Practical use of ion selective electrodes in hydroponics

The achievement of adequate ion concentrations in nutrient solutions, media and plant tissue is key to success in hydroponics. It is therefore important to measure them, so that proper values can be maintained. Up until now, this has been mostly achieved with the use of external lab testing but electrochemical developments made during the past 10 years have made the production of ion selective electrodes with high enough selectivity coefficients viable at a large scale. This means that it is now possible to obtain sensors that yield accurate enough measurements of nitrate, potassium and calcium concentrations, which allows for routine monitoring of these values without having to worry too much about complicated electrode calibration that accounts for selectivity issues. In today's article I am going to be talking about these electrodes and how they can be used in hydroponic crops.



A potassium ion selective electrode manufactured by Horiba An ion selective electrode is an electrochemical device that is sensitive to the concentration of a single ion in solution. This is commonly achieved by coating an electrode with a molecule that can uniquely accommodate that ion, so that the potential measured across that electrode and a reference electrode will change proportionally to the concentration of that ion. A pH electrode achieves this effect with glass — a pH electrode is basically an H_3O^+ ion selective electrode — while to sense other ions the use of other molecules is required. For example Valinomycin — a molecule originally developed as an anti-biotic — is able to accommodate K^+ ions very selectively, reason why an electrode coated with a Valinomycin containing membrane will be sensitive to changes in K^+ concentration.

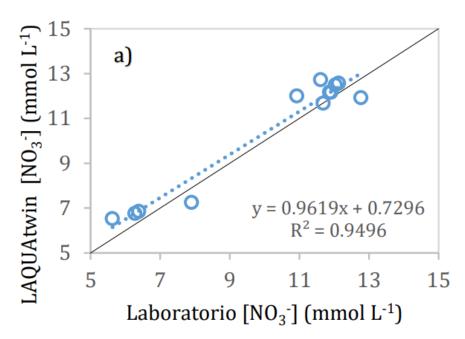
The issue with using these electrodes in hydroponics has always been two fold. First, the electrodes were commonly very expensive (thousands of dollars per electrode) and second, the selectivity of the electrodes was limited enough that the concentrations of other ions in hydroponic solutions caused substantial interference. This meant that accurate use in hydroponics required someone with analytical chemistry training that would calibrate the electrodes to variations in a single ion against a more complicated ionic background, a process which greatly limited the applicability of the technology. However, companies like Horiba have now developed electrodes that overcome both of these issues, with electrodes that have high selectivity coupled with very attractive prices. You can see Horiba's ion selective electrodes for potassium, calcium and nitrate in the links below. These electrodes are very simple to use and come with solutions to perform 2 point calibrations which are good enough given their high selectivity.

Note that Horiba is *not* sponsoring this content, but the links below are amazon affiliate links that will help support this blog at no extra cost to you, if you decide to purchase them.

- Potassium selective electrode
- Nitrate selective electrode
- <u>Calcium selective electrode</u>

Are these electrodes good enough for hydroponics? The answer is, yes! This independent <u>Spanish research thesis</u> looked at the use of two different brands of ion selective electrode for the determination of potassium, calcium and nitrate in hydroponic solutions. Their results show that the Horiba probes achieve good accuracy in the determination of all of these ions, correlating very well with lab measurements of the same nutrient solutions. With these probes you can therefore monitor the concentrations of K, Ca and N as nitrate as a function of time, giving you substantial information about the accuracy of your solution preparations and — probably most importantly in the case of Ca — information about how your water supply calcium content is changing through time, which can be very important if you're using tap water to prepare

your hydroponic solutions. The determinations are instantaneous, which gives you the ability to quickly react, without the need to wait for a long time for lab analysis to come back.



Results for lab measured Vs probe measured nitrate concentrations for hydroponic nutrient solutions using the Horiba probes.

Another very interesting use of these ion selective electrodes is for the monitoring of plant sap to measure nutrient concentrations in tissue. This can be achieved by collecting petiole tissue from mature leaves to perform an extraction — using a garlic press — which then generates sap that can be measured directly using the electrodes. This gives you the ability to perform a lot of tissue measurements, allowing you not only to look at nutrient concentrations of a single plant, but to monitor tissue concentrations from different plants or even different zones in the same plant. You can obtain results from the analysis right away, which allows for much quicker actions to be taken if required. Horiba shows some examples of how this sap analysis can be carried out here.

Although the information given by the above electrodes is not perfect, it has the advantage of being instantaneous and known to correlate very well with lab results measured using ICP.

The ability to carry out 10x more analysis and to monitor these three ions way more closely in tissue, nutrient solutions, run-off, foliar sprays, etc, opens up a lot of ways to improve crop nutrition and to see problems coming way before they become major issues. Imagine being able to monitor the K, Ca and nitrate concentration in your solutions and plant tissue daily, instead of once a week, month or even sometimes even only once per crop cycle, for a fraction of the cost.

Inner leaf tipburn in hydroponic lettuce

The most common problem I get contacted for by hydroponic lettuce growers is the appearance of inner leaf tipburn within their plants. During the past 10 years I have consulted for dozens of growers and helped many of them solve this issue. There can be multiple causes for the problem but a careful evaluation of the crop can often lead to a viable solution. In today's article I am going to talk about the main reasons why inner leaf tipburn is such a big problem with hydroponic lettuce, what can cause it and how it can be fixed.

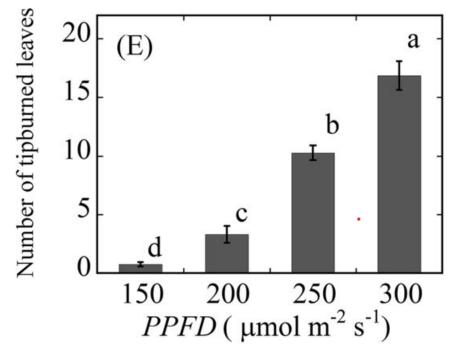


Lettuce showing classic inner leaf tipburn. Image was taken from this article (8)

What is this leaf tipburn issue? It appears as lettuce heads become adult plants, the tips of the inner lettuce leaves die off. This happens because of a lack of enough calcium at the edges of the leaves, which causes the rapidly growing tissue at the center of the lettuce head to start dying of. This does not happen at the outer leaves of the plant because these leaves get much more efficient nutrient transport, while the inner leaves receive a much more limited amount of calcium. In most hydroponic cases this is actually not related at all with a lack of calcium in the nutrient solution, but with the transport of the Calcium from the solution to the leaves. It is often the case in hydroponic crops that conditions are so favorable for fast growth that the leaves of the plant grow too fast and Calcium transport just cannot keep up (5, 6).

Due to the above it is common for measures that help with Ca absorption to also help with the elimination of this tipburn phenomenon. An effective change in the nutrient solution is to reduce the K:Ca ratio if this ratio is significantly high. Going from a solution that has a high ratio (say 3:1) to a solution with a ratio closer to 1.25:1 can heavily reduce tip

burn by reducing the competition of K with Ca and facilitating Ca transport. Making it easier for the plant to move nutrients by reducing the EC of the solution can often lead to improvements in this issue, this is both because lower EC values reduce overall nutrient absorption, making growth slower, therefore enabling the Ca to be absorbed to meet the needs of the plant. You can see experimental evidence for the two suggestions above in (1). This is why lettuce formulated nutrients will generally have K:Ca ratios close to 1.25:1 and why the EC values recommended are usually in the 1-2mS/cm range, even though higher EC levels can indeed be more productive in terms of mass produced per day.



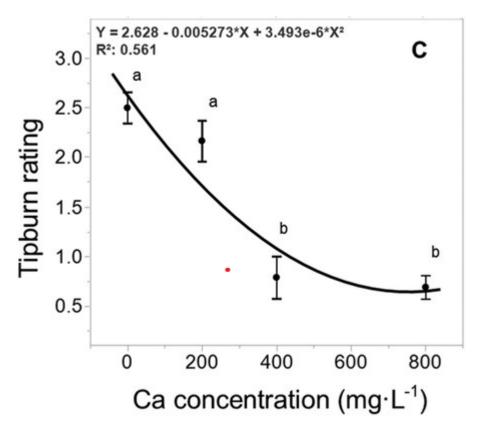
Leaves with tipburn in lettuce as a function of light intensity (taken from $\frac{2}{}$)

Since tipburn is related to how fast plants are grown, it is usually effective to reduce the light intensity in order to alleviate the tipburn problem (2). While growing lettuce at higher PPFD values can generate larger amounts of dry weight per day, it also correlates with a significantly larger amount of tipburn within the crop, precisely because growth is more aggressive. This, in combination with the fact that warmer temperatures further increase growth speed, is an important reason why there is significantly higher incidence of leaf

tipburn in lettuce for crops that are produced during the spring/summer (3).

Environmental modifications to increase Ca transport can also be quite successful at helping prevent leaf tipburn, these can be particularly important when the desire to maximize yields as a function of time is fundamental (for example when growing lettuce in space). Constantly blowing air directly into the inner leaves of lettuce plants has been shown to effectively prevent the tipburn issue, as the constant stream of air increases nutrient transport to the lower leaves, by increasing evaporation and replenishing carbon dioxide (3,4). Note that these experiments are usually done in enriched CO_2 environments, which is a modification that also helps with the issue.

One of the most practical approaches for the control and prevention of tip burn is also the application of calcium foliar sprays, with one of the most effective treatments — as it is also the case for many different crops — being the use of Calcium chloride (7). Treatments of crops twice a week with 400-800 ppm of Ca from calcium chloride can be quite effective in controlling tip burn with minimal decrease in yields. Additionally, calcium chloride can also be effective in the prevention of fungal disease which makes this proposition even more interesting. However, the use of foliar sprays like these requires a careful evaluation of the environmental conditions, as they can cause other problems if they are applied incorrectly.



Tip burn as a function of foliar Ca application rate. Taken from $(\frac{7}{2})$

In my experience, the correction of tip burn should start with an evaluation of the nutrient solution, to evaluate if enough calcium is present in solution, if the ratios of Ca to other cations, such as Mg, K and Na is correct and if salinity due to carbonates, Na, Cl or other such ions is too high. The EC can then be evaluated to determine whether it needs to be decreased to modify the growth rate and help alleviate the issue. Once the nutrient solution aspects are considered, the environmental conditions should be carefully evaluated to determine if changes to either temperature, relative humidity, air circulation, carbon dioxide concentration or light intensity are possible and if so, if they would be helpful. If the environmental conditions allow it, a foliar spray can also be formulated to supplement calcium to the crop using a highly available calcium salt — like Ca chloride — which should also help with the transport of Ca to leaf tissue.

The effect of Seaweed/Kelp extracts in plants

Few bio-stimulants are more popularly used than seaweed/kelp extracts. These are used by many growers to increase plant quality and yields, in particular, extracts from the *Ascophyllum nodosum* species are an all-time favorite of the industry. These extract have also been studied extensively for the past 40 years, with large amounts of evidence gathered about their effects and properties across several different plant species. In this article, I will be talking about what the research says about their use, why these extracts work, how these have usually been applied and what you should be looking for when using this type of bio-stimulant.

Composition of the seaweeds extracts Maxicrop and Algifert (content in mg kg⁻¹). The content of dry matter in the liquid extract of Maxicrop is 8.0-8.2%. Source: Alternatieve Landbouwmethoden (1977).

Element	Maxicrop	Algifert
N	7 200	8 700
P	9 000	1 400
K	26 000	19 000
Mg	3 500	10 600
Fe	2 200	60
Al	60	20
Ca	3 500	11 900
S	23 000	49 600
Cl	67 000	55 400
Si	1 000	1 000
Na	70 000	19 400
I	900	200
Br	800	0.6
Cu	40	0.5
Co	4	2
Ni	24	5
Zn	100	33
Mo	10	0.6
Mn	40	24
В	1	50

Composition of some seaweed extracts in 1991 (taken from (1) linked below)

The use of kelp extracts is so common, that there was already enough research done about their use to publish a review on the subject in 1991 (1), a lot of the information below comes from this source. Seaweed has been used by farmers for hundreds of years, as it could be used as an alternative to lime in order to alkalinize acidic peatmoss soils, due to the high basicity of seaweed extracts (as some are very high in calcium carbonate content). Seaweed extracts also contain a lot of micro and macro nutrients — as shown above — in proportions that are useful for their use as fertilizer. They

are a significant source of potassium and calcium, although the variability of the composition — as shown in the table above — can be quite important. They also contain micronutrients but their low presence relative to plant needs implies that the positive effects of the extracts are most likely not due to them.

Perhaps one of the most important factors surrounding seaweeds is their content of bioactive molecules. These extracts contain an important array of cytokinins, which are plant hormones that will significantly affect plant growth. Auxins, gibberillin-like substances and ethylene precursors like aminocyclopropanecarboxylic acid, have also been detected in seaweed extracts. The cytokinins are usually present in concentrations of around 2-20 ppm in the concentrated extracts, which are enough to cause effects, even if the final diluted versions will be at much lower concentrations. The application of seaweed extracts is usually done through an entire crop cycle and is usually cumulative in nature.

Application rate, frequency, seaweed species and extract processing methods can substantially affect results, with many contradictory results showing up in the literature, with some people showing increases in growth and yields while others show no effects at all. The review quoted above describes many examples of positive results, including examples showing weight gains, yield gains and increases in certain nutrients, like P and N. The review also talks about the ability of seaweed extracts to increase resistance to pests and improve crop quality. A more recent review from 2014 ($\frac{2}{2}$) further expands on a lot of these positive effects, citing extensive literature showing increases in yields, dry weights and quality for a wide variety of plant species. In total, more than 30 different papers showing increases in yields due to the use of kelp extracts are cited in this review. There are also more than 20 articles cited describing increases in disease resistance or other mechanisms of defense elicitation due to the use of the seaweed extracts.

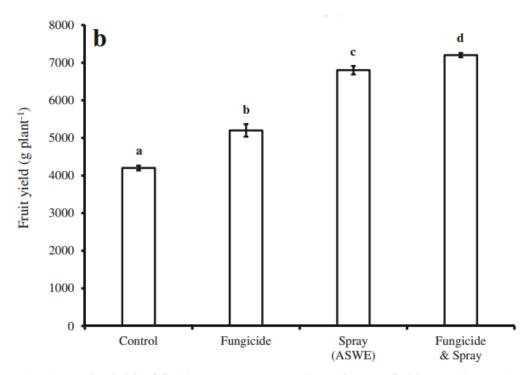


Fig. 2 Fruit yield of field-grown tomato plants from **a** field experiment 1, 90 days after transplantation with eight treatments including seaweed extract made from *A. nodosum* (ASWE) at a concentration of 0.2 % and **b** field experiment 2, 120 days after transplantation with four treatments, including ASWE at a concentration of 0.5 %. Yields are g plant of fresh weight accumulated over several harvests. Data are means \pm SE (n=30 plants); different letters according to Fisher's Least Significant Difference (LSD) test (P=0.05); LSD is 372.3 and 306.1 for **a** and **b**, respectively

Results of a seaweed extract application in tomatoes (taken from (3))

Foliar applications of seaweed can be carried out at varied levels of frequency and concentration. Applications at a 0.2-0.5% w/v of dry extracts are most common, although higher or lower concentrations have also been found to be effective. As a root drench applications will tend to be on the lower side, as the seaweed contains a substantial amount of NaCl, which can be damaging to plants. Timing of applications can also be quite critical, some growers apply the extract equally spaced through the entire growing periods, while others attempt to time the application with a specific growth phase. Success is reported in both cases, although papers that describe different timing of single applications often find

significant differences. To arrive at the optimal usage for a plant species it will be necessary to carry out tests with single applications at different intervals, although single weekly applications are likely to be successful if a less involved approach is desired.

Although the use of seaweed extracts can be very positive, it is also worth mentioning that it is very dependent on the quality and consistency of the extract being produced. Since we know that most of the positive effects of these seaweeds are related to their plant hormone content, their use can sometimes be replaced with specific applications of plant hormones, if the effects are properly understood. The discussion in (2) cited before points to the fact that kinetin applications have been able to match the effects of kelp extracts, at a fraction of the cost and the environmental impact at least in a few cases.

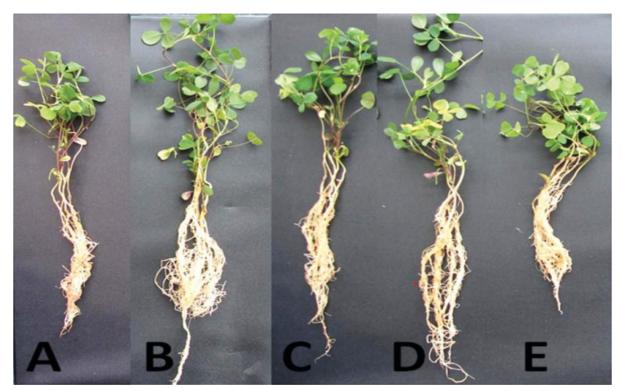


Fig 1: Effects of 1 g L"1, *Ascophyllum nodosum* extract (ANE) and its organic sub-fractions on root nodulation growth and development of alfalfa plants 6 weeks after the treatment: (a) control, (b) *Ascophyllum nodosum* extract (ANE) (c) methanol extract, (d) chloroform, and (e) ethyl acetate. (Khan *et al.* 2013).

Photographs showing the effect of kelp extract on root nodulation in alfalfa. Taken from this review (4)

With all the above said, it is quite evident that kelp/seaweed extracts have been widely confirmed to have positive effects in the growing of plants, beyond any reasonable doubt. This effect is mostly related with the hormones they contain and is therefore dependent on the seaweed species, where it is grown and how the seaweed powder is generated. Although root and foliar applications of kelp can both be used to improve results, the use of foliar applications is often favored in order to avoid the introduction of some undesired ions into the growing media. If you're not using kelp, go ahead, it's bound to help!

Characterizing hydroponic stock nutrient solutions

I've written several articles in the past about how to characterize concentrated hydroponic nutrient solutions using simple yet highly accurate small scale methods. I have now released a video showing how this is all done in practice, using the B solution I showed how to prepare in a previous video.

Why are different hydroponic formulations required for different situations?

Hydroponic growers tend to have very different experiences with nutrient solutions. It is not uncommon to find a grower who "swears" by product A and another who says product A delivers terrible results but product B is "the best". This causes a lot of confusion among new growers since there doesn't seem to be any agreement about what the "best formulation" is. Shouldn't we know by now what the "best nutrients" are? Given how many crop cycles are grown each year and how many iterations growers go through, you would think it would be only a matter of time before we know for certain how to create the "perfect recipe" to maximize yields and minimize problems and diseases. Why haven't we achieved an optimal formulation for each plant species? The answer, is that

nutrition is not only about nutrients and optimal nutrients are only optimal for a very specific set of conditions.



Commercial hydroponic fertilizer manufacturers would want you to believe that they have figured it out. They have a given set of formulations for people using Coco, another for people using rockwool, some for hard water, some for soft water, a whole array of different products to choose from where you will certainly find one that suites your needs if you just follow their guidelines. However, these different products are formulated using very broad assumptions, for example that the Coco you use required initial pretreatment with Ca salt or that your input water will contain substantially large amounts of Ca and Mq, because it's a "hard water" formulation.

Commercial products are also often made with implicit assumptions that depend on the experience of the people formulating the nutrients. For example a nutrient manufacturer might formulate nutrients that delivered excellent results while working at high VPD conditions, without realizing this was even the case. Another might formulate nutrients for the entire opposite case. A person testing a product might also like to only irrigate to a small amount of run-off, while another will irrigate till a large amount of run-off is collected. All these things affect the concentrations of nutrients the plants are exposed to, because they

fundamentally affect the amount of water that the plants have access to and the transpiration demand the plant is subjected to.

This is why a grower might swear by a given nutrient formulation and be completely right in that it delivers amazing results, while another will find this formulation just gives mediocre results with a bunch of nutrient deficiencies. The temperature, humidity, media, irrigations per day, irrigation volumes, input water composition and nutrient ratios, all play a role in determining whether the plant is able to properly uptake nutrients and whether these nutrients are ideal for this case. I've seen a person using a low K, low Ca formulation for rockwool with pretty limited irrigations be quite successful with it, while another using the same formulations under high irrigation volumes had substantial problems. The first person was relying on large dry-backs to increase oxygenation and increase nutrient concentrations to a point that suited the plants very well, the second person failed with this formulation because nutrient concentrations were too low and were never able to reach the same values they reached for the first one with increased irrigation volumes and frequencies.

Nutrient	Hoagland & Arnon (1938)	Hewitt (1966)	Cooper (1979)	Steiner (1984)
	mg L-1			
N	210	168	200-236	168
P	31	41	60	31
K	234	156	300	273
Ca	160	160	170-185	180
Mg	34	36	50	48
S	64	48	68	336
Fe	2.5	2.8	12	2-4
Cu	0.02	0.064	0.1	0.02
Zn	0.05	0.065	0.1	0.11
Mn	0.5	0.54	2.0	0.62
В	0.5	0.54	0.3	0.44
Мо	0.01	0.04	0.2	Not considered

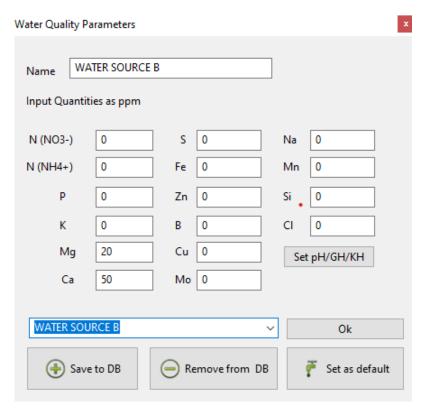
Table 2. Concentration ranges of essential mineral elements according to various authors (adapted from Cooper, 1988; Steiner, 1984; Windsor & Schwarz, 1990).

Different base solutions that have been used in hydroponic research. You can see not even research is homogeneous in terms of the nutrients used.

The development of an optimal formulation for a hydroponic crop is therefore a long process that needs to be guided by a considerable evolution from a given "good guess" base towards what is optimal for the specific conditions. More often than not, the formulation will be optimized alongside some constraints — like those dictated by climate control and light providing abilities — and will therefore be pretty tightly bound to the particular environment. My advice is to start from a good guess base, using the knowledge about the chemistry of the environment — input water, media — and to evolve that base using tissue analysis and crop yield results in order to achieve better and better results. Finding an ideal nutrient solution can take a lot of time and effort but it can substantially increase yields and improve quality levels.

How tap water affects your hydroponic nutrient formulation

Tap water is often the most reliable source of water for hydroponic growers. However, especially in the North America and Europe, tap water can contain a significant amount of dissolved solids. These substances can fundamentally affect the properties of the water and require adjusting the nutrient formulation in order to achieve proper nutrient concentrations in the final nutrient solutions. In this post I'm going to walk you through some of the most important considerations when dealing with tap water and how you should adjust your nutrient formulations to make sure that the final nutrient concentrations are adequate for plant growth.



Hydrobuddy allows you to set water quality parameters to

ensure they are taken into account within your calculations There are four important factors to consider when adjusting a nutrient formulation to your tap water.

Dissolved nutrients. Tap water often contains nutrients that are used by plants. The most common ones are Calcium, Magnesium and Iron. It is often fundamental to adjust your nutrient formulation to account for their presence. If you are using HydroBuddy to prepare your nutrient formulations you can use the "Set Water Quality Parameters" dialogue to introduce the ppm concentrations of these nutrients so that they are properly added when considering your nutrient targets. This will mean that less Ca, Mg and Fe will be added from salts, because the program will assume some will come from the water. An important fact to consider is also that the Ca, Mg and Fe concentrations in the water will tend to change with the seasons, as hotter temperatures means that underground limestone/dolomite deposits will dissolve more and therefore lead to more Ca/Mg rich water. Usually I will advice people to get two analysis - one in August, one in February - so that they can know the two extremes their formulation will be at and adjust accordingly through the year depending on the temperature of the incoming water.

Alkalinity. Your water will also contain a substantial amount of carbonates and will tend to be basic due to this reason. It is often easiest to take the amount of moles of Ca plus the moles of Mg in the water and discount this by the moles of Sulfur, then calculate how much moles of acid you will need to neutralize this amount. This makes the assumption that all Mg and Ca in the water are carbonates, except for the amount that are present as sulfates. Knowing how much moles of acid are needed to neutralize this you can now calculate how much ppm of S, N or P — depending on the acid you are going to be using — will take to neutralize the water and set this into the "Set Water Quality Parameters" box in HydroBuddy. This will account for the acid addition that will be needed to remove all

alkalinity from the water when you prepare the nutrient solution. Note that although HydroBuddy contains fields to set pH/gH/kH within the program, it actually does not take into account any of these values when calculating compensations (these are just there to store for reference).

Dissolved non-nutrient minerals. There can be a lot of minerals dissolved in the water that are not nutrients, which is why a complete chemical panel of the water is required if the water source to be used hasn't been evaluated before. In particular Na, Cl and heavy metals are the most important things to look for, as these can very negatively affect your plants. High presence of these substances will often make the water completely unusable for hydroponics, unless some specific pretreatment steps are taken to fix the issue. Make sure that the ppm of Cl are below 50 ppm, Na is below 100 ppm and all heavy metals are within quantities considered safe for human use.

×

Some typical soft/hard water concentrations of Ca+Mg

Dissolved organics. Perhaps one of the least evaluated aspects of tap water, dissolved organics can be particularly important when considering a tap water source. Substances like chloramines and herbicides can be fundamentally damaging to plant roots. While it is easy to test for oxidative substances like chloramines, normally it is hard to get a lab test for most specific organic substances, reason why the best solution for this problem is adequate pretreatment. Always make sure your tap water runs through both media — sand, ceramic — and activated carbon filters before it is used in your hydroponic crop. An adequate sterilization treatment, UV, ozone, etc, can also help reduce the risk of getting organic molecule contamination.

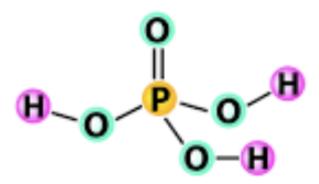
As you can see, tap water is a complex beast. Not only do we need to account for the nutrients and non-nutrients it can

contribute, but we also need to account for its alkalinity and the ways in which these three things might change through the seasons. These complications are the main reason why so many growers end up deciding to use RO water instead — higher reproducibility, less problems — but they are certainly not insurmountable. Creating a hydroponic formulation and infrastructure that accounts for these problems can lead to great cost savings, as you can save both on fertilizers — because the tap water already contains some minerals — and energy.

How much Phosphorous are you adding to your solution to adjust pH?

Phosphoric acid is one of the most commonly used pH down agents in hydroponics. This is because phosphoric acid is available in high purity, is easier to handle and has lower cost. However, phosphorous is a significant plant macronutrient as well, and substantially changing the level of available P in a nutrient solution can have negative effects on plant growth. Since many hydroponic users — especially those that use hard water sources — might be adding significant amounts of acid to correct their pH level, it is important to estimate how much phosphorous you're contributing to your solution by adjusting pH and whether this means you also need to adjust your formulation to use less P within it.

PHOSPHORIC ACID



Schematic representation of a phosphoric acid molecule.

Phosphoric acid is generally available in concentrations from 30 to 80%, most hydroponic users will use pH-down solutions that are in the 35-45% range, which are prepared to be concentrated enough to last a significant amount of time while diluted enough to allow for easier handling and to be less corrosive. You can use the equation given above to calculate the P contribution in ppm from a given addition of phosphoric acid (you can look up the density for a given concentration using this table). Adding 1mL/gal of 45% phosphoric acid will contribute around ~48 ppm of P to your nutrient solution. This is a very large amount of P considering that the normal range for flowering plants is between 30-60 ppm.

Having an excess of P can be very problematic as phosphorous can strongly antagonize certain nutrients, especially if the pH of the solution drifts up as the plants are fed. At P concentrations exceeding 120 ppm, this element can start to antagonize elements like Fe, Ca and Zn very strongly, preventing their absorption and leading to plant issues. Furthermore, excess of P can often cause problems with P absorption itself — as it can become locked up inside the plant as Fe or Ca salts — which can lead to P deficiency-like symptoms. The most tricky thing about P toxicity issues is that they do not show as certain characteristic symptoms, but

mostly as deficiencies for other nutrients or even P itself. The exact symptoms will depend on the VPD and particular environmental conditions as these play an important role in Ca absorption as well.

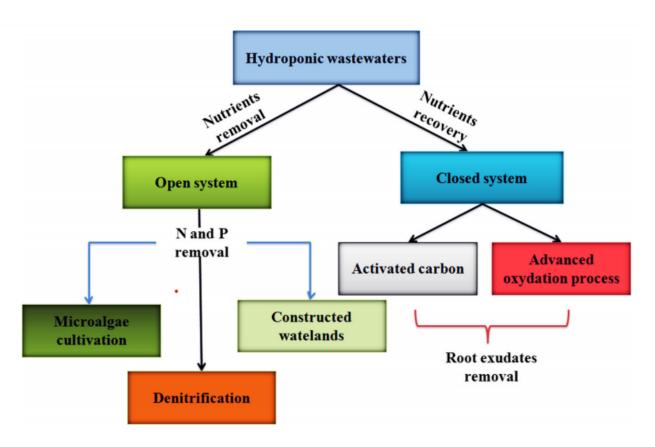
P contribution in ppm = (Acid concentration in % / 100) * 0.3161 * (volume of addition in mL) * (density of acid in g/mL) * 1000 / (total volume of solution in liters)

Many growers will indiscriminately add P without considering how much was required to adjust pH, which is a bad idea due to the above reasons. A water source that is very hard might require almost 1mL/gal to fully adjust the solution to the pH range required in hydroponics, if a normal hydroponic solution is fed — which will contain all the necessary available P (assuming the user adds very little outside of it) — then this means that the final solution might end up with P levels that will strongly antagonize several nutrients. It's therefore no wonder that many hydroponic growers in harder water areas suffer from consistent issues with Ca and Mg, many of these cases could be caused by the presence of excess P within nutrient solutions. While many hydroponic hard-water formulations will adjust for Ca and Mg in hard water, they will generally not adjust for P as they cannot know for certain how the user will lower the pH.

If you're a hydroponic grower using phosphoric acid, keeping track of how much P you're adding to your nutrient solution to adjust pH is going to be very important. If you're adding more than 0.25 mL/gal of 45% phosphoric acid — of course adjust accordingly for higher/lower concentrations — then you should consider adjusting your hydroponic formulation to account for this expected P addition and prevent your formulation from reaching abnormally high levels of P.

How to deal with nutrient solution waste in hydroponics

Hydroponic nutrients contain a wide array of chemicals that are fundamentally contaminating to water sources and can heavily contribute to <u>eutrophication</u>. Both run-to-waste and recirculating systems eventually generate significant amounts of waste as nutrient solutions cannot be infinitely used — even when recirculation is done — due to the many ways in which a solution can deteriorate (<u>see here</u>). Because of this reason, it becomes important to figure out ways to treat this waste and ensure its nutritional content is adequately reduced before it is flushed down the drain. In this post I will go through the ways in which this can be done and which might be the more practical implementations for small/medium sized hydroponic installations. A lot of the content below will be based on information obtained from <u>this review article</u> on the subject.



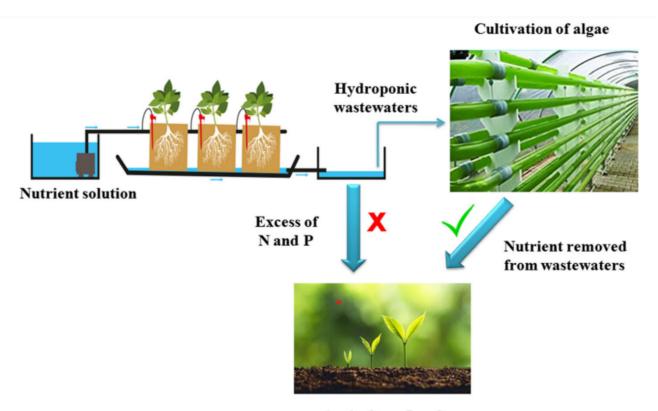
Route for the treatment of hydroponic waste waters depending on whether nutrients are to be removed or recovered (taken from the review mentioned above). Note that eventually solutions need to be changed so the disposal of nutrient solutions cannot be endlessly avoided, even in close systems.

The main problem when dealing with hydroponic waste solutions are the nitrogen and phosphorous content, as these are normally the nutrients limiting plant growth in bodies of fresh water. A hydroponic solution where most N and P is removed can be mostly considered safe for disposal as the contaminating power of the solution will be substantially lower once these two nutrients are removed. This is why most of efforts — both in the academic literature and in real life situations — are focused on the removal of these nutrients whenever nutrient solution is to be discarded. The following are the most tested methods for the treatment of hydroponic waste solutions.

Denitrification using anaerobic organisms. In this process the solution is treated with bacteria that denitrify the nutrient solution by reducing the nitrate to nitrite and then to

nitrogen gas. The process usually requires some sacrificial substance for oxidation — such as a thiosulfate or elemental sulfur granules — the process can be quite successful, removing more than 90% of the nitrogen from solutions. An issue however is that a carbon source is also needed — because the bacteria need to be fed — and this is the most important cost for this method of removal. This process also fails to address the removal of phosphorous from solution as it's mainly focused on the removal of nitrogen.

Artificial wetlands. This is the method with the lowest cost as it makes use of plants to consume all the nutrients left within the solution. It not only addresses N and P but also removes other macro and micro nutrients from the solution, generating the best effluents in terms of mineral content. Usually either common reed (*Phragmites australis*) or common bulrush (*Scirpus lacustris*) are planted and fed the waste nutrient solution so that they can process it for a predetermined period of time before the solution is fully disposed of. This process can achieve a removal efficiency greater than 90% for both N and P. Its main disadvantage is the need for a considerable amount of space and issues working when temperatures drop significantly, as these wetlands are not built inside greenhouse environments to keep costs low.



Agriculture Land

Scheme showing nutrient removal by algae. Taken from the review mentioned in the first paragraph of this post.

Algae. In the same way as artificial wetlands, microscopic algae can also remove N and P from nutrient solutions. The algae are usually grown in transparent tubes, where the waste nutrient solution is run through. The algae can be very efficient at removing these nutrients although they will not be very efficient at removing some micro nutrients from the solution. Efficiencies greater than 90% have been achieved for both N and P removal in the academic literature. These organisms can also then be harvested in order to obtain an additional product for the hydroponic installation, which gives this process the unique opportunity to add value instead of just being an additional cost to the grower. Chlorella vulgaris and Dunaliella salina are the two most studied algae species for hydroponic nutrient solution waste treatment.

Any waste treatment process will introduce an additional cost to a hydroponic crop. However this might not be optional in the future, as regulators in the US and Europe tighten their monitoring of hydroponic waste and restrict the amount of pollutants that might be dumped into the sewage system. With this in mind, it's good to start thinking about ways in which your hydroponic waste could be treated and what might be the lowest cost method to do so. If you have significant amounts of area then an artificial wetland might be the best method to follow while if you arr short on space, algae will offer you the best method to treat your solution with a small footprint. However algae also have light needs, which means you might need to provide artificial light to them if you do not have the outdoor or greenhouse space to accommodate them.

Polluting is something none of us wants to do and ensuring hydroponic waste effluents are properly and economically treated is going to be important for hydroponic cultivation to be sustainable going forward.

Factors limiting the life of a recirculating hydroponic nutrient solution

Hydroponic systems that use recirculating nutrient solutions can be more efficient in terms of water and nutrient usage. However, despite how good the management of a solution is, there are certain factors that will limit the time that a solution can be maintained without performing a full change of the entire recirculating nutrient solution within the system. By performing actions to attenuate some of these factors the life of the nutrient solution can be increased but trying to keep a nutrient solution endlessly is often impractical, both from a technical and economic perspective. In today's post I will talk about the factors that limit the life of a

recirculating nutrient solution and some of the actions that can be taken to increase the life of the solution.

Selective nutrient uptake. Plants will uptake some nutrients significantly faster than they do others. This will lead to a substantial accumulation of certain nutrients within the solution if nutrients are replenished to keep the EC of the solution constant at constant volume. Most commonly phosphorous will tend to accumulate within the solution. This is because plants will uptake this nutrient significantly slower than the others, while it will be replenished in full strength every time nutrients are added. This will tend to increase the ratio of phosphate to other nutrients, eventually causing phosphorous, calcium and magnesium issues within the solution. Micronutrients will also be replenished more than they are consumed and micros like Molybdenum and copper can dangerously accumulate in solutions that are kept for long periods of time (months).

The above is the main reason why nutrients are often replaced every 2-4 weeks in recirculating hydroponic setups. Chemical analysis can help expand this time — by allowing the grower to selectively replace only the things that have been taken — but this requires growers to have experience in the calculation and creation of nutrient formulations and to be able to effectively adapt the nutrients as required.



A small scale, recirculating hydroponic crop

Contamination by pathogens. Nutrient solutions will get contaminated by external pathogens as they recirculate and into contact with the media and the air. This contamination with pathogens might grow to the point that plants start developing disease, which can lead to substantial losses as diseases are spread incredibly efficiently within recirculating nutrient solutions. Potential solutions such as ozone and UV filtration can help eliminate the pathogens, but these oxidative actions will also destroy important aspects of the nutrient solution, such as the chelating agents that are used to wrap around heavy metal ions. This means that — as you destroy pathogens — you will lose heavy metal availability as it will become easier for the free metal ions to precipitate under this circumstances. When using in-line UV or ozone in a reciruclating environment it often becomes necessary to be careful with the analysis and replenishing of chelated heavy metals, especially iron.

Plant root system contributions (exudates). The plants will also contribute chemicals to the nutrient solution, which will increase both the carbon content and the biological activity of the nutrient solution. These substances can severely impact

the growth and development of the plants as well, as these exudates can contain hormonally active molecules that trigger biological processes within plants. You can eliminate most of these molecules by the use of carbon filters and oxidative sterilization processes but this will cause some of the same issues mentioned in the previous paragraph about pathogen contamination. Carbon filters will also need to be checked and replaced regularly otherwise they will just fill up and become ineffective.

Accumulation of non-nutrient substances. Some ions that are added with water will not be used as nutrients and will just tend to accumulate in a nutrient solution until they become poisonous to plants. The most important accumulation problems are related with sodium and chloride in regions where water contains a significant amount of these ions (like Southern Europe, see here). This is problematic because you will always tend to add these ions with new water additions, so you have limited power to control their accumulation. This might require the use of reverse osmosis systems to add water that contains low levels of these contaminants or — often way more economically — will force the replacement of the solution at some point. Note that poisonous heavy metals — like As, Hg, Cd can also accumulate with time, reason why the life of a nutrient solution should always be limited, regardless of the efforts made to never replace it. Impurities in your salt inputs can also play an important role in contributing with this non-nutrient accumulations.

I hope the above serves as a good explanation of the common factors that limit the life of a recirculating solution in hydroponics. Maintaining a recirculating nutrient solution is not just "adding water with nutrients to top it off" or "add nutrients to maintain a certain EC", it requires a substantial amount of care in the evaluation of the nutrient evolution as ions accumulate, other are used and the plants themselves also contribute their own organic molecules to change the makeup of

the nutrient solution. In most cases, the solution to just "change the solution every 2 weeks" is just the most economically viable answer but this can be undesirable if both water usage and contamination of water resources wants to be minimized. With good management, solution lifetimes can often be extended to 8-16 weeks, but going beyond that can be risky due to aspects of ion accumulation that are hard to control (as those mentioned in the last problem).

Preparing your own low cost A+B generic hydroponic nutrients at a small scale from raw salts

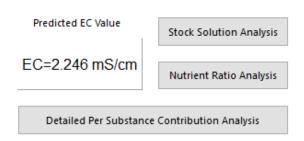
In a <u>recent post</u> about the cost of custom hydroponic nutrients, I talked about the cost of preparing nutrients equivalent to those of a commonly used brand (general hydroponics Flora series) at a small scale. We saw that the cost savings are not very significant when doing this with small amounts of salts, given that the cost of the salts only drops significantly at larger scales. However there are low cost alternatives to prepare viable hydroponic solutions. In today's post I want to write about the DIY preparation of hydroponic nutrients and how you can do this from raw salts to arrive at a generic formulation that you can use for flowering plants.

Substance Name [click for url]	Formula	Mass (g) [Edit to fine-tune]	Preparation Cost
B - Potassium Monobasic Phosphate	KH2PO4	10.985	0.5
B - Ammonium Sulfate	(NH4)2SO4	2.331	0.1
B - Magnesium Sulfate (Heptahydrate)	MgSO4.7H2O	31.694	0.1
B - Potassium Sulfate	K2SO4	25.698	0.5
B - CH - micro	Ch micro	2.225	0.1
A - Calcium Nitrate (ag grade)	5Ca(NO3)2.NH4NO3.10H2O	68.705	0.5

Element	Result (ppm)	Gross Error	Instrumental Error
N (NO3-)	158.296	0%	+/- 0%
K	235	0%	+/- 0%
P	40	0%	+/- 0%
Mg	50	0%	+/- 0%
Ca	208.863	0%	+/- 0%
S	150.686	0.5%	+/- 0%
Fe	2.492	0%	+/- 0%
Zn	0.142	0.3%	+/- 0%
В	0.463	0%	+/- 0%
Cu	0.039	0.4%	+/- 0%
Мо	0.018	-1.1%	+/- 0%
Na	0	0%	+/- 0%
Si	0	0%	+/- 0%
CI	0	0%	+/- 0%
Mn	0.712	0%	+/- 0%
N (NH4+)	20	0%	+/- 0%

Total Cost is 1.8

Values calculated for the preparation of 0.25 liters of A and 0.25 liters of B solution. Please use 4mL of A and B within every Liter of final solution



Generic A+B formulation prepared using

The formulation shown above is meant to be a low cost formulation that is close to a Hoagland solution in as many nutrient concentrations as possible, using as few inputs as possible. The concentrated solution is meant to be prepared in distilled water and it is meant to be used in RO/distilled water as no mineral contributions from the incoming water have been taken into account for its making. The solution is prepared at a 250:1 concentration factor, meaning that a gallon of A and a gallon of B can be used to prepare 250 gallons of final nutrients. This is a concentration factor pretty similar to that of the General Hydroponics Flora series, with an intended dosage of around 15mL/gal of A + 15mL/gal of B. At this dosage the EC is expected to be around 2.2 mS/cm (but this should be experimentally determined!). With 250mL of concentrated solution you can prepare up to

62.5L of final solution (~16.5 gallons).

Note that I have decided to use a "chelated nutrient mix" instead of preparing a solution adding micros one-by-one, as this is not very convenient for people new to nutrient solution preparation, plus, some micros are only available in relatively larger quantities that are unnecessary to store for someone who is only interested in the preparation of small amounts of nutrient solution. The above preparation has a cost of around 25 USD/(gal A+ gal B), which is less than one third the cost of one gallon of Flora series. This cost will be significantly lower if you buy the fertilizers in larger quantities and/or if you buy all the micros and weight them independently.

To prepare this accurately at a small scale — as shown in the image above — you will need the following materials and chemicals:

- Class A Volumetric Flask (250mL)
- Beaker set
- A scale adequate for this range (+/- 0.01g , max 500g)
- Customhydronutrients chelated micro mix
- Calcium nitrate
- Ammonium sulfate
- **Epsom Salt**
- Monopotassium phosphate
- Potassium sulfate
- Distilled water
- air-tight 250mL Glass container for storage

You can follow this process to prepare the nutrients:

- 1. Prepare a clean and dry 250mL beaker, wash with distilled water (no soap)
- Weight each raw salt on your scale, transfer to the beaker (use distilled water as necessary to ensure everything is transferred)

- 3. Add more water and heat if necessary to ensure everything is dissolved (add *less* than 200 mL of water)
- 4. Transfer the liquid to the volumetric flask (use distilled water as necessary to ensure everything is transferred)
- Take to the final volume using distilled water and homogenize
- 6. Transfer to the final storage container

I have also made a video to show you how this entire preparation process is carried out, which I will be sharing shortly! Note I used a potassium sulfate I had previously purchased, which was of significantly low purity (mined potassium sulfate), the link above is for a refined potassium sulfate source, which should give you significantly less problems than it did for me and lead to higher quality solutions (my B solution was cloudy and contained some solids, which were impurities from the potassium sulfate).

If you want to prepare these solutions at a larger scale, then you will face other problems. For example how to accurately measure the final volume of these solutions. Lines in tanks and buckets are terrible volume indicators, flow meters also are also not enough since the salts take a very significant amount of the volume as well (remember we care about the volume of water+salts!). How to properly mix, homogenize, heat and dissolve larger amounts of solution is also not trivial. These are all problems we will be discussing in future posts and videos!