### Using calcium sulfate in hydroponics

Calcium is a very important element in plant nutrition and can be supplied to plants through a wide variety of different salts. However, only a handful of these resources are significantly water soluble, usually narrowing the choice of calcium to either calcium nitrate, calcium chloride or more elaborate sources, such as calcium EDTA. Today I am going to talk about a less commonly used resource in hydroponics – calcium sulfate – which can fill a very important gap in calcium supplementation in hydroponic crops, particularly when Ca nutrition wants to be addressed as independently as possible and the addition of substances that interact heavily with plants wants to be avoided.



Calcium sulfate dihydrate (gypsum)

There are some important reasons why you don't hear too much about calcium sulfate in hydroponics. Some websites actually recommend heavily against using this substance in hydroponic nutrient solutions. Why is this the case? The core issue is calcium sulfate's solubility, with this substance traditionally considered "insoluble" in chemistry. However all substances are soluble to one or another degree – even if to an extremely small degree – but calcium sulfate is actually at the very border of what is considered a soluble substance in regular aqueous chemistry.

At 20C (68F), calcium sulfate dihydrate - the form most commonly available – has a solubility of around 2.4 g/L. In practice this means that you can have up to around 550 ppm of Ca in solution from calcium sulfate dihydrate before you observe any precipitation happening. This is way more than the normal 150-250 ppm of Ca that are used in final hydroponic nutrient solutions that are fed to plants. You could supply the entire plant requirement for calcium using calcium sulfate without ever observing any precipitate in solution. At the normal temperature range that hydroponic nutrient solutions are kept, the solubility of calcium sulfate is just not an issue. To add 10 ppm of Ca from calcium sulfate you need to add around 0.043g/L (0.163g/gal). You should however avoid using calcium sulfate for the preparation of solutions for foliar sprays as it will tend to form precipitates when the foliar spray dries on leaves, the leaves will then be covered with a thin film of gypsum, which is counterproductive.

Calcium sulfate has a great advantage over other ways to supplement calcium in that the anion in the salt – sulfate – does not contribute as significantly to plant nutrition. Other sources, such as calcium chloride or calcium nitrate, will add counter ions that will heavily interact with the plant in other ways, which might sometimes be an undesirable effect if all we want to address is the concentration of calcium ions. Other sources such as Ca EDTA might even add other cations – such as sodium – which we would generally want to avoid. Calcium sulfate will also have a negligible effect in the pH of the solution, unlike other substances – like calcium carbonate – which will have a significant effect in the pH of the solution.



Solubility (g per 100mL) of calcium sulfate as a function of temperature for different crystalline forms (see more <u>here</u>)

A key consideration with calcium sulfate is also that its dissolution kinetics are slow. It takes a significant amount of time for a given amount of calcium sulfate to dissolve in water, even if the thermodynamics favor the dissolution of the salt at the temperature your water is at. For this reason it is very important to only use calcium sulfate sources that are extremely fine and are graded for irrigation. This is sometimes known as <u>"solution grade" gypsum</u>. I advice you get a small amount of the gypsum source you want to use and test how long it takes to dissolve 0.05g in one liter of water. This will give you an idea of how long you will need to wait to dissolve the calcium sulfate at the intended temperature. Constant agitation helps with this process.

An important caveat with calcium sulfate is that its relatively low solubility compared with other fertilizers means that it cannot be used to prepare concentrated nutrient solutions. This means that you will not be able to prepare a calcium sulfate stock solution or use calcium sulfate in the preparation of A and B solutions. As a matter of fact the formation of calcium sulfate is one of the main reasons why concentrated nutrient solutions usually come in two or more parts, to keep calcium and sulfate ions apart while they are in concentrated form. Calcium sulfate should only be added to the final nutrient solution and adequate considerations about temperature and dissolution time need to be taken into account.

### Three ways to judge the quality of powdered hydroponic nutrient products

Commercial hydroponic nutrients are often available as liquid concentrates. These offer a very reproducible experience for the user, with very high homogeneity and easiness of application. However, one big drawback of liquid concentrates is the fact that they contain a significantly large amount of water, meaning that shipping them is often very expensive. The solution to this is to create solid state fertilizers, where a mix of raw salts is shipped, and a concentrated stock solution or final hydroponic nutrient solution is prepared by the user. However, solid preparations have some important issues that liquid concentrates do not have that can significantly affect the quality of the nutrition received by the plants and the reproduciblity of their results. In this blog post, we will talk about what makes a good premixed solid fertilizer and thee ways in which you can judge the quality of one.



This is a poor quality commercial hydroponic nutrient mix. As you can see there are different coarse salts that have been barely mixed (some look like rice grains, others like sugar crystals). There is no proper fine grade mixing of the salts, therefore the standard deviation of the composition of different random samples will be large.

Homogeneity of the product. Having a very finely mixed fertilizer is extremely important because hydroponic fertilizers can contain nutrients with differences in composition of even more than 3 orders of magnitude. A fertilizer might contain 10% of its mass as nitrogen but only 0.01% of its mass as iron. For that fertilizer to work effectively, any random sample draw from it must contain as close as possible to the composition on the label. However, if the fertilizer is not well mixed a random draw might deviate very strongly from the intended composition. This means that one day you might be preparing a batch of solution using a 20%N 0.001%Fe fertilizer and the next day you might be preparing one that is 10% N and 0.5% Fe.

A good quality solid fertilizer product should have a homogeneous look to it. You should be unable to determine the constituent salts from one another in the fertilizer mix. If you notice different types of solids within the product – such as pellets mixed with crystals – or any other sign that the preparation is not homogeneous then this means that the fertilizer is just a very simple mix of the raw salts, meaning that the components may separate relatively easily as a function of time through differences in their properties (such as density). Sometimes a fertilizer might be finely ground, well mixed and then pelleted – which is acceptable – but if this is the case the fertilizers should contain only pellets and all of them should have the same look to them.

If you want to really tell if the fertilizer is of good quality you can take random samples from different parts of the fertilizer – punch different holes in a sealed bag and sample from different sections of it – and send them for lab analysis. The standard deviation of the composition of the different samples will tell you how good the fertilizer is. Good solid fertilizers will have a standard deviation below 5% in analyzed samples.

Stability of the product. A good solid fertilizer product will be stable through time, since it will be formulated with salts that are as close as possible to the lowest thermodynamic state of the mixture of ions being made. Inexperienced people who venture into the fabrication of solid fertilizers will often mix salts that are used in liquid concentrates that can react when put together in solid form. These reactions often happen with a release of water that can change the weight of the fertilizer as it evaporates from the product or can cause very significant caking problems in the mixture as a function of time. In the worst cases, some substances that are hard to put back into solution might form, making the final use of the fertilizer difficult.

You can tell if a fertilizer is reacting if there are changes in the mass of the fertilizer as a function of time or if the appearance or physical properties of the fertilizer change. Are the colors changing? Is the texture changing? All of these things can point to on-going reactions in the fertilizer mixture that can be indicative of problems with the formulation. A good formulation should change as little as possible through time.



Caking of a fertilizer product due to a reaction with atmospheric water

**Easiness of dissolution**. Premixed solid fertilizers for hydroponics need to be prepared to be as easy as possible to dissolve in their final application. This can be problematic depending on the inputs used, but adequate additives need to be put in to ensure that the products will not have a very hard time getting back into solution. This involves adding adequate wetting agents as well as ensuring that chemical reactions that alter solubility do not happen within the final product.

When dissolving raw fertilizers most of the product should go into solution, however — depending on the purity and source of the chemicals used — some insoluble portions might remain. A manufacturer might make the choice of using inputs that are directly mined instead of chemically purified — using for example OMRI grade magnesium sulfate — this will create a product that has more insoluble materials compared to a product that uses more thoroughly refined magnesium sulfate. Whether this is acceptable or not will depend on the type of application required and what the priorities of the grower are, for example MRI compliance might be more important than having better solubility.

As you can see, although solid premixed fertilizers can provide significant savings in terms of shipping over liquid concentrated fertilizers, they can do so at the cost of reproducibility and quality problems. To avoid these problems I recommend you ensure the fertilizer you choose to use has been properly blended to produce low deviations in sampling, has been formulated with thermodynamic stability in mind and has been formulated considering proper solubility in the final application.

## How to control algae in a hydroponic crop

Microscopic algae can be a very annoying problem in a hydroponic crop. As photosynthetic organisms they can cover all exposed surfaces that get wet with hydroponic nutrient solution and can cause a wide variety of different issues for the grower. They can also be hard to control, reason why some growers simply choose to ignore them and learn to "live with them" as a fundamental part of their hydroponic setup. In today's article we'll talk about some of the reasons why microscopic algae are a problem that has to be dealt with, what the different options to solve the problem are and which of these options can be the most effective.



Typical microscopic algae found in hydroponic nutrient solutions

Besides the unpleasant look of algae covered growing media, these microscopic organisms can cause some important problems in your hydroponic crop. They can deprive hydroponic solutions from some nutrients, generate substances that can hinder plant growth, serve as food for some insects (like fungus gnats) and also serve as food for other microscopic pathogens. For more information about algae and their effects you can read <u>this</u> <u>paper</u> that studied some of the effects of algae in hydroponic crops or <u>this white paper</u> that explains some of the main issues associated with algae in hydroponics. <u>This paper</u> also studies nutritional and pH effects in more depth.

The first barrier of defense against algae is to avoid them, cover surfaces that are exposed to light and nutrient solution with opaque covers and ensure that all surfaces are properly sanitized before hydroponic crops are started. Granted this is a limited solution in scope – as places like the top of media are not easy to cover – but it can provide some protection compared to a crop where no attention is paid to surfaces at all.

To deal with surfaces that have algae in them is an entirely different matter. Algae are not easy to get rid of. This paper goes through multiple potential treatments to get rid of algae, including the use of fungicides, insecticides and

algicides and finds that these substances are either not effective, only preventive in nature or actually phytotoxic at the concentration at which they are effective. Hydrogen peroxide is suggested as a potential solution to deal with algae, but hydrogen peroxide also causes significant stress in plant roots and its application is bound to have only limited success, with the algae coming back to recolonize – often more strongly – once the applications are finished. This paper evaluates hydrogen peroxide use even further and also shows some of the potential problems that can happen when using it to control algae and insects.



Image from this article showing plants treated with IBA (a) and plants not treated with it. You can notice the complete absence of algae in the growing media

Thankfully all hope is not lost. Around 20 years ago, experimentation started on the use of some indole derivatives – the same used to stimulate rooting in rooting gel formulations – to control algae populations. This article shows that an application of 3-(3-indolyl)butanoic acid (also known as IBA or Indole-3-butyric acid) at 10 ppm can very effectively control algae populations. The image above shows how the IBA treatment was very effective at reducing all algae growth in the media, even when nutrient solution was directly wetting the media with direct access to light. This is great news since IBA is non-phytotoxic and can therefore be used without having to cause any damage to the plants (unlike peroxide does). There is also additional evidence from independent researchers in Japan showing the effectiveness of IBA for the same purpose (see <u>this article</u>). Additionally there might even be some positive effects of IBA applications in crop yields, as it is shown in <u>this paper</u> where experiments with IBA applications were done on bell pepper. This is not terribly surprising given that the effects of IBA to stimulate root growth are very well known.

Note that although the above articles use IBA as a consistent application during the entire crop, there is little peer reviewed use of IBA applications in plants during their entire crop cycle. To avoid any potentially unknown effects - such as in essential oil substantial changes or product characteristics - it is important to test the effect in the particular plant you are growing and initially apply it only as needed to control any algae growth that might appear. Some areas might also forbid the application of substances like IBA - which is a recognized Plant Growth Regulator (PGR) - so make sure you can also use this in your crop before you even consider it for this application. This 2009 proposal to allow IBA usage in organic food production and handling goes a lot deeper into IBA, its use in plants and its potential effects.

### Can you use regular soil fertilizers in hydroponics?

If you have just started your journey into hydroponics you're probably wondering why you need to spend your money in hydroponic specific nutrients when there are so many cheaply available soil fertilizers sold out there. Certainly there are all plant food and there must be some way you can use all these cheap soil fertilizers to create a suitable replacement to feed your hydroponic crop. In this post I want to explain some of the key differences between hydroponic and soil fertilizers, when soil fertilizers can be used in hydroponics, how they can be used and when it is definitely a bad idea to try to use them.



Some slow release soil fertilizer being added to plants To understand the difference between soil and hydroponic fertilizers we must first understand the difference between both growing setups. In hydroponics we try to grow plants in sterile and chemically neutral supporting media where all the nutrients are expected to be provided by the nutrient solution while in soil the media is not intended to be inert - it contains organic matter, minerals that can dissolve and living microbes - and we expect some of these to provide nutrition to our plants. Fertilizers for soil are intended to aid this process - provide material for microbes to process and supplement some of the lacking elements in the soil - while hydroponic fertilizers intend to provide all required nutrition in the forms that are mostly favorable for plants. Fertilizers for soil are often also meant to be applied once or very occasionally, while fertilizers for hydroponics are expected to be fed to the plant very frequently.

In chemistry terms, this means that fertilizers for soil will

tend to contain forms of nitrogen that can be processed slowly by microbes in soil - urea and ammonium salts - while hydroponic fertilizers contain mostly nitrate salts. It is rare for soil fertilizers sold to home growers to contain large amounts of nitrates because these are easily washed aware by rain, are strong pollutants of underwater ground sources and are only shortly available for plants due to their high mobility in soil. However ammonium and urea are a terrible idea in hydroponics since ammonium fed frequently strongly acidifies the media and plants supplied their nitrogen only from ammonium in solution will tend to show toxicity issues quickly. Soil fertilizers rely on bacteria to convert this ammonium and urea to nitrate in a slow process, hydroponic fertilizers do not, they contain nitrate which is the final form of nitrogen that plants prefer for healthy growth.

- GUARANTEED ANALYSIS - F1144
Total Nitrogen (N)
1.62% Ammoniacal Nitrogen
2.46% Nitrate Nitrogen
13.89% Urea Nitrogen
0.03% Other Water Soluble Nitrogen
Available Phosphate (P <sub>2</sub> O <sub>2</sub> )
Soluble Potash (K <sub>2</sub> 0)
Magnesium (Mg) 0.50%
0.50% Water Soluble Magnesium (Mg)
Boron (B) 0.02%
Copper (Cu) 0.05%
0.05% Water Soluble Copper (Cu)
Iron (Fe) 0.10%
0.10% Chelated Iron (Fe)
Manganese (Mn) 0.05%
0.05% Chelated Manganese (Mn)
Molybdenum (Mo) 0.0005%
Zinc (Zn) 0.05%
0.05% Water Soluble Zinc (Zn)
Derived from Ammonium Sulfate, Potassium Nitrate, Urea, Soy Protein Hydrolysate, Monopotassium Phosphate, Sulfate of Potash, Magnesium Sulfate, Boric Acid Conper Sulfate Iron FDTA Mannanese
EDTA, Sodium Molybdate, and Zinc Sulfate.
Information regarding the contents and levels of metals in this product is available on the Internet at http://regulatory-info-sc.com

Guaranteed Minimum Analysis	
Total Nitrogen (N)	20%
Nitrate Nitrogen	12.1%
Ammoniacal Nitrogen	7.9%
Urea Nitrogen	0%
Available Phosphoric Acid (P <sub>2</sub> O <sub>5</sub> )	8%
Soluble Phosphorus	3.4%
Soluble Potash (K <sub>2</sub> O)	20%
Soluble Potassium	16.6%
Calcium (Ca)	0%
Magnesium (Mg)	0.25%
Chelated Iron (actual) (Fe)	0.100%
Chelated Manganese (actual) (Mn)	0.050%
Chelated Zinc (actual) (Zn)	0.050%
Chelated Copper (actual) (Cu)	0.050%
Boron (actual) (B)	0.020%
Molybdenum (actual) (Mo)	0.015%
EDTA (chelating agent)	1.24%

Comparison between a couple of typical water soluble soil (left) and hydroponic (right) fertilizer labels.

The image above shows you a comparison between the labels for a water soluble soil and hydroponic fertilizer. In terms of NPK they both seem to be similar fertilizers, but the hydroponic fertilizer will have most of its nitrogen as nitrate while the other fertilizer has most of its nitrogen as urea. There are some other differences, mainly that the amount of phosphorous in the soil fertilizer is more than double that of the hydroponic fertilizer, which is also common given that phosphate is fixed rapidly in soil and therefore a higher excess is often added to ensure plants get enough supply. At an application of 1g/L the soil fertilizer would provide 75+ ppm of phosphorous while the hydroponic one would provide around 35. Also note that none of these two fertilizers would be enough to provide total plant nutrition since they both lack a source of Ca, which is commonly provided via a separate product in both cases.

So can any soil products be useful in hydroponics? Yes. First you need to completely avoid products that contain N mainly as urea or ammonium. Useful products to get for your hydroponic grow will be fully water soluble and will either contain nitrogen solely as nitrate or no nitrogen at all. A very coarse DIY formula can usually be put together using something like a micro nutrient containing 0-10-10 bloom fertilizer (which contains no nitrogen) coupled with a source of nitrate, like agricultural grade calcium nitrate. You can use <u>Hydrobuddy</u> – my open source hydroponic nutrient calculator – to figure out the nutrient contributions of each one of the products you decide to get or have easily available and create an acceptable formulation from their use. The program also contains a long list of readily available raw salts that you can use to make your own fertilizer formulations from scratch if you wish to do so.

In the end, soil products for home growers are not designed for hydroponics use and should therefore be avoided except as a last resort if raw salts or hydroponic specific nutrients cannot be purchased. If you're interested in saving money, learning how to prepare your own fertilizers from raw salts will always be the best and cheapest option, provided you have the time and desire to learn how to do it properly.

### Accurately preparing large quantities of concentrated hydroponic nutrients

When preparing concentrated solutions for hydroponics it is important to have a reproducible process that always generates the exact same results. If this is not done, you'll obtain different nutrient concentrations between different batches and the concentrated nutrient additions to create the final nutrient solutions will yield inconsistent results. To address the potential variability of the concentrated solution manufacturing process we need to understand the different sources of error present and come up with ways to modify the process to generate more reproducible results. In this blog post I will talk about the largest source of error when preparing larger batches of concentrated nutrient solutions and how this error can be greatly reduced in order to obtain both more precise and accurate results.



Picture of a type A 250mL volumetric flask.

The process of preparing hydroponic concentrated solutions involves two steps. First, you dissolve raw fertilizer salts into some volume of distilled or RO water and then you take this volume of solution to a desired final volume of solution using the same source of water. In a small scale setup this process is very simple to carry out, since we can just weight and dissolve all our salts in some fraction of the desired final volume and then use a precise instrument to measure total volume – most typically a volumetric flask – to take our solution to the final desired volume. For example if we desire to prepare 250 mL of concentrated nutrient solution and we use a well calibrated scale with +/- 0.001g of precision and an A grade volumetric flask with a precision of +/- 0.3 mL, the error we expect to get from a 500mg salt will be +/- 4.77 ppm with a 99% confidence. Since the concentration of this salt in the concentrated solution is 2000 ppm, we get a final result of 2000 +/- 4.77 ppm. If both instruments are calibrated this is a very precise and accurate result.

When we move to larger amounts of solution we usually get better on the side of mass. This is because we can still get scales that weight with +/-0.1g precision even at weights exceeding 50kg, so our error as a fraction of the total measurement remain in the 0.01% to 1% region pretty easily. However things get way worse in terms of volume. If you are preparing 100 gallons of nutrient solution – around 378 liters – you will be able to weight the salts precisely and accurately but when it comes to measuring final volumes of solution, you are not going to be very lucky. The volume marks in tanks are widely inaccurate and are not even standardized to any level of significant precision or accuracy plus accurately measuring whether water is at a given level in a tank is a very error prone process because of how wide the tank area is.

Although we don't usually have a way to adequately measure final volume, we do have a way to measure volume going into a tank in the form of flow meters, which can give us significant accuracy and precision. However, to be able to properly use the flow meter — know how much volume we need to actually get to the final volume we want — we must obtain information from a precise and accurate low scale process. To do this you can carry out the following steps:

- Get a precise and accurate scale (calibrated and at least +/- 0.001g in precision)
- Get a scale that can weight up to 500g that can measure with at least +/- 0.1g precision (if the one above does not).
- Get a 250 mL type A volumetric flask (should be around +/- 0.3 mL in precision).
- Get a 250mL beaker
- Get a plastic lab washing bottle and fill it with distilled water
- Calculate the salts you would need to dissolve to arrive at your desired concentrations at a 250mL final volume of concentrated solution
- •Weight those salts and put them in a beaker, take note

of all the exact weights added.

- Weight the dry, empty volumetric flask
- Add approximately half the volume of distilled water to the beaker and dissolve the salts
- Transfer to the volumetric flask, use the washing flask to fill the volumetric flask up to the calibration line (bottom of water meniscus is touching the line when viewed at eye level).
- Weight the flask with the solution
- Calculate the weight of water (weight of flask with solution – weight of flask – sum of weight of salts)

If the procedure above was carried out between 10-25C (50-77F) we can approximate the density of water to 1.0g/mL with little error (around 0.003g/mL). This means that we know the volume of water that was required to get to the desired final volume and we can then transfer this volume to our preparation procedure when we use a large tank. If the volume of water required for the preparation of the 250mL solution was just 230mL, then we can assume that the volume required to prepare 100 gallons will be 92 gallons, as the salts, when proportionately scaled, will take up the same volume and will require the same amount of water proportionately to reach the final desired volume.

When this type of procedure is done and an accurate and precise flowmeter is used, we can usually achieve concentration values at large scales that will be in the 0.1-1.0% error range, which is way better than anything that can be achieved by just using lines in tanks or procedures that use flow meters but ignore what the actual amount of water added needs to be in order to reach the desired concentration (many people achieve the salts take up no volume, which is a mistake). Having low errors in concentrated solutions means there will be less variability in final nutrient solution composition and therefore more reproducibility in crops. Calcium EDTA and its problems in hydroponics

Calcium is mainly used in hydroponics as calcium nitrate, given that this is a very soluble and abundant form of calcium. However this is not the only way calcium can be fed to plants and a myriad of other calcium sources exist. Among this we find calcium sulfate, calcium chloride, calcium hydrogen phosphate, calcium citrate, calcium gluconate and calcium EDTA. This last form, a chelate of calcium with EDTA, is one of the most cheaply available forms of chelated calcium but carries with it some substantial problems in hydroponic culture. In this article we are going to talk about Ca EDTA, its advantages and challenges when used as a supplement for calcium in hydroponics.



Model representation of the CaEDTA<sup>-2</sup> anion in the Ca EDTA salt. When talking about Ca EDTA we should first understand that this is not simply a calcium ion with an EDTA molecule wrapped around it. In reality, the product we purchase as Ca EDTA, that contains 9.7% Ca by weight, is actually represented chemically as  $C_{10}H_{12}O_8CaN_2Na_2\cdot 2H_2O$ . The Ca EDTA product is actually four parts, a few waters of crystallization, the Ca<sup>+2</sup> cation, the chelating agent anion that wraps around it (EDTA<sup>-4</sup>) and two sodium cations, Na<sup>+</sup>, that are used to counter the two excess negative charges coming from the Ca EDTA (which we should more accurately call (CaEDTA)<sup>-2</sup>). When adding Ca EDTA we are actually adding four things, a little water, Ca, EDTA and Na. Most importantly Ca EDTA is in reality 12.15% sodium, meaning you're adding more Na than you're adding Ca when you use it.

Because of the above, thinking about Ca EDTA as any significant portion of a plants Ca nutrition is going to be a problem. Adding 100 ppm of Ca through this chemical would imply adding more than 100 ppm of Na. This addition of sodium can start to be heavily detrimental to plants as higher and higher values are reached (read my article on <u>sodium in hydroponics</u> to learn more). Although there is not much in the way of scientific literature using Ca EDTA, we do find <u>some reports</u> talking about heavy toxic effects at concentrations near 2.5 mM (940.7 ppm), which would contribute around 90 ppm of Ca to a solution.

Another important aspect to consider is the EDTA molecule itself. The EDTA chelate is not passive by any means and is not covalently attached to the Ca, so can easily move away. Since it binds pretty weakly with Ca, it will want to exchange Ca with anything else that seems more attractive to it. This poses an important problem when applying it in solution, as the EDTA in Ca EDTA might dissociate from Ca and attach to another ion that it finds more attractive, it prefers heavy metals so this can actually cause extraction of things like lead from the media. This might be an important consideration when used in cases where the media might contain significant amounts of heavy metals. Yet another interesting issue — that I haven't seen mentioned anywhere else and only know experimentally — is that the actual CaEDTA<sup>-2</sup> anion can form insoluble salts with Ca itself. This means that you can actually precipitate Ca(CaEDTA) in solutions that are highly concentrated in both ions. This is an important reason why concentrated solutions of Ca EDTA and Ca nitrate are very hard to prepare right, because as soon as you pass the solubility limit of Ca(CaEDTA) you will start to see it crystallize out of solution. Many people wonder why something is precipitating out of a solution made of two very soluble Ca salts, the reason is that Ca EDTA is not a neutral entity but can actually form a salt with free Ca. The Ca EDTA definitely requires its own concentrated solution most of the time.

So why would anyone use CaEDTA given the above set of very important problems? There are a some advantages to it that make it a good salt for some applications, particularly foliar sprays. The first is that it is not going to precipitate easily out of solutions because of anions, so it can remain at a high concentration with anions that would normally precipitate as Ca salts in the presence of free Ca. This can be interesting in the case of some anions, like salicylates, that are often used as plant growth promoters (you can see this specific use in this paper). It is also one of the only forms of Ca that is taken in by the plant as an anion, so it is Ca that can get into the plant without having to compete with other cations in their transport channels. There are therefore some cases where Ca can be used very successfully in foliar applications (1).

Although there might be some niche applications for CaEDTA, particularly allowing some experiments that would be impossible with regular Ca salts, there are also some very important issues with its use in hydroponic culture. If you're contemplating using it, I would suggest you carefully consider its chemistry in solution and interactions with other substances that will be with it, particularly in stock solutions. You should also consider the amount of sodium being added and preferably avoid using it in feeding solution applications unless you have carefully considered all of the above and its advantages are more important for your particular use case.

### How to prepare a low cost chelated micronutrient solution

Micronutrients constitute only a small portion of a plant's nutritional requirements but are still vital to growth and development. They are mainly comprised of heavy metals (Fe, Zn, Mn, Cu, Mo) as well as a single non-metal, boron (B). Since they are used in such small concentrations – normally in the 5 to 0.01 ppm range – they are normally put into concentrated nutrient solutions in small proportions and included with other components such as Ca and Mg, which are present in concentrations much more in line with macro nutrients like N, P and K.



Metal IonEDTAChelateSimple model of the metal chelating process

The advantage of micro nutrients is that they are available cheaply and in high purities as heavy metal sulfate salts. These however have the problem of leading to relatively unstable cations in solution, making the preparation of concentrated micro nutrient solutions with pure sulfates impractical (unless you want to see how a gallon of rust looks like). However we can chelate the cations as they come out of these sulfates, using a chelating agent, in order to prevent any precipitation issues. In this article I am going to walk you through the preparation of a DIY chelated micronutrient concentrated solution. This is much cheaper than buying the heavy metal chelates, which can be 3+ times more expensive. To prepare this solution you'll need to buy the chemicals shown in the table below. The table includes links to buy all the different substances mentioned plus their cost (without shipping).

Link	Price USD/lb	Weight g/gal
<u>Disodium EDTA</u>	22.96	17.0600
Ferrous sulfate heptahydrate	15.99	9.4211
Zinc sulfate monohydrate	9.49	0.1039
Manganese sulfate monohydrate	14.99	1.1646
<u>Copper sulfate pentahydrate</u>	20.99	0.0595
<u>Sodium Molybdate</u>	19.99	0.0191
<u>Boric acid</u>	10.95	3.3384
Total Cost	115.39	

List of salts to prepare a DIY chelated micronutrient concentrated solution. This concentrated solution is to be used at 5mL per liter of final feeding solution.

In order to prepare the solution you also need a scale that can weight with a precision of +/- 0.001g (this is my low cost recommendation) and a container where you can store 1 gallon of solution. Please note that these solutions have to be prepared with distilled water, with RO water you might still run into some issues in the process. To prepare the solution carry out the following steps (the weights to be used are specified in the table above):

- Wash your container thoroughly with a small amount of distilled water
- Fill your container with half its volume of warm distilled water (30C, 86F)
- 3. Weight and add the disodium EDTA, stir until it is completely dissolved (this can take a while).
- 4. Weight and add all the remaining micro nutrients one by one in the order given above, stirring till each one is fully dissolved before adding the next.
- Fill the container to its final volume using warm distilled water.
- 6. Let the solution cool before closing the container.
- For longer half-life transfer to a container that is opaque to UV light.

This solution is prepared to give you the heavy metal concentrations of the <u>Hoagland nutrient solution</u> (a very common set of ratios used in scientific research for growing plants) when used at a ratio of 5mL per every liter of final feeding solution (18.92mL per gallon). The links given above are for 1lb of each product, with this you should be able to prepare at least 53 gallons of the concentrate, which will allow you to prepare 10,600 gallons of final feeding solution. The first salt you will run out of is Fe, but some are used so sparingly that you should be able to use them for the rest of your life without needing to buy any more (like copper sulfate and sodium molybdate). For less than 120 USD you will be able to have enough solution for probably the rest of your life – if you're a hydroponics aficionado – or even an entire crop cycle if you're a commercial grower.

This preparation is not without problems though, since the chelates are all prepared *in situ* they will take a substantial amount of time to reach their thermodynamic equilibrium, meaning that it cannot be used to soon or some of the metals

might not be fully chelated. To obtain the full metal chelating effect an excess of around 25% of disodium EDTA is also used, which means that this micro nutrient solution contains more free EDTA than a solution prepared with the chelates. Another issue is that all heavy metals are chelated with EDTA, which might not be optimal depending on your growing conditions. The EDTA chelates are also less stable against UV light and are also more easily attacked by oxidants. Another final issue is that the solution above contains no preservatives and fungi generally like to feast on this sort of micronutrient containing solutions. It is therefore reasonable to avoid preparing any large amounts of the above, as a solution prepared as instructed is normally expected to spoil in 3-4 weeks.

With this in mind, the above is not a perfect but a low cost and practical solution for those who want to start preparing their own nutrient solutions and avoid paying the high prices of some commercial nutrients just because of their micro nutrient contents. The above gives you a versatile micro nutrient concentrate that is bound to be adequate for growing almost all plants.

# Understanding the carbonic acid/bicarbonate buffer in hydroponics

I have written several articles before about pH and it's importance in hydroponic culture (1, 2, 3, 4). However I have yet to write a detailed explanation of one of the most important buffering systems in hydroponics, which is the

carbonic acid/bicarbonate buffer. This buffer is significantly more complicated than the simpler buffer created using phosphoric acid species, as it not only relies on ions present in solution but also on the partial pressure of carbon dioxide in the atmosphere. In this article I will attempt to explain this buffering system in detail, shining some light into the limitations of this buffer and how changing different key variables can fundamentally affect the way it works in hydroponics.



#### composite carbonic acid

Chemical reactions involved in the carbonic acid/bicarbonate buffer. Taken from <u>here</u>.

A buffer is nothing more than a pair of chemical species in solution that are present at a certain pH, that can react with additional  $H_3O+$  or OH- ions that are introduced into the solution. Since these ions control the value of pH, anything that prevents their concentration from changing will keep the pH stable. Distilled water, for example, has absolutely no buffering capacity since within it there is nothing that can react with incoming  $H_3O^+$  or  $OH^-$  ions that are added to the solution. Distilled water should therefore have a pH of 7.0, it does not because we live in an environment where an acid can always be generated from the air. This acid – carbonic acid – is generated in water whenever it's put into contact with a carbon dioxide containing atmosphere. *This makes distilled water have a pH of around 5.6*.

To be able to calculate the pH we need to consider all the chemical equilibrium reactions that happen, these are summarized <u>here</u> and in the image above. We must consider that carbon dioxide will dissolve in water to always satisfy Henry's law, that dissolved carbon dioxide will be in equilibrium with carbonic acid, that carbonic acid can dissociate into a  $H_30^+$  ion and a bicarbonate ion and that a bicarbonate ion can further dissociate into an additional  $H_30^+$  ion and a carbonate ion. To solve all of this we must also consider that charge neutrality must be preserved, meaning that the sum of all molar charges of all positive ions must be equal to the molar charges of all negative ions. To carry out these calculations I routinely use the freely available <u>Maxima software</u>. Below you can see the code I use to solve this system in Maxima (constants are taken from <u>here</u>):

```
[kw : 10^(-14.0), kh: 1.7*10^(-3.0), kc1: 2.5*10^(-4.0), kc2:
4.69*10^(-11.0), co2: 1.32*10^-5];
log10(x) := log(x)/log(10) ;
pH(x) := float(-log10(x));
```

float(solve([h\*oh=kw, h = 2\*co3+hco3+oh, kh=h2co3/co2, kc1=(hco3\*h)/h2co3, kc2=(co3\*h)/hco3],[oh, co3, hco3, h2co3, h]));

This is the solution obtained for the molar concentrations (rounded for clarity):

```
oh = 4.21*10^{-9}

co3 = 4.68*10^{-11}

hco3 = 2.36*10^{-6}

h2co3 = 2.24*10^{-8}

h = 2.37*10^{-6}
```

After executing this code you will get several different possible solutions, but the only one that interests us is the one where the  $H_3O^+$  (h) concentration is a positive number (this

solution is showed above). We can then use the pH function to calculate the value of pH for this  $H_30+$  concentration, which gives us a value of 5.62, this matches the real measurement of a distilled water solution at 25C under a 387ppm carbon dioxide atmosphere. Note that the amount of none dissociated acid in solution is very small. Taken to mass, the concentration of carbonic acid is 0.00138 ppm. However the concentration of bicarbonate is significantly greater, at 3.6 times the concentration of undissociated carbonic acid. This explains why the pH drops so much, since a significant amount of the generated carbonic acid ends up dissociating and contributing  $H_30^+$  ions to the solution. This also shows you how little acid is needed to drop the pH of an unbuffered solution.

To create the buffer with the biggest possible strength we would need to add enough strong base to shift the pH to the point where the pH equals the pKa (which is just - Log(equilibrium constant)) of the joint reactions created from the reaction of carbon dioxide with water to create carbonic acid and the subsequent dissociation of this acid into bicarbonate and  $H_30^+$ . This point is at 6.3 under atmospheric conditions at 25C. This can be achieved with the code below:

[kw :  $10^{(-14.0)}$ , kh:  $1.7*10^{(-3.0)}$ , kc1:  $2.5*10^{(-4.0)}$ , kc2: 4.6910^(-11.0), co2:  $1.32*10^{-5}$ , h: $10^{(-6.3)}$ ]; float(solve([hoh=kw, base+h = 2co3+hco3+oh, kh=h2co3/co2, kc1=(hco3h)/h2co3, kc2=(co3h)/hco3],[oh, co3, hco3, h2co3,base]));

This is the solution obtained for the molar concentrations(rounded for clarity):

oh =  $1.99*10^{-8}$  co3 =  $1.04*10^{-9}$ hco3 =  $1.11*10^{-5}$  h2co3 =  $2.24*10^{-8}$ base =  $1.07*10^{-5}$  The pH here is set to 6.3 and we can see that to get there we would need to add a base at a concentration of  $1.07*10^{-5.0}$ . If this base was KOH this would imply adding it at a rate of 0.6 ppm. We can see how the pH changes as a function of adding base or acid from this point. If at this point we decided to double the addition of strong base we would get to 6.57, tripling it would take us to 6.73 and adding 10 times more base would take us to 7.25. The buffer is indeed resisting the increase in pH by basically drawing CO<sub>2</sub> from the air to react with the incoming base as base is added to the solution. *However you might notice that under equilibrium conditions the buffering capacity of this system is very low.* Just 6 ppm of a KOH equivalent strong base addition can strongly affect the pH – taking it from 5.6 to 7.25 – so how can the carbonic acid/bicarbonate buffer be effective at all in hydroponics?

The answer is in the first image in this post. The equilibrium reaction between carbonic acid and water plus carbon dioxide in water (k23/k32) is fundamentally slow. We can take advantage of this by generating larger amounts of carbonate species in solution through the use of exogenous carbonate or bicarbonate additions and then setting the pH at a lower value to generate more carbonic acid, this acid will then take some significant time to reach equilibrium. This is the reason why using tap water with a significantly high alkalinity can provide a surprisingly stronger buffer than what would be expected at equilibrium and it also has some interesting consequences in the use of nutrient solutions.

Let's consider a case where there is no decomposition of carbonic acid – let's suppose it's extremely slow – and say we add 100 ppm of potassium carbonate into a solution and then set the pH back to 5.8 using phosphoric acid. In this case the predominant reactions in solution would be the dissociation of dihydrogen phosphate to hydrogen phosphate and  $H_3O+$  and the carbonic acid dissociation discussed before. In order to properly consider this case we must also introduce two

additional equations, mainly the mass balance equations for the phosphate and carbonate species, since this time we are assuming no carbon dioxide is ever lost to the atmosphere. Note that I have changed the equilibrium constant for the carbonic acid reaction here to  $10^{-6.3}$  where carbonic acid is now "apparent carbonic acid". You can see the equation system and solution below:

[kw : 10^(-14.0), kh: 1.7\*10^(-3.0), kc1: 10^-6.3, co2: 1.32\*10^-5, kp:10^-7.2, total\_p: 1.7\*7.2310^-4, total\_c: 7.23\*10^-4];

float(solve([h\*oh=kw, total\_c=hco3+h2co3, total\_p=h2po4+hpo4, 2\*total\_c+h = hco3+oh+h2po4+2\*hpo4, kc1=(h\*co3h)/h2co3, kp=(hpo4\*h)/h2po4],[hco3, h2co3, h2po4, hpo4, h, oh]));

This is the solution obtained for the molar concentrations(rounded for clarity):

hco3	= 1.72* <i>10</i> ^- <i>4</i>
h2co3	= <i>5.50</i> *10 <sup>-4</sup>
h2po4	= 0.00118
hpo4	= 4.64*10^-5
h	= 1.60*10^-6

The final pH of this solution is very close to 5.8 and the concentration of P is 47.9 ppm with K at 38.10 ppm. Notice however that apparent carbonic acid has a concentration of

5.50\*10<sup>-4</sup> M, which implies that the system is not at equilibrium since this amount is significantly larger than what we would expect from Henry's law. If we reduce the concentration of carbonic acid to half then the pH will increase to 6.01, as we would expect from extracting an acid from the solution. The implication is that – with time – the pH of this solution is going to slowly increase, as carbonic acid decomposes and the solution reaches an equilibrium with the atmospheric carbon dioxide level. This is also why nutrient solutions that are prepared with tap water high in carbonates and then aerated will tend to show a rapid increase in pH – even if the solution is not fed to plants – as the reaching of equilibrium is accelerated by the agitation of the solution and the contact with air (that allows  $CO_2$  in solution to escape).

As soon as the above solution is prepared it offers a substantially superior buffering capacity when compared with a solution containing only phosphates. This is why water with high alkalinity tends to provide better pH stability in drain to waste type systems when compared with solutions prepared with RO water. This water contains a significant amount of carbonates that are turned into carbonic acid and bicarbonate as soon as the pH is lowered to the pH range used in hydroponics. As long as the solution is used quicker than the carbonic acid decomposes, there will be a substantial increase in pH stability.

If you are using RO water or water with low alkalinity to prepare your solutions you can obtain a similar effect by adding 100-200 ppm of potassium carbonate before you start preparing the nutrient solution, you can similarly use bicarbonate but I would recommend using potassium carbonate, as it is cheaper. It would also be advisable to use the solution as fast as possible, since time will cause the solution to reach equilibrium and the pH to increase. This effect will take much longer if the  $CO_2$  concentration is higher – which is true for setups that use enriched  $CO_2$  – or if the temperature is lower, which increases the solubility of  $CO_2$ .

### A guide to different pH down

### options in hydroponics

The control of pH in hydroponic nutrient solutions is important. Plants will tend to increase the pH of solutions in most cases — as nitrate uptake tends to dominate over the uptake of other ions — so most growers will tend to use pH down much more than they use pH up. While most growers prefer to use concentrated strong acids, there are a wide variety of different choices available that can achieve different outcomes at different cost levels. In this post I want to talk about different pH down options in hydroponics, along with some of their advantages and disadvantages.



Hydrangeas change color as a response to different pH values in soil

The first group of pH down chemicals are strong acids. These are technically acids with very low pKa values, meaning they react instantly with water to generate at least one mole of hydronium for each mole of added acid. They offer the strongest ability to drop pH per unit of volume, which makes them more cost effective. However the fact that they often need to be diluted to make the pH addition process practical – because of how much the concentrated forms can change pH – can make their use more difficult than other forms of pH down. These are the most common options:

Phosphoric acid (from 20 to 85% pure): This acid doubles as a

plant nutrient, meaning plants will be affected by the phosphorus added. It is commonly used in food — so food grade phosphoric acid can be bought cheaply — it also has additional deprotonations with strong buffering at a pH value of 7.2 with buffering capacity against bases getting stronger as the pH goes down all the way to 6.2. This is the most commonly used acid by hydroponic growers.

Sulfuric acid (from 20 to 98% pure): This acid is commonly used in car batteries and offers the largest pH dropping ability per unit of volume among all the strong acids. It is however important to use food grade sulfuric acid in hydroponics as normal battery acid can include some metallic impurities - from the fabrication process of sulfuric acid that might negatively affect a hydroponic crop. Food grade sulfuric acid is safe to use in hydroponics. A big advantage is that plants are quite insensitive to sulfate ions - the nutrient provided by sulfuric acid - so adding sulfuric acid does not really affect the nutrient profile being fed to the plants. Note however that most battery acid products in developed countries are also ok, as the quality of these acids demands the metallic impurities (more commonly iron) to be quite low. If in doubt, you can do a lab test of the sulfuric acid to see if any impurities are present.

Nitric acid (from 30-72% pure): This acid also provides nitrate ions to plants, so it also contributes to a solution's nutrient profile. It is however more expensive than both phosphoric and sulfuric acids and more heavily regulated due to its potential use in the fabrication of explosives. The acid itself is also a strong oxidant, so storage and spillage problems are significantly worse than with phosphoric and sulfuric acid. Although this acid can be used in hydroponics, it is generally not used by most growers due to the above issues.



Diagram showing the dissociation of a strong vs a weak acid The second group of pH down chemicals are weak acids. These are acids that do not generate at least one mole of hydronium ions per mole of acid when put in solution, but do provide a pH down effect as some hydronium ions are generated. This means that larger additions will be needed to cause the same effect but at the same time their handling is usually much safer than for strong acids. Here are some options that could be used as a pH down.

**Common food grade organic acids (citric acid, acetic acid, etc):** Organic acids are a very low cost way to lower the pH of a hydroponic solution as many of these are available off the shelf in super markets in food grade qualities. The main issue with organic acids – which anyone who has used them has probably experimented – is that the effect of the acids does not seem to hold (pH goes up quickly after the acid is added and the solution comes into contact with plants). This is actually caused by the fact that plants and microbes can actually use the conjugated bases of these ions nutritionally, causing an increase in pH when they do so. The initial addition of say, citric acid, will drop the pH – generating citrate ions in the process – these will then be absorbed by microbes and plants, increasing the pH again rapidly. *The use of these acids is therefore not recommended in hydroponics*.

**Monopotassium phosphate (MKP)**: This salt contains the first conjugate base of phosphoric acid and is therefore way less acidic than it's full on acid partner. Since it's a solid its addition is way easier to control compared to the acid and it can also be handled safely with minimal precautions. It provides both potassium and phosphorous to a solution – both important nutrients – and therefore needs to be used carefully when used as a pH down agent (as it significantly affects the nutrient profile of the solution). Since it adds both a cation that helps counter pH increases by plants and phosphate species it provides a double buffering effect against future pH increases. It is a very common ingredients of commercial pH down solutions for this reason.

**Monoammonium phosphate (MAP)**: Similar to the above, except for the fact that this salt adds nitrogen as ammonium, which is a nitrogen form plants are very sensitive to. Plants will uptake ammonium preferentially over any other cation, so MAP provides a very strong buffering effect against nitrate absorption, with potential problems if too much is used (although this depends on the plant species being grown). When MAP is used as a pH down its addition therefore needs to be carefully controlled in order to avoid excess usage. Due to the presence of this powerful ammonium buffer, MAP is generally very effective at preventing future increases in pH, although this might be at the expense of yields or quality depending on the crop.

**Potassium bisulfate:** This salt contains the first conjugate base of sulfuric acid and is therefore a powerful tool to decrease the pH of a solution. The resulting sulfate ions provide no chemical buffering effect, so the only buffering effect in terms of plant absorption comes from the addition of potassium ions, which can help mitigate nitrate absorption. This salt is also considerably expensive compared with the two above – which are commonly used fertilizers – and is therefore seldom used in hydroponics.

Which is the best pH down solution? It depends on the characteristics of the growing system. Generally a pH down solution needs to be easy to administer, cheap and provide some increase in buffering capacity overtime – to make additions less frequent – so the pH down product or combination of products that best fits this bill will depend on which of the above characteristics is more important for each particular user.

People who use drain-to-waste systems usually go for stronger acids, since they only adjust pH once before watering and then forget about the solution. This means that additional buffering capacity in the solution is probably not going to be very important and cost is likely the most important driving factor. If injectors are used then the strong acids are often diluted to the concentration that makes the most sense for them and most commonly either phosphoric or sulfuric acids are used.

For growers in recirculating systems options that adjust pH with some added buffering capacity are often preferred, because the same solution is constantly subjected to interactions with the plants. In this case it's usually preferred to create a mixture of strong and weak buffering agents so that both quick decreases in pH and some increased protection from further increases can be given to the solution. In automated control systems using something like a concentrated MKP solution is preferable over any sort of solution containing phosphoric acid, as issues from control failures are less likely to be catastrophic.

### Nutrient solution conductivity estimates in Hydrobuddy

People who use Hydrobuddy can be confused by its conductivity estimates, especially because its values can often mismatch the readings of conductivity meters in real life. This confusion can stem from a lack of understanding of how these values are calculated and the approximations and assumptions that are made in the process. In this post I want to talk about theoretically calculating conductivity, what the meters read and why Hydrobuddy's estimations can deviate from actual measurements.

Calendary	Norma		Farmela	Manage (and 100 all the film of here all	Descention Cost
Substan	ce ivame		Formula	Mass (g) [Edit to fine-tune	Preparation Cost
Yara Cald	tium Nitrate		Yara_Ca(NO3)2	1028.04	102.8
Potassiu	m Nitrate		KNO3	491.68	49.2
Potassiu	m Monobasic Phosph	ate	KH2PO4	148.47	14.8
Magnesium Sulfate (Heptahydrate)		irate)	MgSO4.7H2O	486.815	48.7
Boric Acid			H3BO3	2.86	0.3
Iron EDTA			Fe(EDTA)	19.231	1.9
Copper	Sulfate (pentahydrate		CuSO4.5H2O	0.079	0
Zinc Sulf	Zinc Sulfate (Dihydrate) ZnSO4.2H2O		ZnSO4.2H2O	0.151	0
Sodium Molybdate (Dihydrate) Na2MoO4.2H		Na2MoO4.2H2O	0.025	0	
Mangan	ese Sulfate (Monohyd	rate)	MnSO4.H2O	1.538	0.2
	2101105	2.570	., .,.		
N (NO3-)	216.165	2.9%	+/- 0%		
К	232.791	-0.9%	+/- 0%	Values calculated for the p	reparation of 1000
P	232.791 33.789	-0.9% 9%	+/- 0% +/- 0%	Values calculated for the p liters	reparation of 1000
K P Mg	232.791 33.789 48	-0.9% 9% 0%	+/- 0% +/- 0% +/- 0%	Values calculated for the p liters	reparation of 1000
K P Mg Ca	232.791 33.789 48 195.328	-0.9% 9% 0% -2.3%	+/- 0% +/- 0% +/- 0% +/- 0%	Values calculated for the p liters	reparation of 1000
K P Mg Ca S	232.791 33.789 48 195.328 63.661	-0.9% 9% 0% -2.3% -0.5%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0%	Values calculated for the p liters	reparation of 1000
K P Mg Ca S Fe	232.791 33.789 48 195.328 63.661 2.5	-0.9% 9% 0% -2.3% -0.5% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1%	Values calculated for the p liters	reparation of 1000
K P Mg Ca S Fe Zn P	232.791 33.789 48 195.328 63.661 2.5 0.05	-0.9% 9% 0% -2.3% -0.5% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1% +/- 6.6%	Values calculated for the p liters	reparation of 1000
K P Mg Ca S Fe Zn B Cu	232.791 33.789 48 195.328 63.661 2.5 0.05 0.5 0.05	-0.9% 9% 0% -2.3% -0.5% 0% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1% +/- 0.1% +/- 6.6% +/- 0.4%	Values calculated for the p liters Predicted EC Value	reparation of 1000 Stock Solution Analysis
K P Mg Ca S Fe Zn B Cu Mo	232.791 33.789 48 195.328 63.661 2.5 0.05 0.5 0.05 0.02 0.02	-0.9% 9% 0% -2.3% -0.5% 0% 0% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1% +/- 0.1% +/- 0.4% +/- 0.4% +/- 12.7%	Values calculated for the p liters Predicted EC Value	reparation of 1000 Stock Solution Analysis
K P Mg Ca S Fe Zn B Cu Mo Na	232.791 33.789 48 195.328 63.661 2.5 0.05 0.5 0.02 0.01 0.01 0.005	-0.9% 9% 0% -2.3% -0.5% 0% 0% 0% 0% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1% +/- 0.1% +/- 6.6% +/- 0.4% +/- 12.7% +/- 39.7% +/- 0%	Values calculated for the p liters Predicted EC Value EC=1.8 mS/cm	reparation of 1000 Stock Solution Analysis
K P Mg Ca S Fe Zn B Cu Mo Na Si	232.791 33.789 48 195.328 63.661 2.5 0.05 0.5 0.02 0.01 0.001 0.005 0 0	-0.9% 9% 0% -2.3% -0.5% 0% 0% 0% 0% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1% +/- 0.1% +/- 6.6% +/- 0.4% +/- 12.7% +/- 39.7% +/- 0%	Values calculated for the p liters Predicted EC Value EC=1.8 mS/cm	reparation of 1000 Stock Solution Analysis Nutrient Ratio Analysis
K P Mg Ca S Fe Zn B Cu Mo Na Si Cl	232.791 33.789 48 195.328 63.661 2.5 0.05 0.5 0.02 0.01 0.005 0 0 0 0 0 0 0 0 0 0 0 0 0	-0.9% 9% 0% -2.3% -0.5% 0% 0% 0% 0% 0% 0% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0.1% +/- 0.1% +/- 6.6% +/- 0.4% +/- 12.7% +/- 39.7% +/- 39.7% +/- 0%	Values calculated for the p liters Predicted EC Value EC=1.8 mS/cm	reparation of 1000 Stock Solution Analysis Nutrient Ratio Analysis
K P Mg Ca S Fe Zn B Cu Mo Na Si Cl Mn	232.791 33.789 48 195.328 63.661 2.5 0.05 0.5 0.02 0.01 0.005 0 0 0 0 0 0 0 0 0 0 0 0 0	-0.9% 9% 7% -2.3% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0% 0%	+/- 0% +/- 0% +/- 0% +/- 0% +/- 0.% +/- 0.1% +/- 6.6% +/- 0.4% +/- 12.7% +/- 39.7% +/- 0% +/- 0% +/- 0%	Values calculated for the p liters Predicted EC Value EC=1.8 mS/cm Detailed Per Substance C	reparation of 1000 Stock Solution Analysis Nutrient Ratio Analysis

Standard Hoagland solution calculation using HydroBuddy with a set of basic chemicals.

The images above show the use of HydroBuddy for the calculation of a standard Hoagland solution for a 1000L

reservoir. The Hoagland solution's recipe is expressed as a series of elemental concentrations, all of them in parts per million (ppm) units. The results show that the final conductivity of this solution should be 1.8 mS/cm but in reality the conductivity of a freshly prepared full strength Hoagland solution will be closed to 2.5mS/cm. You will notice that HydroBuddy failed to properly calculate this value by an important margin, missing the mark by almost 30%. But how does HydroBuddy calculate this value in the first place?

Conductivity cannot be calculated by using the amount of dissolved solids in terms of mass because charges are transported per ion and not per gram of substance. To perform a conductivity calculation we first need to convert our elemental values to molar quantities and then associate these values with the limiting molar conductivity of each ion, because each ion can transport charge differently (you can find the values HydroBuddy uses in the table available in <u>this</u> <u>article</u>). This basically means we're finding out how many ions we have of each kind and multiplying that amount by the amount each ion can usually transport if it were by itself in solution. The sum is the first estimate in the calculation of conductivity.



Conductivity calculations carried out by HydroBuddy, also

showing conductivity contributions per ion. This is done by converting ppm quantities to moles, then multiplying by limiting molar conductivity values here.

The image above shows the result of these calculations for an example with a perfectly prepared Hoagland solution. You can see that the estimate from limiting molar conductivity is initially 2.7 ms/cm - much closer to the expected 2.5 mS/cm but then HydroBuddy makes an additional adjustment that lowers this down to 1.8 mS/cm. This is done because limiting molar conductivity values make the assumption of infinite dilution what the ion conducts if it were all by itself in solution but in reality the presence of other ions can decrease the actual conductivity things have in solution. HydroBuddy accounts for this very bluntly, by multiplying the result by 0.66, in effect assuming that the measured value of conductivity will be 66% of the value calculated from the limiting molar conductivity values. This is of course wrong in many cases, because the reduction in activity due to the presence of other ions is not as strong. However it can also be correct in many cases, primarily depending on the substances that are used to prepare the formulations and the ratios between the different nutrients.

In my experience HydroBuddy tends to heavily underestimate the conductivity of solutions that receive most of their conductivity from nitrates, as this example, but it tends to do much better when there are large contributions from sulfate ions. When I first coded HydroBuddy all my experiments were being done with much more sulfate heavy solutions, so the correction parameter value I ended up using for the program ended up being a bad compromise for solutions that deviated significantly from this composition. With enough data it might be possible to come up with a more advanced solution to conductivity estimations in the future that can adjust for non-linear relationships in the conductivity and activity relationships of different ions in solution.

If your measured conductivity deviates from the conductivity calculated in HydroBuddy you should not worry about it, as HydroBuddy's values is meant to be only a rough estimate to give you an idea of what the conductivity might be like but, because of its simplicity, cannot provide a more accurate value at the moment. The most important thing is to ensure that all the salts, weights and volumes were adequately measured in order to arrive at the desired solution.