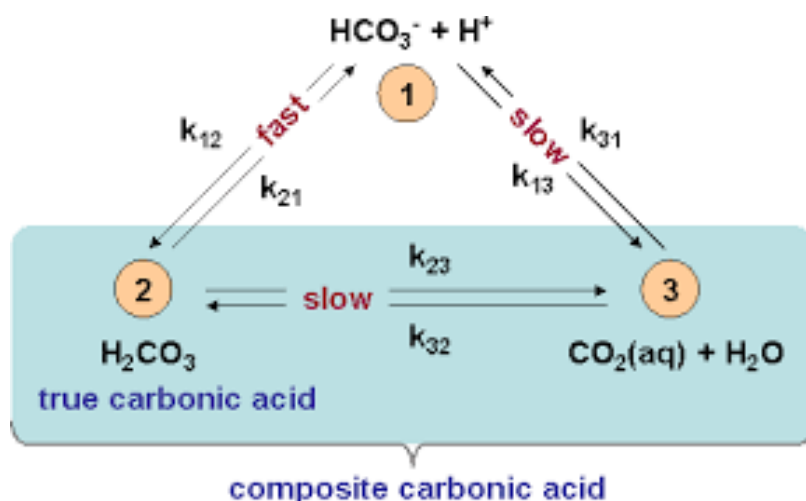# Understanding the carbonic acid/bicarbonate buffer in hydroponics

I have written several articles before about pH and it's importance in hydroponic culture ([1](#), [2](#), [3](#), [4](#)). However I have yet to write a detailed explanation of one of the most important buffering systems in hydroponics, which is the carbonic acid/bicarbonate buffer. This buffer is significantly more complicated than the simpler buffer created using phosphoric acid species, as it not only relies on ions present in solution but also on the partial pressure of carbon dioxide in the atmosphere. In this article I will attempt to explain this buffering system in detail, shining some light into the limitations of this buffer and how changing different key variables can fundamentally affect the way it works in hydroponics.

Chemical reactions involved in the carbonic acid/bicarbonate buffer. Taken from [here](#).

A buffer is nothing more than a pair of chemical species in solution that are present at a certain pH, that can react with additional H_3O+ or $OH-$ ions that are introduced into the solution. Since these ions control the value of pH, anything that prevents their concentration from changing will keep the

pH stable. Distilled water, for example, has absolutely no buffering capacity since within it there is nothing that can react with incoming H_3O^+ or OH^- ions that are added to the solution. Distilled water should therefore have a pH of 7.0, it does not because we live in an environment where an acid can always be generated from the air. This acid — carbonic acid — is generated in water whenever it's put into contact with a carbon dioxide containing atmosphere. *This makes distilled water have a pH of around 5.6*.

To be able to calculate the pH we need to consider all the chemical equilibrium reactions that happen, these are summarized [here](#) and in the image above. We must consider that carbon dioxide will dissolve in water to always satisfy Henry's law, that dissolved carbon dioxide will be in equilibrium with carbonic acid, that carbonic acid can dissociate into a H_3O^+ ion and a bicarbonate ion and that a bicarbonate ion can further dissociate into an additional H_3O+ ion and a carbonate ion. To solve all of this we must also consider that charge neutrality must be preserved, meaning that the sum of all molar charges of all positive ions must be equal to the molar charges of all negative ions. To carry out these calculations I routinely use the freely available [Maxima software](#). Below you can see the code I use to solve this system in Maxima (constants are taken from [here](#)):

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

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

This is the solution obtained for the molar concentrations

(rounded for clarity):

```
oh    = 4.21*10^-9
co3   = 4.68*10^-11
hco3  = 2.36*10^-6
h2co3 = 2.24*10^-8
h     = 2.37*10^-6
```

After executing this code you will get several different possible solutions, but the only one that interests us is the one where the H_3O^+ (h) concentration is a positive number (this solution is showed above). We can then use the pH function to calculate the value of pH for this H_30+ concentration, which gives us a value of 5.62, this matches the real measurement of a distilled water solution at 25C under a 387ppm carbon dioxide atmosphere. Note that the amount of none dissociated acid in solution is very small. Taken to mass, the concentration of carbonic acid is 0.00138 ppm. However the concentration of bicarbonate is significantly greater, at 3.6 times the concentration of undissociated carbonic acid. This explains why the pH drops so much, since a significant amount of the generated carbonic acid ends up dissociating and contributing H_3O^+ ions to the solution. This also shows you how little acid is needed to drop the pH of an unbuffered solution.

To create the buffer with the biggest possible strength we would need to add enough strong base to shift the pH to the point where the pH equals the pKa (which is just -Log(equilibrium constant)) of the joint reactions created from the reaction of carbon dioxide with water to create carbonic acid and the subsequent dissociation of this acid into bicarbonate and H_3O^+. This point is at 6.3 under atmospheric conditions at 25C. This can be achieved with the code below:

```
[kw : 10^(-14.0), kh: 1.7*10^(-3.0), kc1: 2.5*10^(-4.0), kc2: 4.69 10^(-11.0), co2: 1.32*10^-5, h:10^(-6.3)];
```

```
float(solve([hoh=kw, base+h = 2co3+hco3+oh, kh=h2co3/co2,
kc1=(hco3h)/h2co3, kc2=(co3h)/hco3],[oh, co3, hco3,
h2co3,base]));
```

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

```
oh    = 1.99*10^-8
co3   = 1.04*10^-9
hco3  = 1.11*10^-5
h2co3 = 2.24*10^-8
base  = 1.07*10^-5
```

The pH here is set to 6.3 and we can see that to get there we would need to add a base at a concentration of $1.07*10^{-5.0}$. If this base was KOH this would imply adding it at a rate of 0.6 ppm. We can see how the pH changes as a function of adding base or acid from this point. If at this point we decided to double the addition of strong base we would get to 6.57, tripling it would take us to 6.73 and adding 10 times more base would take us to 7.25. The buffer is indeed resisting the increase in pH by basically drawing CO_2 from the air to react with the incoming base as base is added to the solution. *However you might notice that under equilibrium conditions the buffering capacity of this system is very low*. Just 6 ppm of a KOH equivalent strong base addition can strongly affect the pH — taking it from 5.6 to 7.25 — so how can the carbonic acid/bicarbonate buffer be effective at all in hydroponics?

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

expected at equilibrium and it also has some interesting consequences in the use of nutrient solutions.

Let's consider a case where there is no decomposition of carbonic acid – let's suppose it's extremely slow – and say we add 100 ppm of potassium carbonate into a solution and then set the pH back to 5.8 using phosphoric acid. In this case the predominant reactions in solution would be the dissociation of dihydrogen phosphate to hydrogen phosphate and H_3O+ and the carbonic acid dissociation discussed before. In order to properly consider this case we must also introduce two additional equations, mainly the mass balance equations for the phosphate and carbonate species, since this time we are assuming no carbon dioxide is ever lost to the atmosphere. Note that I have changed the equilibrium constant for the carbonic acid reaction here to $10^{-6.3}$ where carbonic acid is now "apparent carbonic acid". You can see the equation system and solution below:

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

float(solve([h*oh=kw, total_c=hco3+h2co3, total_p=h2po4+hpo4, 2*total_c+h = hco3+oh+h2po4+2*hpo4, kc1=(h*co3h)/h2co3, kp=(hpo4*h)/h2po4],[hco3, h2co3, h2po4, hpo4, h, oh]));

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

hco3 = 1.72*10^-4
h2co3 = 5.50*10^-4
h2po4 = 0.00118
hpo4 = 4.64*10^-5
h   = 1.60*10^-6

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

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

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

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

— which is true for setups that use enriched CO_2 — or if the temperature is lower, which increases the solubility of CO_2.

# Controlling pH in hydroponics using only electricity

The ability of plants to assimilate nutrients changes as a function of pH. This makes maintaining the pH of nutrient solutions within an acceptable range — most commonly 5.8 to 6.2 — one of the most important tasks in a hydroponic crop. This is commonly done with the addition of strong acids or bases to decrease or increase the pH when it drifts away from the intended value. This requires either manual monitoring with careful addition of these substances or automated processes using pumps to ensure the pH always remains at the correct value. However both of these methods lack fine control, require a lot of maintenance and monitoring and can lead to costly mistakes. Today I want to discuss an alternative method that relies on a completely different idea to control pH, the idea that we can oxidize or reduce water using electricity to achieve changes in pH. **Yes, you can change pH using literally only electricity**.

A modern anion exchange membrane. Fundamental to the idea of an electricty-only pH control system

Let's start by discussing pH and talking about how it is changes. The pH of a solution is calculated as -Log($|H^+|$) where $|H^+|$ is the molar concentration of H^+ ions in solution. In water, the dissociation constant 1×10^{-14} (at 25C), always needs to be respected, so we always know that the product of $|H^+|$ and $|OH^-|$ needs to give us this number. When you add acids you increase $|H^+|$ conversely $|OH^-|$ decreases and the pH goes down, when you add bases $|OH-|$ increases, $|H+|$ decreases and the pH goes up. *In simpler terms everything you need to decrease pH is a source of H^+ and everything you need to increase pH is a source of OH^-.*

This is where electrochemisty gives us the simplest solution we could hope for. Water can be oxidized or reduced. When you run a current through water — above the minimum required voltage — water splits into hydrogen and oxygen molecules. In the image below you can see how the water oxidation reaction generates H+ ions while the reaction on the right generates OH- ions. When you do this in a single cell — as shown below — the H+ ions generated at the anode react with the OH- ions generated at the cathode and the pH of the solution remains neutral while oxygen is produced at the anode and hydrogen is produced at the cathode.

$$2 H_2O \, (l) \rightarrow O_2 \, (g) + 4 H^+ (aq) + 4 e^-$$

$$2 H_2O \, (l) + 2 e^- \rightarrow H_2 (g) + 2 OH^- (aq)$$
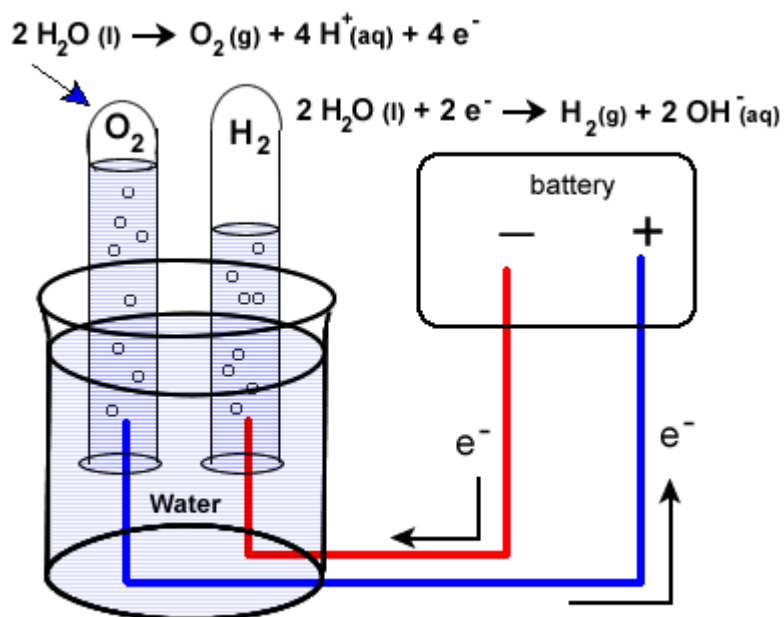
The image above shows the half reactions involved in the oxidation (left) and reduction (right) of water.

However, we can take advantage of ion exchange membranes to separate these two processes, allowing us to control where each reaction happens and where the acid or base is generated (preventing them from just mixing and neutralizing). As a matter of fact, all we need is to have an electrode in our nutrient solution and another electrode in an auxiliary cell, separated from our nutrient solution by an ion exchange membrane. This concept is actually not new and was already proposed in a 1998 paper to control pH in hydroponic systems. Although it was never tried in a production system, all the concepts were validated and were shown to perform adequately in test solutions.
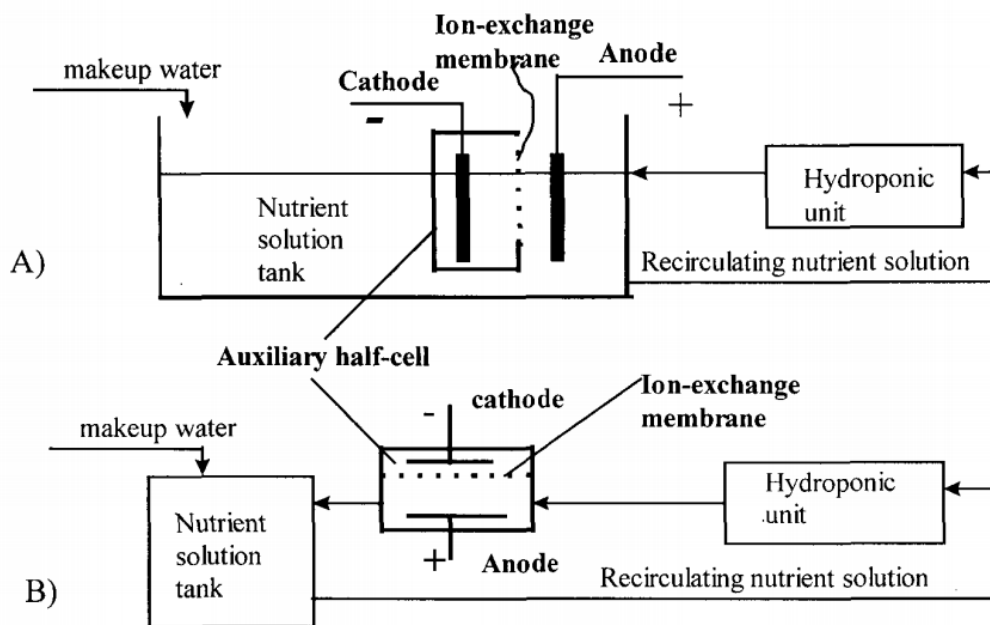
Image taken from [this paper](#), which discussed the topic of electrochemical pH control in hydroponic systems at length.

One of the big challenges of this setup is that the cathode side involves hydrogen gas evolution — which could be dangerous — but can be completely avoided by replacing the cathode's half reaction with much more benign chemistry. As an example — also suggested in the paper above — you can replace the cathode half-cell with a copper sulfate solution with a copper electrode, with an anion exchange membrane. This would allow you to have your reduction reaction be the reduction of copper onto a copper place, which is a very tame reaction. Since the membrane only exchanges anions you would only have sulfate go to your nutrient solution, which is a benign anion in hydroponic culture. This of course means that your half-cell electrode and solution would need to be replaced with time, but this is completely independent from the control process (much more like refilling a tank of gas). The anode would only evolve oxygen in your nutrient solution, which is a potentially beneficial side effect.

Using a copper sulfate half-cell would however limit the control system to lower pH but this is not a problem since this is the most commonly used operation in hydroponics (very rarely do people have to increase the pH of their solutions).

If a proper venting system or catalytic recombination system is used on the cathode side you could also go with the simple water oxidation/reduction route and be able to increase or decrease the pH using basically, pure electricity.

I am definitely planning to build one of this setups in the future. Coupled with modern sensors and micro controllers this could make it extremely easy to maintain very fine control over the pH of the solution, compensating — in real time — all the changes in pH carried out by plants without the risk of heavily over or under compensating (as it happens when you use acid/base additions).

Better understanding pH dynamics in hydroponic culture

Plants require specific conditions within their root zones to give optimal yields. The negative of the logarithm of hydronium concentration (a.k.a pH) is a very important measurement that tells us if the root zone is too acidic or too basic for our plants. However pH is affected by many different variables, making the calculation, theoretical understanding and modification of this variable difficult — and often very puzzling — for a significant percentage of growers. Today I want to go into how we can understand these pH changes from a qualitative perspective to get an idea of how pH can be expected to change in solution if we modify one variable within our hydroponic crop.

The final pH in the root zone of a hydroponic crop will mainly depend on the following factors: Chemical species in solution, plant absorption/secretion and media reactions. Basically we need to consider the chemistry of the solution, the way plants absorb nutrients and the chemistry of the media. The size of these effects relative to one another is also very important to consider.

In a normal hydroponic crop with a nitrate rich solution plants will tend to absorb more nitrate than any other ion, which will tend to increase pH as plants will excrete bases when they take anions in. Since the effect of nitrate in pH is very small the net effect is a substantial increase in the pH of the nutrient solution. Anions like citrate can also cause increases in nutrient solution pH due to a similar reason, they can be strongly taken in by plants and generate upside drifts.

Model of a citrate ion molecule.

The effect of anion absorption can be offset by acids present in solution. Phosphorus is most commonly present in hydroponics at a pH of 5.8-6.2 as $H_2PO_4(-)$ which is a weak acid that is able to react with the bases excreted by plants. This means that higher P containing solutions will tend to drift less towards the upside than solutions that contain more

P. This is a common reason why yields are usually better for less experienced growers when higher P solutions are used, because they are more forgiving to pH drifts due to their higher buffering capacity towards the upside at the pH used in hydroponics. When we add P the effect of the buffer is way bigger than the effect of P absorption, as P is not absorbed in very high concentrations by plants.

When you increase or decrease the concentration of an ion in solution you need to consider if it will be absorbed, how strong its absorption will be relative to other ions and how this relates to the chemistry of this ion in solution. For example citrate provides a relatively strong buffer towards both upside and downside moves at a pH of 5.8-6.2 but its absorption by plants negates this effect and generates a net drift towards the upside in solution in most cases.

Species that are not absorbed so significantly — like bicarbonate ions — are better at buffering moves towards the upside, since they provide a weak acid to react with plant secretions without providing a very significant source of anions for the plant to absorb and exchange for more basic species.

This exact same logic can be applied to positive ions that are easily absorbed by plants. Adding ammonium generally causes strong decreases in the pH due to plants exchanging ammonium with hydronium ions. However this effect can be compensated by adding things that cause upside drifts either through absorption or through buffering effects. Adding ammonium citrate to a nutrient solution causes a rather balanced effect due to both the ammonium and citrate absorption/buffering compensating.

The media is also very important to consider as non-neutral behavior will tend to strongly drift pH due to the mass of the media within the hydroponic setup. To prevent this problem it is not uncommon to treat media with a buffer before use,

although this can become prohibitively expensive quickly if large volumes of media are used. It is more common to deal with the quirks of the media using nutrient solution chemistry. To get an idea of how your media affects pH you can let your media soak in nutrient solution and notice how pH evolves as a function of time. If the pH increases or decreases you'll get an idea of what you should expect and the think about how you might want to handle it.

Peat moss

Media that decompose — particularly peat moss — will tend to acidify and become more and more acidic with time. This effect can be so strong that the only reliable solution is to amend with some low solubility base that can offset this effect with time (such as limestone). This is however problematic since the base will tend to run out towards the flowering stages of crops, where its help is most needed to offset potassium absorption. For this reason it's usually more manageable to use a media like coco coir, which has a more stable pH profile and will not tend to "fight growers" through the crop cycle.

As you can see pH in hydroponics can be a complicated issue. When it starts to drift you need to immediately think about what the source of the ions is. If the pH increases you have a contribution of basic ions that exceeds the strength of the weak acids in solution, while the exact opposite is the case if the pH decreases. What is the source of these ions? Is the plant absorbing more of something? Do we need to add something to counter the effect? Is the media the culprit? Start asking and trying to answer these questions and it will become easier to understand why your pH is drifting and what you might be able to do about it.

Creating a robust pH/EC monitor for hydroponics using Atlas probes and an Arduino

A few months ago I talked about how you could build a simple sensor station for your hydroponic projects using an arduino (see [here](#)). However this small project used the relatively cheap — but I have found not very robust — pH/EC probes and boards from gravity which makes it a poorer choice for a more professional project aiming to constantly monitor the pH/EC of a production hydroponic setup. Today I am going to tell you how you can build a dedicated pH/EC monitor using the robust pH probes from Atlas, which also have several important advantages we will be discussing within this post. *I would also like to point out that Atlas is not paying me anything to write this post, I write just because of my experience using their probes.*

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The pH/EC probes from gravity have several problems when looking for a robust sensing setup. The first issue they have is that the probes are not rated for constant immersion, so they are damaged if you place them within solution the whole time which is probably what you want to do within a production hydroponic setup. The second issue is that the boards require cable connections to the Arduino which introduces a significant amount of noise that can causes problems with measurements. Due to poor isolation there can also be issues with the gravity boards when measuring EC/pH at the same time. To overcome these issues we can use probes and boards from

atlas which have the advantage of having no cable connections to the Arduino – connections are through pins directly – plus the probes are rated for constant immersion and are much more robust. These are the things we would need to build this project:

- [Arduino UNO R3](#) – 23.90 USD
- [LCD 12864 screen shield](#) – 24.05 USD
- [Mini tentacle shield](#) – 85.00 USD
- [pH kit from Atlas](#) – 149.15 USD
- [EC kit from Atlas](#) – 195.71 USD
- [Arduino headers](#) – 12.99 USD

As you notice this sensor project is much more expensive than the sensor station I had discussed before, with a price tag of around 490 USD (not including shipping). However when looking for a robust setup you definitely should favor the additional expense as this will likely be paid off with much longer service times.

When you get the pH/EC kits the first thing you want to do is change your EZO boards (the small circuit boards that come with them) to i2C mode so that you can use them with your mini tentacle shield. To do this follow the instructions [here](#), follow the instructions in the "Manually switch between UART and I2C" section, use [female jumpers](#) to make this process easier. Note that you can use your LCD shield analogue 5V and ground pins when you need power within the process.

```
//Libraries
#include <U8glib.h>
#include <stdio.h>
#include <Wire.h>
#include <Arduino.h>

#define TOTAL_CIRCUITS 2

///---- variables for pH/EC tentacle shield ------- //
```

```
#define TOTAL_CIRCUITS 2

char sensordata[30];
byte sensor_bytes_received = 0;

byte code = 0;
byte in_char = 0;
int channel_ids[] = {99, 100} ;
// ------------------------------------------- //

// EC values // CHANGE THESE PARAMETERS FOR EC PROBE
CALIBRATION
#define EC_PARAM_A 0.00754256

//pH values // CHANGE THESE PARAMETERS FOR PH PROBE
CALIBRATION
#define PH_PARAM_A 1.0
#define PH_PARAM_B 0.0

#define XCOL_SET 55
#define XCOL_SET2 65
#define XCOL_SET_UNITS 85

//-------------------------

U8GLIB_NHD_C12864 u8g(13, 11, 10, 9, 8);
float pH, EC;

//-------------------------

void draw() {
  u8g.setFont(u8g_font_04b_03);
  u8g.drawStr(0,11,"pH:");
  u8g.setPrintPos(XCOL_SET,11);
  u8g.print(pH);
  u8g.drawStr(0,21,"EC:");
  u8g.setPrintPos(XCOL_SET,21);
  u8g.print(EC);
  u8g.drawStr( XCOL_SET_UNITS,21,"mS/cm" );
}
```

```cpp
void read_tentacle_shield(){

  for (int channel = 0; channel < TOTAL_CIRCUITS; channel++) {
    Wire.beginTransmission(channel_ids[channel]);
    Wire.write('r');
    Wire.endTransmission();
    delay(1000);

    sensor_bytes_received = 0;
    memset(sensordata, 0, sizeof(sensordata));

    Wire.requestFrom(channel_ids[channel], 48, 1);
    code = Wire.read();

    while (Wire.available()) {
      in_char = Wire.read();

      if (in_char == 0) {
        Wire.endTransmission();
        break;
      }
      else {
        sensordata[sensor_bytes_received] = in_char;
        sensor_bytes_received++;
      }
    }
    if (code == 1){
      if (channel == 0){
        pH = atof(sensordata);
        pH = pH*PH_PARAM_A + PH_PARAM_B;
      }
      if (channel == 1){
        EC = atof(sensordata);
        EC = EC*EC_PARAM_A;
      }
    }
  }
}

void setup()
{
```

```
    pinMode(13,OUTPUT);
    Serial.begin(9600);
    u8g.setContrast(0);
    u8g.setRot180();
}

void loop()
{

  digitalWrite(13, HIGH);
  delay(800);
  digitalWrite(13, LOW);
  read_tentacle_shield();

  u8g.firstPage();
    do  {
      draw();
    }
      while( u8g.nextPage() );
}
```

Once you have changed the EZO boards to i2C you can now plug everything into the arduino and upload the code into your arduino. Plug the EZO boards into the mini tentacle shield and then plug that shield into the arduino. You'll notice that the EZO boards make it impossible to plug the LCD screen directly on top – as the EZO circuits make the shield too tall – so you should use stackable headers to extend the connections so that you can plug the LCD screen on top without any problems. Make sure you download and install the U8glib library in your arduino IDE before uploading the code.

As with the previous code you'll notice there are variables called PH_PARAM_A, PH_PARAM_B and EC_PARAM_A within the beginning of the code that you should change in order to calibrate your probes. Follow the instructions about calibration I gave in the previous post in order to figure this out. Using the calibration solutions that come with your kits you'll be able to perform this calibration procedure. Whenever you want to calibrate your probes you should reset

these variables to their original values, reupload the code and retake measurements.

Following this guide you will have a very robust sensor setup using very high quality probes. These probes are also coupled with a board that has no wire connections with the arduino, offering very high quality readings with very small amounts of noise. Additionally the LCD shield opens up the possibility to add more sensors to your station so that you can monitor, temperature, humidity, and carbon dioxide potentially from a single place.

Five dos and don't's for automated pH control in hydroponics

The pH is one of the most important variables to control in hydroponic culture as it plays a key role in the availability of different ions and their absorption dynamics. Although most growers control pH manually it is often desirable to implement automatic pH control so that you can ensure that your solution always stays within an optimum range. This is especially true in recirculating systems where correcting the pH of the solution after it goes through the plants' roots is necessary. Today I want to share with you five dos and don't's when implementing automated pH control in hydroponic culture.

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Do test your pH meter frequently with a buffer solution. In hydroponics pH meters can lose calibration rather quickly as a consequence of being immersed in a nutrient solution that is at a lower ionic concentration than what's ideal for most glass electrodes. This means that testing your pH meter with a buffer solution often — every week is ideal — is necessary in order to ensure that you are getting accurate readings. If the reading is not accurate you can then recalibrate the meter.

Do recondition your pH meter every month. In line with the above and in other to increase the life of a pH meter and each calibration it's necessary to immerse the pH electrodes in a pH 4 or 7 buffer solution every month — for at least 2-3 hours — to ensure that the ionic content of the electrode is restored and the glass membrane's responsiveness remains accurate. If you do this your electrode will be happier and you will need to calibrate less frequently. If an electrode is covered in biofilm the putting it in a hot bleach solution for half an hour before the buffer immersion is also necessary.

Do use electrodes designed for constant immersion. Regular pH electrodes — including those sold with some automated pH controllers — are not meant to be immersed the whole time and therefore get damaged and lose calibration much more quickly when used in this manner. To get best results use pH electrodes that are fabricated with long term immersion in mind. I wrote a blog post about [these electrodes](#) and why they are different than traditional pH electrodes.

Do place your electrode as far as possible from your pH changing inputs. When using a pH controller you should place the pH probe as far away as possible from the place where your pH up/down solutions will enter the hydroponic system. This is so that your pH electrode can get a slow change in pH as the pH up/down is mixed with the entire reservoir. Placing the probe close to the inputs will cause very erratic changes in the pH that do not really reflect the effect of the addition across the entire reservoir.

Do have addition limits in your controllers. Allowing a pH controller to add as much substance as needed to correct the pH can be a very bad thing to do. This is because several things can go wrong – pH probe losing calibration, controller getting damaged, electrical noise etc- that can cause unnecessary levels of addition that can kill an entire crop. Always have controllers where maximum additions per unit of time can be specified so that the possibility of this happening is minimized.

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Don't rely on a single pH probe. Although single probe controllers are the most common they can also be the most dangerous. A pH probe can get damaged, it can lose calibration or it can give erratic readings due to other reasons (for example electrical interference from other things in the reservoir). Therefore it's always best to use two-probe controllers where readings are always verified across the two probes to ensure that the reading the controller is getting is accurate. If you have a commercial enterprise then this is a must, you wouldn't want to lose an entire crop due to a bad pH probe adding a ton of acid/base to your solution.

Don't aim for a specific pH value. A pH controller should not aim for a specific value of pH but to maintain pH within an adequate range. Usually the best way for a controller to act is to have a range with high/low thresholds where the controller will act to take the pH to the middle of the range when these thresholds are exceeded. For example a controller can be told to maintain pH in the 5.6-6.4 region and then it will act whenever the pH reaches 5.6 or 6.4 to take it back to 6 when any one of these two thresholds is breached. However if the pH is at 6.4 and the controller drops it to 5.8 it will

not try to then bring the pH up (because it's above the lower threshold).

Don't place your pH probes near pumps or other electrical equipment in reservoirs. A pH probe takes an electrical measurement and is therefore prone to electrical interference. Having a pH probe close to other electrical equipment — especially those that draw significant current — can cause those wires to induce currents in the pH probe wires and generate all sorts of issues with pH readings. Always place pH probes away from pumps and ensure the pH probe and pump wires are never tangled together.

Don't use very concentrated acid/base input solutions. A pH controller will be doing very fine control over a small pH range so it won't need a very large amount of acid/base to do this job. Using very concentrated acid/base can cause the pH controller to completely overshoot its targets and cause it to either cause the system to get into an undesirable state — for example a very low pH if the controller can only add acid — or enter a loop where acid additions are followed by base additions in an endless cycle. Usually you want your acid/base mixtures to be concentrated enough to shift the pH over their addition volume but not much more than that. Strong acids/bases in the 10-20% concentration range are usually more than enough for this job.

Don't ignore your controller's data. A pH controller will do its job — control pH within a range — but it will not tell you whether your system is doing ok or not from a plant-health perspective. How often your pH controller has to add acid/base and how much acid/base it's using to perform its job are important pieces of information that you need to take into account in order to ensure that your system is working properly. Remember that pH controlling substances often also contribute nutrients — like phosphorous or potassium — so it's important to keep all these additions in check.

Of course pH control is no simple task and different pH controllers will have different advantages and disadvantages. However doing what you can to ensure proper maintenance – cleaning, conditioning electrodes, having proper placement, etc – can go a long way in ensuring that your setup behaves as ideally as possible. If you can then I would advice you build your own controllers using things like arduinos, raspberry pi computers and robust immersion pH probes so that you can have an optimum setup that can deliver all the advantages of pH control with as few disadvantages as possible. I'll write about building your own pH controller in a future post.

Probes for constant immersion in hydroponic nutrient solutions

If you have a hydroponic crop then you probably have to measure and monitor the pH and EC of your nutrient solutions. This means taking probes out of storage, ensuring they are calibrated and then carrying out measurements. This process can be very inconvenient, reason why growers might prefer to carry it out less often, even if this means they will have a lot less data. However there are several solutions that can enable constant monitoring of hydroponic nutrient solutions without the need to constantly take out, calibrate and then store away probes. Today we will talk about why regular probes are not suited for this and what types of probes are needed if you want to do this.

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Usually low quality EC/pH pens cannot be kept within nutrient solutions because they are not built to withstand constant contact with nutrient solutions. This is both due to the electrode composition — the actual glass or metal electrodes not being robust enough — and the actual junctions and other components not withstanding the nutrient solution as well. Although hydroponic nutrient solutions are not particularly harsh environments — with a slightly acidic pH and moderate ionic strengths — probes for constant monitoring of nutrient solutions must be designed with constant immersion in mind.

For constant monitoring of pH in nutrient solution tanks you want a proper submersible electrode assembly like this one. These electrodes are usually mounted on PVC fixtures and can be easily mounted on tanks to provide constant readings for the nutrient solution. The electrode comes with a standard BNC connector meaning that it is compatible with a wide variety of pH controllers. If you don't want to mount it on the tank but you just want the electrode to be like a normal probe but constantly submerged then you can use something like this industrial probe which comes with a pH controller as well that can be used with any other probes you purchased and interfaces with an arduino or raspberry pi to get and store readings. For probes like this last one I usually wrap the entire outside body of the probe in electrical tape to give further strength to the probe/cable junction.

For conductivity readings you will want to go with electrode-less EC probes (like these ones) which over PVC mountings as well with the advantage that they do not suffer from polarization issues — like normal EC pens use — so they lose calibration much more rarely and can give much more accurate readings across a wide range of different solution types and conductivity values.

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For the grower who wants it all there are also probes like the [Mark I-A probe](#) which is a tank-mounted probe assembly that does EC, pH and ORP readings, all in one single fixture. This is incredibly practical since it is able to implement all the readings you need in one single fixture. The problem of course is that calibration of any reading requires you to remove all three sensors so this can be a bit inconvenient when you want to ensure that any of the readings are indeed accurate.

Of course submersible robust probes are more expensive but they are much more convenient. They get damaged much less frequently, require much less maintenance, provide constant readings and need to be calibrated only a few times a year. For example the industrial EC and pH probes I use in my home hydroponic setup have only required calibration once a year, even then the loss in calibration was only around 0.2 units for the pH sensor and 0.3 mS/cm for the EC one so I probably could have continued using the probes without calibrating them for 2 years without having to face any dramatic consequences. If you spend 300-400 USD on high quality robust probes you will probably have them for much longer, with far more accurate results along the way.

Five things that will damage your pH probes

Since pH is one of the most important variables to control in hydroponic culture almost all hydroponic growers have and use pH probes. There are however several things that can go wrong with these probes due to the very nature of the sensor and the way in which other substances interact with it. Today we will learn about some of the worst things that you can do to your pH probes and how you can potentially avoid these issues.

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1. Let them dry. These probes are made from glass and the readings depend on the potential difference between the inside and outside surfaces of the sensor. These are determined mainly by pH since hydronium (H_3O^+) ions interact strongly with the glass surface. For measurements to be accurate the surface needs to be in equilibrium with the media that is being measured. If you let the electrode dry then the hydration of the surface will be lost and the equilibrium state will be much harder to achieve (a dry probe should be placed in a KCl solution for at least 4 hours before being used). Any junctions within the probe might also dry which will require further stabilization before the probe can be used . Dry pH probes are therefore a big no no.

2. Keep them in water. Although keeping pH probes in water is better than letting them dry this has a similar effect in that it alters the composition of the glass with time. Since the solution around the probe is much more diluted, with time ions in the glass will have no problem migrating away from the probe, creating defects within the glass that will mess with

your sensor's calibration. Ideally you will want to store your pH probes in a concentrated KCl solution (usually around 150-300g/L) which will prevent any of these migration effects and will ensure that your probe remains stable in the longer term. If you buy KCl you can use distilled water to prepare your own pH probe storage solution.

3. Measure very basic solutions. Since pH probes are made of glass and glass is mainly made of silicates this means that basic solutions will tend to react with your pH probe. When the pH goes above 10 a pH probe will start to dissolve in solution, completely altering the surface and making the sensor lose calibration very quickly. In general avoid measuring the pH of any solution above 10 so that this effect can be kept to a minimum.

4. Measuring solutions with chemicals that react with glass. Besides basic solutions — where hydroxide ions dissolve glass — there are a variety of substances that can affect the performance of pH probes by reacting with the glass. This includes solutions containing silicate species and solutions containing fluoride ions. If the solution has ions that can react with glass then the pH probe's lifetime will be diminished and much more frequent calibration will be required. Try to avoid long term measurements of solutions containing large amounts of these ions and beware that weekly calibration might be necessary.

5. Not cleaning the probe. When measuring solutions such as hydroponic nutrient solutions the pH probe is usually subjected to an environment filled with potentially microorganism contaminants. If the probe is not properly cleaned then microbes can form a biofilm over the glass that will seriously affect the accuracy of pH readings. A probe can be cleaned with a bleach or hydrogen peroxide solution to remove these contaminants but the probe will then need to be recalibrated as the film will have effectively changed the glass surface to some extent.

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Having pH probes that give accurate reading for a long time is not a difficult task if you take proper care of your sensors. Storing them adequately, ensuring they are not exposed to harmful conditions and cleaning them ensures that they will last for a much longer time. IF you keep track of your pH sensor calibrations you might notice changes in the calibration slope – as in the first image in this post – which indicates a loss of sensor sensibility (the slope becomes less pronounced). You can use a sensor until around 20% of the sensor's sensibility is lost, time after which you'll need to buy a new probe.

There are also several sensors that can be used for long term continuous measurements – which are made in a much more robust manner – we will talk about industrial quality and in-line sensors in a future post.

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.

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.

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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.

Chemical Buffers in Hydroponics : What is the Best, Cheapest Buffer

One of the biggest questions people ask when starting to grow hydroponic crops deals with the stabilization of pH and the use of chemical buffers to keep pH levels at acceptable ranges during long periods of time. The question is very relevant since changes in the pH of a nutrient solution can cause a lot of problems related to nutrient availability and having to add large quantities of acids or bases to correct the deviations is also not something plants will enjoy very much. What we need to do then is to keep pH levels within an acceptable range, for a period at least long enough to last a few weeks.

On previous posts I have talked about the way in which I do this using ion exchange resins but these can be too expensive or hard to find for most hydroponic growers out there. More over, chemical buffers are often much easier to use, get and apply although their actual mechanism of action is much less effective and much more aggressive than that of the ion exchange resins. A chemical buffer is mainly a substance which is added into your solution that distributes itself as different ionic species that can react either with acids or

with bases at certain pH levels. The buffer however is also available for your plants to absorb and therefore we are limited to chemical buffers which are not phytotoxic (toxic to plants) and which allow us to control pH within the range we want.

From the very large library of chemical buffers available to the modern chemist, only a handful are suitable for their use in hydroponics and — even then — most of these are actually not practical in the sense that they are extremely expensive for the home grower. Certain organic buffers [like MES](#) offer extremely good results although they are hard to buy and very expensive, a reason why they are not used widely in hydroponic culture (this buffer is used mainly on hydroponic research where precision — and not cost — is the main determinant factor).

The buffers we are left with are then very simple organic and inorganic substances that have low phytotoxicity and some compatibility with the other ions present in our hydroponic setup. From these ions phosphate species, citrate species and carbonates are the most important ones we can use within our hydroponics setup. However we are limited by the actual concentration values of each we can use and for this reason we cannot have unlimited buffering capacity from these sources.

Which one is best ? We can actually carry out simulations to show us the pH vs acid-base addition for different hydroponic solution constitutions using mathematical equations. Running these simulations requires the solution of highly complex systems of equations which contain all the information relative to the chemical equilibrium of all the different existing ionic species. The below shown simulations were carried out using the Mathematica computer program (all solutions are assumed to be adjusted to an initial pH of 5.8 with a strong acid or base).

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The blue curve represents the behavior of a poorly buffered

hydroponic solution with only about 0.002M phosphate concentration (about 50 ppm of P). The red and yellow curves represent two solutions with increasing levels of carbonate showing us that if you are battling pH increases, having more carbonate will definitely help you deal with this. However it is also clear that carbonate concentrations at pH 5.8 are restricted to around 100 ppm since values above this are bound to cause toxicity due to the very large presence of the hydrogen carbonate ion. The green curve represents an increase in the amount of phosphate from 0.002 to 0.004M (about 100 ppm) with carbonate, showing us that phosphates are not good at buffering increases towards the upper side but they do increase buffering towards acid territory. Overall I also noticed that citrate concentration increases to the maximum threshold allowed by calcium citrate solubility did not afford a very good buffering effect with only a mild effect that prevented shifts towards the downside.

In the end, the conclusion seems to be that in a regular hydroponics system where pH increases generally happen towards the upside it is better to use carbonate as a buffering agent than to use citrate or phosphate although phosphate at its regular concentration in hydroponic does provide some buffering against pH moves (without phosphate increases are much more dramatic). For this reason I believe that a phosphate/carbonate buffer seems to be the best choice for most hydroponic growers, taking care to keep the concentrations at levels that do not cause precipitation or phytotoxicity problems.