Hydroponic micro and macro nutrient sufficiency ranges

When you want to prepare a nutrient solution one of the first things you want to know is which concentration ranges are appropriate for the growth of the specific plant specie you want to cultivate. You will definitely want to make sure that you do not feed either too much or too little of any of the essential nutrients a plant requires. Lucky for you there is a ton of research surrounding what we call "sufficiency ranges" in hydroponic culture. The sufficiency range of a nutrient is simply the range of concentration where a plant does not show a toxicity or a deficiency but develops in a normal manner. On this blog post we will talk about the different sufficiency ranges that are provided across the scientific literature and what they tell us about plant nutritional needs.

Table 4.3. Target nutrient levels in NFT solution in ppm. (Beam et al. 1990, Ministry of Agriculture and Food, Ontario 1988)

pН		5.5	6.0	6.5	
Conductivity (µS/cm)		1800	2000-2500	3500	
		Minimuma	Optimum	Maximum	
Nitrate nitrogen	(NO_3^N)	50	150-200	300	
Ammonium nitrogen	(NH_4^+-N)	5	10-15	20	
Phosphorus	(P)	20	50	200	
Potassium	(K)	100	300-500	800	
Calcium	(Ca)	125	150-300	400	
Magnesium	(Mg)	25	50	100	
Iron	(Fe)	1.5	6	12	
Magnesium	(Mn)	0.5	1	2.5	
Copper	(Cu)	0.05	0.1	1	
Zinc	(Zn)	0.05	0.5	2.5	
Boron	(B)	0.1	0.3 - 0.5	1.5	
Molybdenum	(Mo)	0.01	0.05	0.1	
Sodium	(Na)	_	< 30	<90	
Chloride	(Cl)	_	< 50	<150	
Sulfur	(S)	_	50-200	_	

^aThe concentrations listed as minimum are the approximate lower limit of a preferred range; in general, these minimum values are above those at which deficiency symptoms would develop

The first thing to be clear about is that there is no single "sufficiency range" table. There have been many people who have worked on this subject using different plants and each one of them will tell you that the sufficiency range is different. The above hydroponic concentration table shows you the minimum, optimal and maximum nutrient values that were determined by the Canadian ministry of Food and Agriculture using NFT systems. These requirements were determined for flowering plants - mainly tomatoes reason why you can see the optimum Ca range at 150-300 and the optimum K range at 300-500. Also notice the very high optimal Fe requirement of 6 ppm. This is almost certainly using either a form of unchelated Fe or an Fe chelate that is not so stable in the hydroponic conditions under study. The sufficiency range of micro-nutrients also depends on exactly what form of the micro nutrients you use since some forms are absorbed much more efficiently than others (it's not the same to have 3 ppm of simple Fe+2 or 3ppm of FeEDDHA).

In general you'll see that micro-nutrient sufficiency ranges have the most disparity between different sufficiency range tables. This is mainly because both the form of the micro nutrient and the specific cultivation media play a huge role in determining sufficient and toxic levels in hydroponic culture. For example a media like peat moss will contain a far greater amount of micro-nutrients than something like say, rockwool, so it is very important to account for media contributions when assessing micro-nutrient sufficiency ranges. While plants require so much macro nutrients that the sufficiency ranges are fairly coherent between different studies in the case of the micro nutrients the media choice itself could provide the entire requirement of a micro-nutrient through the plant's growth cycle.

Table 4.4. Nutrient concentrations and chemicals for tomatoes in NFT

Element	Desirable concentration (ppm)	Chemicals		
Nitrate nitrogen	150-200	KNO ₃ , NH ₄ NO ₃ , Ca(NO ₃) ₂		
Ammonium nitrogen	0-20	NH ₄ NO ₃ , (NH ₄) ₂ SO ₄		
Potassium	300-500	KNO ₃ , K ₂ SO ₄ , KH ₂ PO ₄		
Phosphorus	50	KH ₂ PO ₄ , NaH ₂ PO ₄ , CaHPO ₄		
Calcium	150-300	Ca(NO ₃) ₂ , CaSO ₄ , CaHPO ₄		
Magnesium	50	$MgSO_4$, $Mg(NO_3)_2$		
Iron	3	FeEDTA, FeEDDHA		
Manganese	1	MnSO ₄		
Copper	0.1	CuSO ₄		
Zinc	0.1	ZnSO ₄		
Boron	0.3-0.5	H ₃ BO ₃		
Molybdenum	0.05	(NH ₄) ₆ MO ₇ O ₂₄		
Sodium	Maximum 250			
Chlorine	Maximum 200			

The second image shows another sufficiency range table for hydroponic nutrients. This time we can see the source salts being used. As you can see we have a fairly good agreement in the macro-nutrients — with perhaps the exception of the ammonium minimum being set at zero — but in the case of the micros we see that the recommended amount of Fe is actually 3 ppm instead of the 6 ppm that were recommended before. This is most probably because in this case some percentage of this was given as FeEDDHA, which is much more effectively absorbed than either unchelated Fe sources or Fe EDTA. The boron range is exactly the same and this is undoubtedly because boron is always supplied in the same manner in hydroponic crops, therefore its sufficiency range tends to be coherent as long as the same plant specie is used for determination.

Macro nutrient suggestions are also not free from variations. Depending on the method used to determine the sufficiency range there can also be differences. The table below shows you yet another sufficiency range table which was geared towards maximum yields in terms of product weight. In this case You can see optimum K concentrations in the 50-200 range which is confusing given that the two tables before had suggested a much higher range of 300-500 ppm. Who is right here then? Do plants require 300-500 ppm of K for optimum growth or can they

TABLE 8.1 Ranges of the Essential Element Concentrations in Nutrient Solutions and Plant Tissues, and the Required Annual Amounts for Maximum Yields

Element	Chemical symbol	Form available to plants	Nutrient solution	Plant tissues	Annual consumption
Macroe le ments			$mg L^{-1}$	$g kg^{-1}$	kg ha ⁻¹ y ⁻¹
Calcium	Ca	Ca ⁺²	40-200	2.0-9.4	10-200
Magnesium	Mg	Mg ⁺²	10-50	1.0-2.1	4-50
Nitrogen	N	NO ₃ -, NH ₄ +	50-200	10-56	50-300
Phosphorus	P	HPO4-2, H2PO4-	5-50	1.2-5.0	5-50
Potassium	K	K ⁺	50-200	14-64	40-250
Sulfur	S	SO ₄ -2	5-50	2.8-9.3	6-50
Micronutrients			mgL^{-1}	$\mu g g^{-1}$	g ha-1 y-1
Boron	В	H ₃ BO ₃ , HBO ₃ -	0.1-0.3	1.0-35	50-250
Copper	Cu	Cu+, Cu+2	0.001-0.01	2.3-7.0	33-230
Iron	Fe	Fe+3, Fe+2	0.5-3	53-550	100-4000
Manganese	Mn	Mn ⁺²	0.1-1.0	50-250	100-2000
Molybdenum	Mo	MoO ₄ -2	0.01-0.1	1.0-2.0	15-30
Zinc	Zn	Zn ⁺²	0.01-0.1	10-100	50-500

The answer is that both can be right. Under some growing systems plants might require the solution to have more K because the setup might make K absorption harder while in other setups you might want to have lower K. This sort of contradiction surfaces constantly in hydroponic nutritional studies, simply because the variability in the subject of study (yields of a certain plant) will tend to vary very significantly depending on exactly which plant is grown and under which conditions. Just the plant and its development phase can make a huge difference in what has actually been found to work better.

Checkout for example the Israeli service recommendations for growing three different plants across their life cycle. You can see that the amount of nutrients they use can be different from what we have learned before. In this case their recommendations for all plants fall within the sufficiency ranges in the previous table but notice how for strawberry plants we use a potassium level that is at most 90 ppm while for tomatoes we go as high as 250 ppm within the fruit ripening stage. Also notice how in the case of sweet peppers the P can go as high as 150 ppm while for tomatoes we always stay within the 30-40 ppm range. If we had followed the previous recommendations we would have never considered

something like a 150 ppm of P to be an acceptable value for this element, since all of these sufficiency range studies point to the optimum P being 50 ppm. However a sweet pepper is not a tomato. In the same way that a house cat isn't a tiger.

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TABLE 8.2 Recommended Nutrient Solution Compositions Matched to the Growth Phase in Soilless Culture in Israel

Growth phase	N	P	$(\text{mg } L^{-1})$	Ca	Mg
Strawberry in greenhouse					
Transplanting	55-60	20-25	45-60	60-70	35-40
Anthesis and first fruit wave	70-85	20-25	70-90	100	45
Second fruit wave	80-85	25-30	80-90	100	45
Third fruit wave	80-85	25-30	80-90	100	45
Fourth fruit wave	55-60	20-25	55-60	80	35
Summer sweet pepper in greenhe	ouse and net-ho	use			
Transplanting to blooming	50-60	50-60	75-80		
Anthesis to fruit growth	80-100	80-100	100-120		
Fruit ripening and harvesting	100-120	100-120	140-160		
Fruit harvesting	130-150	130-150	180-200		
Fall-winter tomato					
Transplanting	80-90	30-40	120-140	180-220	40-50
Blooming and anthesis	120-150	30-40	180-220	230-250	40-50
Fruit ripening and harvesting	180-200	30-40	230-250	180-220	40-50
Fruit harvesting	120-150	30-40	180-220	180-220	40-50

Source: Israeli Extension Service Recommendations.

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So although sufficiency range tables are good to determine starting points, you should be well aware that these tables need to be considered in the context in which they were created. The plant used, the exact nutrient salts used and the growing system can all play significant roles that may cause two sufficiency studies to tell you very different things. In the end the best thing that can be done is to use the values for the plant that is taxonomically closest to the one you want to study in the system that resembles your system the most and then go from there to establish what the best values are in your particular case.

What is the effect of chloride in hydroponics?

I recently wrote <u>a post</u> about the effect of sodium ions in hydroponics and how it is important to keep an eye on sodium levels due to the potentially negative effects they can have on plants. However you may have noticed that sodium is never added alone into nutrient solutions and there is always a counter-ion that accompanies sodium, which is — more often than not — chloride. This ion is very special and it has some clear effects in hydroponic culture. Today we are going to be talking about chloride, how it can dramatically affect plants and why it does so in such a special way.

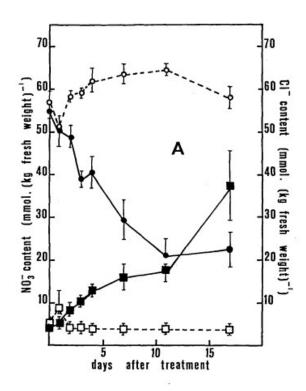


FIG. 3A: Effect of substituting chloride for ntirate in the nutrient solution on the nitrate content () and the chloride content () in leaf blades of lettuce plants, compared with the nitrate () and chloride content () of untreated plants. Light intensity: 65 W.m., temperature 17°C and rel. humidity 70%. All values are averages of 3 determinations. Vertical bars indicate + 1 SE of the mean.

Chloride — not to be confused with chlorine — is a reduced form of the element Cl, an ion with negative charge (Cl-). Unlike elemental chlorine, which is a strong oxidant, chloride is extremely inert in terms of its chemical reactivity and does not appreciably react with anything in a hydroponic nutrient solution. This however does not mean that it is inert when you put it in contact with plants, as a matter of fact chloride is a micro-nutrient — essential for plant life — but it plays such a small role that any important increase in concentration can be detrimental. Usually there is no need to add chloride but simply the chloride present in the water — or as impurities within the other salts — will be more than enough.

But what effect does chloride have? Chloride is special in that it behaves chemically in a similar way to ammonium when in contact with plants, that is, chloride can go through plant cells very easily. This means that whatever chloride you put in solution is very readily absorbed, meaning that it counteracts the absorption of other anions very strongly. This is why the expected effect of plants dropping a solution's pH due to the addition of ammonium is completely negated if instead of ammonium sulfate you add ammonium chloride. This is because you add both an anion and a cation that are absorbed very fast, hence you do not affect the cation/anion absorption balance of the plant and the pH will continue to drop or increase in exactly the same manner as before.

This anion absorption of chloride implies that it readily competes with anion absorption. This means that if you have chloride and nitrate in solution plants will tend to absorb the chloride instead of the nitrate and you will see symptoms of nitrogen deficiency — not because you don't have enough in solution — but because nitrogen absorption is being hindered by the presence of a very competitive anion. Not only this but other anions, particularly phosphates, will also suffer and therefore you will also start seeing problems with P

absorption as well. If you're interested in reading more about this I recommend <u>this chloride replacement study</u> showing the dramatic effect it has on nutrient absorption.

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In many cases, deficiency problems in salinity studies can be attributed to the action of chloride and not so much the direct action of sodium ions. See here for a study that does a direct comparison on seedlings. However since sodium and chloride are very often present in equimolar ratios it is important to always search for both to know what type of problems you are dealing with. Chloride can cause problems at much lower concentrations than sodium, with just chloride concentrations above 20-30 ppm already causing very substantial issues for a wide variety of plants. If you have chloride it is wise to consider this when gauging the concentration of the other anions in solution as their concentration will need to be increased to account for the presence of this ion.

As in the case of sodium there is not much you can do to decrease the amount of this ion in solution since almost all chlorides are soluble. Some zeolites — like <u>clinopitolite</u> — might be able to remove some of these ions from solution but the most effective method if your water contains an important concentration of chloride is to use a reverse osmosis machine.

If this is not possible — due to costs or water availability — then the best chance you have is to try to increase anion concentrations to try to compensate for chloride absorption. However this will not work if the Cl concentration is very high as the osmotic pressure will be too high for the plants to handle after compensating.

Some things you should know about sodium in hydroponics

Sodium is a ubiquitous element, you can find it in your tap water, in the sea and in most eatable foods. It is also necessary for animal life where it plays a key role in many biological processes. However — despite its overwhelming abundance — sodium is in fact not required for plant life in general (although some species, like C4 plants, do require it in small measure), meaning that it can act in a detrimental manner when present in significant quantities in hydroponic culture. Today I want to talk about what problems sodium can cause, how they can be attenuated and how we can deal with it in hydroponic crops.



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So what is the problem with sodium? Sodium in its cation form (Na+) is an extremely soluble ion with an ionic radius that is intermediate between those of lithium and potassium. Being from the same group it chemically behaves in a similar way to these two elements and can therefore act in a similar manner when in contact with plants. Sodium — when present in large enough quantities — will enter plants in significant quantities and replace potassium in some biological roles. Although this might work in your favor when potassium is scarce it does not replace it very well and ultimately costs you dearly in terms of plant growth when compared to plants grown without sodium. You can read this 1976 review for some good information about some general effects of sodium on plants.

Since sodium is so ever-present it is a significant concern in agriculture. This is a reason why there are so many salinity studies — which is what the abundance of salts like sodium chloride is usually called — often aimed at finding ways to attenuate the effects of sodium to make plants grow effectively under high salinity conditions. This is not because people will add things like table salt to agricultural crops but because many areas around the world simply don't have a choice and need to deal with higher salinity

conditions. Things like additives, substrates, irrigation cycles and light treatments are investigated to figure out how they affect plant behavior under these conditions. For example this recent study sought to find out if silica nano-particles could help with this problem (and they do!).

In your hydroponic crop sodium might be an important concern in two main ways. The first is if your water source contains a significant amount of sodium. In general sodium starts to be worrisome above 5 mM which is around 120 ppm which is the point where it can start to significantly affect yields and growth. However sodium even at 12 ppm can start having some micro-nutrient like effects, but these can be mostly beneficial in flowering plants like tomatoes and peppers, even increasing fruit quality when given in moderation (see here). However many plants are resistant to even moderate levels of sodium if these are not kept for too long so if your source water has something like 20-60 ppm of sodium (common in the US), you shouldn't really worry too much about it. In reality huge problems usually start at around 75mM of NaCl which is closer to 1725ppm of Na, although with some Na sensitive crops this might be much lower (like lettuce where 100ppm is already very detrimental to growth).



The second problem you might face only happens if you have a system that recirculates nutrient solution. Since sodium is not absorbed so readily by plants it can easily accumulate in a nutrient solution that is recirculated for a significant period of time. During one month of operation a 1 gallon per plant deep water culture system can increase the concentration from tap water 5 fold. This presents a problem since this implies that a hydroponic system that initially had 50 ppm of Na can easily end up with 250 after a single month of solution recirculation. This poses a limit to the life of a nutrient solution, even if other nutrient concentrations are adequately controlled through routine lab analysis. This means that if you want to keep solutions for longer than a few weeks you probably need to use reverse-osmosis water to avoid this problem — although more about the issue of solution life in a future post.

In the end sodium is an element that might be good to have in small measure in most cases, if you are growing C4 plants — like maize or sugar cane — then it is essential in a small amount (20-60 ppm) but you will want to avoid having sodium in any bigger amount or it can start to affect your growth. For plants where sodium isn't biologically necessary it can still provide some useful supplemental roles but in this case it might be best to keep it close to micro-nutrient levels, at 5-15 ppm. However if you are growing a halophilic plant — like say swiss chard — then you might want to have even more than 1000ppm of sodium to increase your growth (see here).

Using UV sterilization in your recirculating hydroponic crop

In general most growers want their hydroponic setups to remain fairly sterile. This is because maintaining a sterile environment discourages problems such as algae growth and can eliminate bacterial and fungal problems even before they appear. This is especially important in recirculating hydroponic setups where algae can cause important nutrient balance issues within hydroponic solutions and root pathogens can spread very quickly across an entire hydroponic operation. Today we will be talking about one of the least invasive methods to maintain sterility within a hydroponic solution, UV light.



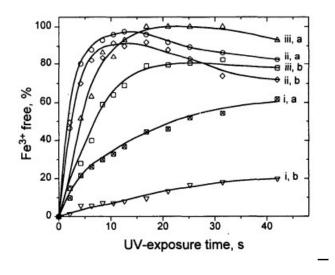
This days hydroponic growers have access to a wide variety of in-line UV lamps that can be used in all hydroponic system sizes. An inline UV lamp like the one above — which uses 18 Watts of power — can be used to effectively sterilize at a 750

GPH flow rate and can therefore provide appropriate sterilization for even moderate system sizes of 200-300 gallons. Larger inline setups also exist but if you cannot find them there is also no reason why you cannot use several of these — each one with its own pump — in order to maintain an even larger reservoir sterilized.

Research has also shown that UV light sterilization is effective in reducing bacterial and fungal populations (see here). But this research also shows that the use of UV lights also affects native bacterial populations so if you're using any type of beneficial microbes these will need to be systematically replenished to compensate for their loss due to the sterilization system. There have been some reports of 99.99% of pathogen inactivation in water in hydroponic crops when using adequate doses of UV radiation, so this is definitely a good way to keep pathogens at bay, even if it can somewhat compromise root bacteria populations.

Iron stability has also been an important concern in UV sterilization for a while. This is because UV irradiation of chelated iron species can destabilize and destroy the chelate, leading to non-chelated forms of iron that can much more readily precipitate from solution. The image below — taken from this article — shows the degradation of 3 different Fe chelates at pH values of a (3.0) and b (6.0) as a function of time. Note that the fact that free Fe is generated does not mean that the Fe is precipitated but merely that the chelate has been destroyed, which is the first step before the Fe can precipitate. From this it is clear that different chelates have very different stabilities and in this case chelate i-Fe-EDDHA had the largest stability while other chelates had much poorer stability against UV radiation.

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In the end UV sterilization offers many advantages with only a few disadvantages if the formulation is properly prepared and the crop is properly managed. Fe depletion can be a problem if chelates like EDTA and DTPA are used but this problem can be alleviated in great measure by using a chelate like Fe-EDDHA. Micro-organism depletion from the roots can also be a problem if symbiosis are important for yields but this can also be alleviated by the periodic introduction of new beneficial microbe populations within the plant root environment.

However UV is definitely not the only way to go for nutrient solution sterilization. There are other methods that can be used, some of which do not generate the problems that UV has — but different problems — and others that are less generic in their protection, implying that they must be somewhat targeted towards a particular pathogen in order to be effective. You can read this review about nutrient solution sterilization in hydroponics if you want to learn more before I post about these alternatives.

What is an ORP meter and why is it useful in hydroponics?

Hydroponic growers are used to using pH and EC meters to control their growing conditions but very few use ORP meters in order to learn more about their nutrient solution. An ORP meter can give you very useful information and cheap ORP meters can usually be bought on ebay or amazon for less than 20 dollars each. Today we will talk about ORP meters, what they are, what they are useful for and how you can use them in your hydroponic crop.



An ORP meter or "Oxidation-Reduction Potential" meter characterizes the electrochemical environment within a solution. An ORP meter has two electrodes, a traditional reference electrode with a known potential and a platinum electrode whose potential changes depending on how hard the solution is pushing either to take electrons from the platinum electron or give it electrons. A solution that has a lot of substances that are willing to give electrons will tend to

give a more negative reading and a solution that has more substances willing to take electrons will tend to give a more positive reading. The ORP reading is given in mV.

So how is this useful in hydroponics? It is useful in the sense that we can know exactly how the chemical environment is behaving. The ORP of potable water is generally around 600-700mV, this is because oxidants — substances that are willing to take electrons — are added to solutions in order to kill pathogens. The chemical environment needs to have an ORP of above 600mV to eliminate harmful fungal spores and bacteria. Of course this means that if you want to run a sterile hydroponic environment you'll want to keep the ORP of your solution probably in the 300-500mV range, large enough to prevent any micro-organisms from growing but low enough to prevent any damage from happening to your roots.

In this way you can use things like hypochlorous acid and hydrogen peroxide to increase the "killing power" of your solution while knowing how harsh you're making the chemical environment. The ORP will also give you signs about water oxygenation and biological activity within the water. A reductive environment — ORP below 100mV — will mean that there is a significant number of substances in the solution that want to give electrons and these substances are generally organic acids, bacteria, viruses or other organics molecules, like reductive sugars. If this is the case then it means that oxygen in solution has a short lifetime so you will want to increase your oxygenation significantly or your roots might be starved of this essential nutrient.

Half-Reaction	€° (v)	Half-Reaction	& (A
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^{-} \rightarrow Cu$	0.34
$\text{Co}^{3-} + \text{e}^- \rightarrow \text{Co}^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^{-} \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^{-} \rightarrow Cu^{+}$	0.10
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.0
$e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^{-} \rightarrow Fe$	-0.03
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^{-} \rightarrow Pb$	-0.1
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^{-} \rightarrow Sn$	-0.1
$^{9}bO_{2} + 4H^{+} + 2e^{-} \rightarrow Pb^{2+} + 2H_{2}O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.2
$cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.3
$2c_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cc^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^{-} \rightarrow Cd$	-0.4
$0_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^{-} \rightarrow Fe$	-0.4
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.5
$O_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.7
$8r_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.7
${}^{\prime}O_{2}^{+} + 2H^{+} + e^{-} \rightarrow VO^{2+} + H_{2}O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.8
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.1
$10_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.6
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.2
$Hg^{2+} + 2e^{-} \rightarrow Hg_{2}^{2+}$	0.91	$Mg^{2+} + 2e^{-} \rightarrow Mg$	-2.3
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^{-} \rightarrow La$	-2.3
$1g_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.7
$e^{3+} + e^{-} \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^{-} \rightarrow Ca$	-2.7
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^{-} \rightarrow Ba$	-2.9
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.9
$_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.0
$Cu^+ + e^- \rightarrow Cu$	0.52		

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The chemical environment is determined by the sorts of half reactions that can happen in solution and this is also determined by the pH of your solution. The above table shows some of the most common electrochemical half-reactions that can happen in solution. For example in order to reduce molecular oxygen and obtain 4 electrons we need to produce hydroxide ions. This means that oxidation reactions will tend to increase the pH and therefore they are expected to become harder as the pH rises. We also have the opposite case for hydrogen peroxide where a more acidic solution is bound to prevent the oxidation of peroxide to molecular oxygen. It is worth noting that these are half reactions so in reality what always happens is that two half-reactions — for example oxygen reduction and Fe oxidation — are brought together to generate a chemical change in the environment.

In the end the ORP measurement gives you something that pH and EC measurements do not tell you, which is what the chemical environment looks like from an oxidation-reduction perspective. With this information it becomes easier to tell things like whether you're lacking enough oxygenation, whether

you're adding too much hypochlorite or peroxide and whether or not you should be adding more or less microbes to your environment.

How to prepare your own solutions for EC meter calibration

On a <u>recent post</u> I talked about how you can prepare your own solutions for the calibration of your pH meter. However hydroponic growers not only need to calibrate their pH meters but they also need to use EC meters to control their growing environment. Today I want to talk about how you too can prepare solutions for the calibration of your EC meter so that you don't need to depend on expensive commercially prepared solutions for EC calibration. I will also give you some important tips about how to maintain these solutions so that they last for a longer time period.



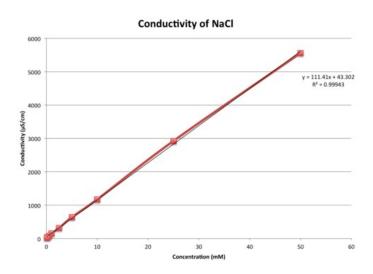
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As in the case of pH meters the correct calibration of an EC meter ideally requires the use of two solutions. Most people however use only one solution or use two solutions in a rather wide range. Ideally both solutions would need to be within the range in which we would want to measure so ideally we would want to have solutions in the 0.5-3.0 ms/cm range for the calibration of an EC meter used in hydroponic. We also need to make sure we use substances that show both a linear relationship between EC and concentration and that do not affect the pH of the solution considerably as the EC can also vary significantly with the pH of a solution.

As in the case of pH meters the easiest — but definitely not most analytically correct — way to carry out this preparation is to work with a calibrated EC meter to start with. In order to do this buy a single calibration solution so that you can ensure that your EC meter is at least calibrated properly over a single point. After the EC meter is calibrated we will use it to prepare a calibration solution with a specific EC level that we can then use for calibration. Since there is nothing special about any specific EC points — not the same case as with pH electrodes where pH 7 is the

electrodes isoelectric point — preparing EC calibration solutions is easier.

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Start with a water source — distilled would be preferred — and add around 1g per liter of NaCl, you can use any store-bought variety to carry out this process (the small amounts of additives won't affect this process significantly). This should give you a conductivity reading in the range that is generally used in hydroponics, depending on your tap water it should be somewhere between 1.5-2.5 mS/cm. You can also prepare another solution with 0.5g per liter of NaCl which should allow you to perform a two solution calibration. Note that the addition values do not need to be exact. If you are using tap water make sure you let it sit for around a day before using it so that any chlorine is eliminated from the water.

After preparing the solutions take note of their EC levels, these are the levels you will use for calibration. A problem with EC solutions is that they have a fundamental dependence on the concentration of ions in solution and cannot compensate for this so the EC values will vary and become unknown if you let the solutions evaporate. When storing EC solutions it is therefore important to use airtight containers and

additionally put electrical tape around the cap after every use, this will make sure that the loss of ions within the bottle is minimal. After some volume of solution is used make sure you discard it and never put it back inside the same bottle.

As in the case of pH meter calibration solution preparation this is definitely not the way in which these solutions would be prepared in a lab — as you can prepare solutions with extremely accurate predicted conductivity if you have very pure salts and double distilled water — but it's a very good way to create cheap calibration solutions that offer low enough errors to allow for their use in hydroponic culture.

Preparing your own buffer solutions for pH calibration

If you are interested in learning how to prepare buffers without needing a previously calibrated pH probe, please read this post.

One of the most common tasks that hydroponics growers have to carry out is to calibrate their pH meters in order to ensure that the readings are accurate. To do this it is generally necessary to buy somewhat expensive pH buffer solutions that will only last for a relatively small while before new solutions have to be bought. However the fact of the matter is that you don't need to buy these solutions forever and you can actually make your own using a few chemicals. This will be a ton cheaper than buying buffer solutions and will allow you to prepare solutions whenever you need them.

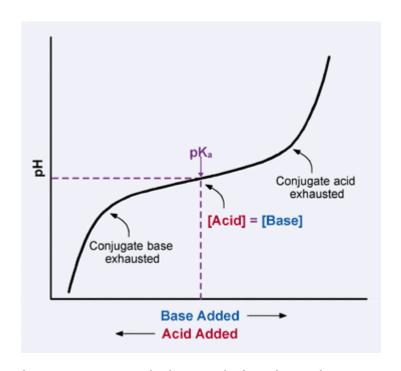


To calibrate a pH meter for hydroponics we generally need two different buffer solutions. One of these solutions needs to have a pH of 4 and another one needs to have a pH of 7. You can actually calculate the exact amount of chemicals you need to add to create these buffer solutions but this assumes that your water source is very pure (distilled water) and that your chemicals are also very pure and standardized. To make buffer solutions in less-than-ideal conditions we need to have a calibrated pH meter, which means you will need to purchase some buffer solutions, but only once.

After you have calibrated your pH meter ensure that the pH meter measures the exact value that you want to prepare within the buffer solution you have purchased. So make sure that the pH meter when placed in the pH 7 buffer solution measures 7 if this the solution you want to prepare and make sure it measures 4 when placed in the pH 4 buffer solution if this is what you want to make. Once you have the pH meter in a coherent state with the solution you want to prepare we can now proceed to make a new buffer solution.

To do this first fill a contained with tap water, make sure you don't fill it to more than 80% of its volume (to account for some volume expansion when we add the solids) and use your calibrated pH meter to measure its pH. For the pH 7 buffer add 10g of mono potassium phosphate per liter of solution (this

doesn't need to be exact) and stir the solution until it dissolves. Then add KOH slowly, add it flake by flake, while you measure the pH until your pH reaches 7.00. You will notice that as the pH approaches 7 you will need more KOH to change the pH. If you go a bit above the intended pH you can add mono potassium phosphate to decrease it to 7.00. For the pH 4 solution you can perform the same procedure but instead add 20g per liter of citric acid and then add KOH slowly to increase the pH up to 4.00. After preparation leave the buffers to rest for a few hours and measure the pH again to ensure that your solution pH remains stable. Remember to store any prepared buffers in air-tight bottles and store these bottles in dark places.



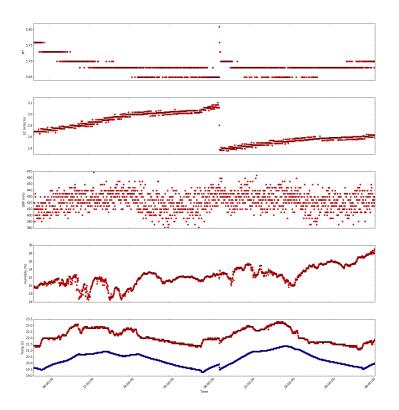
What we are doing with the above procedure is basically adding two acidic substances which have pKa values close the pH values that interest us. Close to 7 (mono basic phosphate) and close to 4 (citric acid). We then generate the necessary amount of conjugate base to reach the necessary pH level by adding KOH. The buffer strength is established by the initial amount of the acidic substance we add and the role of the KOH is basically to move the buffer pH to the point where we want it, a point that has a very high buffer capacity given the pKa values of the acids used.

Of course the above is very far form the ideal analytical procedure to prepare a buffer but it's the easiest, cheapest and most effective way to prepare a buffer that is accurate enough for pH meter calibration use in hydroponics at a minimum cost. Sure, it requires an initial pH calibration — which can be a bit inconvenient — but you can buy a small couple of buffer bottles to calibrate and then prepare 2 gallons worth of pH buffer that you can then use to calibrate your pH meters for a long time. If you use tap water to prepare the above and some solids precipitate you can filter them before storing your solutions. Then measure the pH again after filtering to ensure that everything remains stable.

Automating a hydroponic system: Sensors and monitoring

Hydroponic systems benefit greatly from gathering more information as this gives the grower the ability to better diagnose problems and better understand the evolution of their hydroponic crops. Usually growers limit the information they gather to single sensor measurements carried out either at different points during the day or even only when nutrient solutions need to be changed. These measurements are often not recorded and are difficult to analyse in a wider context. Today I am going to talk about the automation of sensors in a hydroponic crop and the benefits this can yield you in the longer term. I will give you some advice regarding how to do this and will in a later post provide some practical steps to achieve an automatically monitored setup. Below you can see a picture of the output of my home hydroponic setup monitoring

pH, EC, ORP, humidity, ambient and solution temperatures.



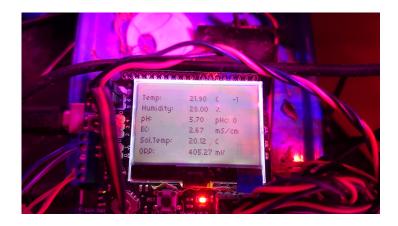
Automating sensors is not only having sensors that can take readings at predefined intervals but also making sure that the reading from these sensors are stored so that they can be used for analysis and diagnosis later on. Thankfully these days we have Arduino micro-controllers which are compatible with a wide variety of sensors that can be used for automated monitoring. We also have very cheap raspberry pi computers which we can use to store this information and build a database with our sensor information. Ideally we would like to monitor as many variables as possible but we are somewhat limited both by cost and the sensor capabilities of the Arduino micro-controllers. If you want to perform automated monitoring then you would definitely want to buy pH, EC, ambient temperature, solution temperature, humidity and carbon dioxide sensors. If you have more money or want to have more data then I would also advice getting a dissolved oxygen sensor and an ORP sensor. If you have a large grow room then you might want to place several CO2 and temperature sensors to properly monitor the entire

crop. Here is a small shopping list with sensors and micro-controllers you could use for this:

- Temperature and humidity sensor 5.20 USD
- Arduino UNO 23.90 USD
- Raspberry Pi 39.95 USD
- ORP sensor 89.05 USD
- pH sensor 56.95
- EC sensor 69.90 USD
- Arduino LCD shield 24.95 USD
- Dissolved Oxygen 257.45 USD
- Real-time clock module 13.55 USD
- CO2 sensor 56 USD

Although the LCD shield isn't really necessary for the setup it does allow you to write an Arduino program that displays readings right away. This is very useful as you can see readings as they happen within your hydroponic crop. The image below shows you how this looks like within my home hydroponic setup. In this setup I have all the sensors constantly taking measurements from the crop, which are displayed in this LCD screen. There is also a raspberry pi connected to this Arduino that records one measurement every 2 minutes. I don't record measurements any faster since this would cause the memory usage to grow very fast within the Raspberry pi without any important gains in the amount of knowledge gained from the information taken.





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It is also important to know that the sensors should be industrial quality sensors designed to be kept submerged all the time. For example the above ORP, dissolved oxygen and EC meters are not designed for being constantly submerged so after a while they will stop working and you will need to change them. However if you clean the sensors around once a week and cover the body of the sensor — especially where the cable goes out the back — with electrical tape you can significantly extend their service life. After they run out you can still use the interface to connect an industrial grade sensor. It is worth noting that all sensors can lose their calibration so you want to calibrate your pH/EC sensors at least once every month within this setup. Also when taking sensor measurements you will want to take the median of a large number of measurements (>100) in order to ensure better stability.

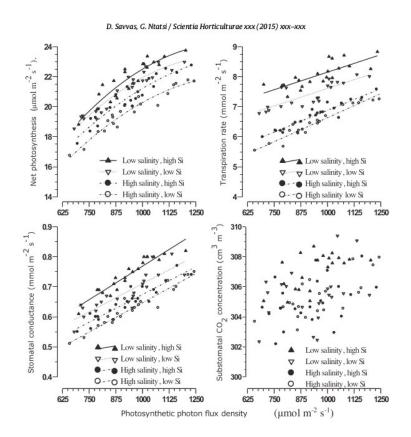
Within a followup post I will share the code I use for my automated home setup as well as some additional information dealing with the automatic use of peristaltic pumps to automatically adjust pH/EC and ORP. For a few hundred dollars automated monitoring can greatly increase your ability to understand your hydroponic crops.

Is ortho-silicic acid worth the additional expense in hydroponics?

Silicon is all the rage right now and different silicon product manufacturers are racing to produce commercial

products that contain more and more biologically active silicon. The idea is mainly that potassium silicate — the most commonly used form of silicon in hydroponics — has some problems maintaining high bioavailability at the pH levels used in hydroponics and therefore more stable silicon sources are needed to meet plant needs. However we need to ask ourselves if this is actually true and whether it is actually worth it to go to much more expensive Si sources when supplementing plants with silicon products. Today I want to talk about the Si research up until now and what it tells us about silicon and stabilized silicon products.

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Without a doubt there are some proven benefits to using silicon supplementation. As explained within this recent literature review from 2015 about silicon's role in plants the benefits from silicon application include increased photosynthesis, resistance to abiotic stress as well as

increased resistance to several fungal pathogens. It is also clear that foliar application of Silicon does not lead to large increases in tissue concentration and root applications tend to yield the biggest benefits. The above image shows some of the benefits of high (1mM) and low Si (0.1mM) treatments under different conditions for hydroponically grown Zucchini plants. The review also mentions the exploration of stabilized silicon forms and the current lack of scientific evidence regarding their efficacy when compared with traditional non-stabilized forms of silicon.

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So if silicon from potassium silicate can show benefits why may we need a better form of silicon? The problem with silicates is that under low pH values the silicate ion gets protonated and converted into silicic acid but silicic acid is unstable and will tend to polymerize and form molecules with limited bioavailability under these conditions. If we use a form of silicon that does not suffer from this problem then we might be able to get some additional benefits. There are indeed a few studies in lettuce and tomatoes showing that choline stabilize orthosilicic acid (ch-OSA) can indeed improve plant responses under Mn stress and even a study about the use of ch-OSA improving seedling growth but these results lack controls against potassium silicate so we don't know if the response would simply be equal than that of a traditional graphical silicate application. Below you can see a representation of a choline molecule's structure, choline is basically a beta aminoacid that is able to stabilize silicic acid by binding to its oxygen atoms through the positive trimethyl amine group, inhibiting polymerization.

Choline

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We know however that not all forms of stabilized silicon sources would work well. For example there is a <u>study</u> involving alkyl silicic acids (another form to stabilize silicon) that shows that the application of these compounds produces even worse results than controls with no silicon supplementation. Plants do not seem to deal well with this type of stabilized compounds, where the silicon is stabilized by the introduction of simple alkyl groups. Some of these forms of silicon — dimethyl silicic acid — were even highly toxic to plants at low concentrations.

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Up until this point there is basically no scientific evidence that shows how stabilized silicon sources like ch-OSA may provide a benefit over using a simpler and cheaper source of silicon like potassium silicate in higher plants. If potassium silicate is dissolved at the appropriate concentration and in an adequate manner then there is no doubt that it can provide significant benefits at a fraction of the cost. Companies producing ch-OSA and similar silicon stabilized sources generally say that they contain "more bioavailable silicon" and while it may be true that they may allow for the larger abundance of some silicon species in solution, what they should show is an increase in benefits when compared with a potassium silicate control since this is in the end what

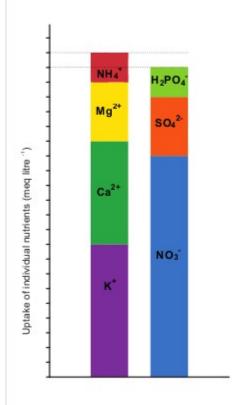
interests most hydroponic growers. While this evidence is lacking it is certainly not worth it to pay the extra cost, given that benefits using potassium silicate have been proven while benefits using ch-OSA haven't been proven to be greater than those obtained with these cheaper Si sources.

Nitrate, Ammonium and pH in hydroponics

The stability and variability of pH in hydroponic solutions has always been a complicated topic to discuss. There are many reasons why pH may change in a hydroponic system, ranging from the media being used, the micro-organisms present and the amount of carbon dioxide in the air. However the most agressive contributing factor in a healthy hydroponic system with no important pH altering media is plant nutrient absorption. Today we are going to talk about this and how the ratio of ammonium to nitrate heavily affects plant nutrient absorption.

FIGURE 6

Balance between the uptake of cations and anions by plants when the NH₄-N/total-N in the supplied nutrient solution is high, thereby imposing a higher total cation uptake in comparison with that of anions



Under these conditions, the pH in the root zone tends to decrease, because the difference between total cation and anion uptake by the plant is compensated for by release of H+ by the root cells to avoid imbalances of their electrochemical potential.

As I have discussed in the past in my blog, plants will always compensate ion absorption by releasing a pH altering ion of the same charge. If a plant absorbs nitrate (NO3-) it will release an OH- ion in order to balance the charge. This ion will increase the pH. The same happens when the plant absorbs a cation — like K+ or Ca+2 — as it will release H3O+ ions in order to compensate (one in the case of K+ and two in case of Ca+2). However plants do not absorb all ions equally and therefore if there is more cation than anion absorption pH will decrease while in the opposite case pH will increase.

The image above shows how plants usually distribute their cation/anion absorption. In the case of anions the largest contributing factor is nitrate while in the case of cations

the largest contributions come from potassium and calcium. Since adding ammonium to replace nitrate will cause the balance to shift to the cation side we can indeed cause the pH behavior to change significantly by changing the ammonium to nitrate ratio. For many plants — especially fruiting plants like tomatoes or cucumbers — the ideal ammonium to nitrate ratio has been established to be around 2:8 and this usually implies that pH will tend to increase as a function of time since the amount of anions absorbed will be larger. Using larger ammonium to nitrate ratios — like 5:5 — may bring you more pH stability but this may be at the cost of crop productivity. If you want to increase the amount of ammonium in solution ammonium sulfate (shown below) is usually the cheapest source. Adding 0.05g/L (0.18 g/gal) will increase your NH4+ concentration by around 10 ppm.

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It is also important to note that you cannot easily affect ion absorptions by shifting solution concentrations. Ammonium affects the pH quite directly because adding more ammonium to the solution almost immediately adds that ammonium to the plant's cation absorption — because it's taken up very readily — but adding other cations might not increase their absorption because either environmental or plant regulatory mechanisms may stop this from happening. For example increasing potassium

may not increase the overall size of the cation absorption column because the plant might simply compensate by reducing calcium absorption. Such a compensatory mechanism does not exist for ammonium, reason why it is so effective in changing the relative size of one column against another.

In the end the nitrate/ammonium ratio is perhaps one of the biggest weapons you have in controlling how your plants change the pH of your nutrient solution. However aiming for the most stable pH — in terms of cation/anion absorption — might not be the best bet since this might reduce your crop's yield. At optimum nitrate to ammonium concentrations most crops tend to experience some moderate pH increases as a function of time. Nonetheless different crops respond to ammonium to nitrate ratios differently so you might want to give different ratios a try to see what works best for you, both in terms of yields and easiest crop management.