:

- Physical incompatibility of products with the water carrier or with other products in the spray tank, such as slowly soluble or insoluble dry fertilizer materials, or layering of immiscible liquid components with different densities
- 2) Chemical incompatibility of products due to acid-base reactions, reduction-oxidation (RedOx) reactions, and precipitation due to ion pairing
- 3) **Biological incompatibility** of some biofungicide products using live bacterial cultures with chemicals in the tank mixture

Don't store a mixed spray tank overnight before use.

Physical, chemical and biological incompatibilities of spray-mixture components can introduce substantial inefficiencies in the grove-spraying operation. Inefficiencies include direct loss of expensive products by neutralization reactions in the tank, and/or phytotoxicity to the trees due to altered activity of some active ingredients in the presence of other chemicals in the mixture. For example, copper fungicides may become phytotoxic to trees at low spray mixture pH caused by the addition of acidic fertilizer products in the tank.

Spray product incompatibilities and phytotoxicities are also affected by concentration, temperature, contact time and water quality. Never mix concentrated products. High-volume (dilute) spray mixtures will reduce product interaction when compared to low-volume (concentrated) spray mixtures. Many spray mixtures become more phytotoxic at elevated temperatures. Spray groves at moderate air temperatures and avoid greater than 94°F with mixtures containing petroleum oil.

Any chemical degradation through component interaction takes time, and therefore mixing a spray tank just prior to use is the best strategy. Don't store a mixed spray tank overnight before use. Use the cleanest water available for spray mixtures; turbidity and salinity may interact adversely with some spray chemicals, and water pH should be measured and adjusted if necessary according to product labels. An example instruction cutout from the product-label directions of OxiDate, a broad-spectrum bactericide/fungicide, is shown below.

DIRECTIONS FOR USE

 OxiDate works best when diluted with water containing low levels of organic or inorganic materials, and with water having a neutral pH.

The directions clearly indicate that *only clean water of neutral pH* should be mixed with OxiDate. Adding any other pesticide, fertilizer or SAR product to OxiDate would create antagonistic chemical reactions,

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including RedOx, acid-base and organic matter oxidation, leading to the mutual degradation of OxiDate and the other products. For example, some biofungicide products use live bacterial cultures such as *Bacillus subtilis*, which would be completely destroyed in mixtures containing OxiDate, and some OxiDate would be consumed in the oxidation process.

Spray tank mixtures to avoid:

- Do not mix strong oxidizers with divalent iron (ferrous) or manganese (manganous) fertilizer compounds, phosphites, salicylic acid, ascorbic acid or other antioxidants, biofungicides and other oxidizible organics.
- *Do not* mix copper, manganese and zinc fungicides/bactericides with live biofungicides (e.g., *B. subtilis*).
- *Do not* mix fertilizer calcium, phosphorus and sulfates; insoluble precipitates may result (e.g., calcium nitrate +



magnesium sulfate produces insoluble gypsum).

Additional tips for preventing spray tank compatibility problems:

- Alternate different products at different times to keep compatible groups together and incompatible ones apart.
- Use different spray application options [aerial low volume, ultralow ground, air-blast high volume (HV)] to apply different products. Use HV for the most unstable mixtures that will benefit from the high dilution rate.
- Supply most macronutrients through fertigation and granular fertilizer application to the roots instead of the foliage (e.g., calcium nitrate). In general, micronutrients are more compatible with spray mixtures than macronutrients because micronutrients are only needed in small amounts.

SOIL OR WATER ACIDIFICATION

Excessively alkaline soil and irrigation water is detrimental for the uptake of essential plant nutrients, such as phosphorus, iron, manganese, zinc, copper and boron. Additionally, at common pH ranges of 7 to 9 found in alkaline soils and natural waters, bicarbonate ions predominate and interfere with the normal uptake of calcium and magnesium by the roots. Therefore, alkaline soil and irrigation water acidification is a remedy used by citrus growers to enhance nutrient uptake by tree roots that are affected by HLB.

Soil acidification can be achieved by direct addition of acid chemicals or indirectly by oxidation (conversion) of fertilizer chemicals in situ to release acid (H+ or hydrogen ions), usually with the help of soil microbes. Examples:

- Direct: sulfuric, nitric or phosphoric acid addition via fertigation
- Indirect: in situ oxidation of sulfur, thiosulfate, ammonium

fertilizers by soil bacteria (e.g., *Thiobacillus* spp., *Nitrobacter* spp.)

sulfur \rightarrow sulfate; thiosulfate \rightarrow sulfate; ammonium \rightarrow nitrate

Direct soil acidification is very rapid, while indirect acidification occurs over a longer time (slow release, and therefore is safer to crops).

During water acidification, irrigation water is acidified by direct addition of acid chemicals releasing H+ (e.g., liquid sulfuric, nitric or phosphoric acids). Solid sulfur can be used in special controlled combustion (oxidation) devices to generate sulfurous acid in situ and inject it into the irrigation water. These "sulfur burners" are quite popular in the western agricultural regions where bicarbonate concentrations in irrigation water are excessive.

A common misconception about fertilizer chemistry regarding acidification is "ammonium sulfate acidifies soil due to the sulfate content." The statement is incorrect because the real acidification mechanism involves the oxidation of ammonium to nitrate, which releases H⁺(acid).

Another false statement is "gypsum $(CaSO_4)$ will acidify soil due to the sulfate content."

No part of the gypsum molecule can be further oxidized, and thus it releases no acidity. This is because fertilizer sulfates (SO_4^{2-}), phosphates (PO_4^{3-}) and nitrates (NO_{3-}) are fully oxidized states and don't acidify soil, unless the compounds also contain H⁺ (acids).

Fertilizers with partially oxidized oxyanions like sulfites (SO_3^{2-}) and phosphites (PO_3^{3-}) can release additional acidity upon further oxidation. The capacity for different fertilizers to acidify soil or irrigation water varies greatly. Consult the product labels to obtain the correct application rates.

CALCIUM NUTRITION, HLB AND ROOTS

The following characteristics of calcium (Ca) nutrition are important

when addressing the critical Ca deficiencies found in trees that are affected by HLB:

- Ca is taken up mainly behind the root tips; therefore actively growing roots are necessary for proper Ca nutrition of trees.
- Ca moves upward from the roots in the xylem, driven by transpiration.
- Ca is not translocated in the phloem, so it cannot move from one part of the canopy to another or downward to the roots.
- Disruption of transpiration flow leads to deficiencies of Ca and may be caused by cloudy humid weather, cold, drought, flooding, over-irrigation, root injury, soil compaction and root disease.
- Ca deficiencies cause rapid meristem death, including root tip dieback. This can trigger a "vicious cycle."
- HLB results in root damage, exacerbated by critical Ca deficiencies, root tip dieback and, consequently, even less Ca uptake. A self-perpetuating decline cycle begins.

What can be done to improve calcium nutrition in HLB-affected citrus trees?

- Proactively include Ca in granular fertilizer blends (e.g., calcium nitrate, which is a central part of the Orange Hammock nutrition program).
- Include slow-release Ca such as coated granular calcium nitrate in blended controlledrelease fertilizers.
- Use gypsum applications to soil or as a constant feed through irrigation water.
- Consider rock phosphate application, which provides both Ca and phosphorus to the soil and roots in a very slowly soluble (constant supply) natural form.
- Foliar spray application of Ca is not effective because it is not translocated to the roots, and the amount of Ca which can be

applied in spray coating on leaves is minimal and transient.

The above discussions highlight some of the important chemical concepts and management considerations for growers to optimize when using the many fertilizers, pesticides, SAR inducers and pH adjusters that are available to mitigate HLB-affected citrus groves. Correct use of agrochemicals improves their performance and reduces production costs, while minimizing waste and environmental impacts.

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