Supplementary Information 4 - Best practices for long-term pH monitoring and control

pH controller

We have used a pH controller (Hanna Instruments, Woonsocket, RI) with a recorder output. These controllers are available as high-voltage (115 V, model 931700-1) or low-voltage (12 V, model 931700-0). If the controller is not mounted in an electrical panel, the 12 V model should be used to reduce electrical shock hazard. Both models attach to a pH electrode using a BNC connector and allow for electrode calibration and a set-point to two decimal places. The price is similar ($225; 2022).

Electrodes

The pH electrode is at the core of the control system. A durable and reliable electrode is essential. pH electrodes measure the activity of hydrogen ions in solution and transmit a voltage to the controller. The voltage is determined by the electrochemical potential of the hydrogen ions (Nernst Equation). The pH electrode must be continually immersed in solution to avoid desiccation, which causes rapid aging of the bulb. The inlet tube from the acid column should be close to the glass bulb so acid rapidly contacts the bulb after injection and the valve closes (Figure S1). This results in small, frequent doses of acid and stable pH in the bulk solution.

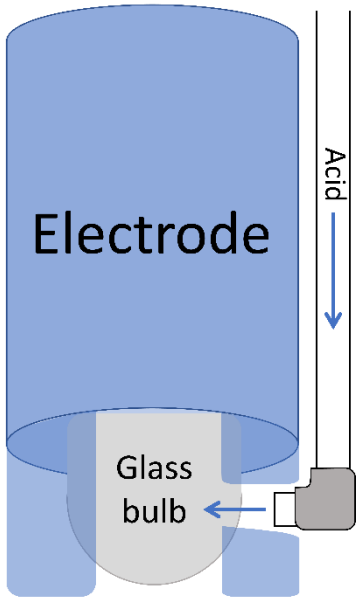

Figure S1. The acid outlet tube should be close (about 5 mm) to the electrode bulb for fast response times and accurate acid dosing. Response time is much longer as the distance between the inlet and bulb increases.

We have used single-junction combination pH electrodes (e.g., Oakton pH electrode, Cole Palmer, Vernon Hills, IL). We have found no benefit to using double junction electrodes. Combination electrodes have the pH electrode and reference electrode contained as one unit and are easier to implement. These electrodes are dependable for about 6 to 15 months before requiring reconditioning.

Electrode calibration

We have found calibration to be stable for more than a month in continuous use in nutrient solutions. Calibration solutions (pH 4 and 7) need to be replaced every 1 to 2 months to minimize fungal growth and maintain accuracy. We use pH reference tablets and make the calibration standards with

deionized water. Fungal growth in calibration solutions can reportedly be minimized by adding a fungal inhibitor (Color key buffer preservative, MicroEssentialLabs.com), but we have found the use of this fungal inhibitor to promote fungal growth rather than suppress its development.

Electrode reconditioning

Over time both organic and inorganic materials adhere to the glass bulb and can cause slow response times, unstable readings, and inaccurate measurements [1]. Periodic cleaning can extend electrode life. Protein deposits can be removed by soaking the glass bulb in 0.4 M HCl for 30 minutes followed by a deionized water rinse. Microbial biofilms and oils can be removed by soaking in a mild detergent (dishwashing soap) for 10 to 30 minutes followed by a soak in 1% HCl for 10 minutes. See the following link for specifics on electrode reconditioning: https://www.coleparmer.com/tech-article/how-to-store-clean-and-recondition-ph-electrodes A microbial biofilm can develop around the electrode bulb, which decreases response time and can clog the acid tube outlet. We have not found a solution to this problem other than manual rinsing of the electrode once a week during continuous use.

Solenoid valves

We have used two types of solenoid valves: pinch and flow-through. Pinch valves have an electromagnetic shaft that pushes against a piece of soft tubing to restrict flow. This eliminates contact between the valve and the solution. Flow-through valves allow the solution to pass through the valve. Although our pH control solution is only 50 mM acid, we have found that even acid resistant valves start to develop leaks after about a year of continuous use. We now use pinch-type valves, which have been more reliable.

Tubing

Tubing for pH control must have acid and base resistance, minimal gas permeability, and adequate flexibility. Resistance and minimal permeability are required regardless of valve type, but flexibility is particularly important if using pinch valves. The tubing must be compressible to be pinched, yet rigid enough to open the valve when released. The low permeability of silicon tubing coupled with its flexibility (lower durometer) makes it a good choice for pinch valve use. If sufficient time exists between successive activations of the solenoid pinch valve, the low durometer tubing has the potential to remain compressed upon release. Pinch valves need a small backward pressure on the ram to release the electromagnet, and the compressed tubing cannot overcome this force. This is typically not an issue in mature systems where small frequent doses are constantly added but is a concern early in the life cycle when dosing is low. Pinch valves do not need to be activated until the plants are established as there is generally no need for pH adjustment during early growth.

pH control fail safe

Electrodes can fail and give incorrect readings, which may cause inadvertent acid dosing. If the electrode measures a pH higher than the setpoint it will continually let acid into the tank with no change in apparent pH. Although the pH is decreasing, the electrode does not sense the decrease and continues to dose acid. We have observed pH values below 4 following failures of an electrode.

We have prevented this problem by installing a time delay relay between the pH controller and solenoid. When the pH controller activates the solenoid to open the acid reservoir, the relay interrupts the signal and begins a countdown. Power is cut to the valve after a set time and no more acid is allowed to enter the tank. The relay then resets until the pH again crosses the set point. A time delay of 1 second is often sufficient to allow acid to flow while still preventing potential overdosing. We have used the Timer Relay (DROK) sold on Amazon.com for about $14 (2022). This is an inexpensive insurance policy to avoid a costly problem.

Continuous monitoring of pH

Continuous monitoring and graphing of pH provide an indication of the health of the plants and can indicate ammonium levels in solution (see Figures 3 and 4 in the main text). The pH controllers have a recorder output that can be connected to a data logger with a graphical capability (e.g., model CR1000X, Campbell Scientific, Logan, UT). A multiplexer can be attached if more than eight electrodes are needed.

Reference

1. Munro, W.A.; Thomas, C.L.P.; Simpson, I.; Shaw, J.; Dodgson, J. Deterioration of PH Electrode Response Due to Biofilm Formation on the Glass Membrane. *Sensors and Actuators B: Chemical* **1996**, *37*, 187–194, doi:10.1016/S0925-4005(97)80137-2.