

Supplementary Material

Mathematical modelling and simulation

It was shown in Section 3.3 that the rate of nitrate depletion is related to the concentration of nitrate in solution. This may be the result of higher ammonium uptake rates by the plants at lower nitrate concentrations (since the ammonium-to-nitrate concentration ratio in the solution is higher). To demonstrate, consider the conditions employed in run 4. A δ value of 1.5 resulted in slow depletion of nitrate in solution while the ammonium concentrations remained low. As ammonium uptake relative to nitrate is related to the concentration ratio of ammonium-to-nitrate in solution (Imsande, 1986), higher ammonium uptake rates by the plants are expected as the nitrate concentration approaches that of ammonium. From Fig. 2, it can be shown that if the pH and nitrogen concentrations remain constant: $\delta = (\eta_1 + \eta_2 - \eta_3)F_{NH_4^+}^P + (\eta_3 - \eta_1)$. Where, $F_{NH_4^+}^P$ is the fraction of the total ammonium dosed which is absorbed by the plant (the rest being taken by the bacteria). This function is plotted in Fig. S1 (a) in which $\eta_1 = 0.5$, $\eta_2 = 1$, and $\eta_3 = 2$. Since ammonium and hydroxide dosing is intended to produce an acidic effect (lowering the pH when it rises above a setpoint), high δ values will result in nitrate accumulation and low δ values will lead to nitrate depletion in solution. Therefore, if the δ required for constant nitrate concentration is lower than the actual δ being dosed, nitrate will

accumulate in solution and vice versa. So as the nitrate concentration decreases, $F_{NH_4^+}^P$ increases and the employed δ becomes “too high” which tends towards nitrate accumulation. This may be difficult to conceptualise initially and thus it is shown mathematically below by modelling the flux diagram depicted in Fig. 2.

The nitrate balance over the solution at constant volume, assuming that all ammonium consumed by the bacteria is converted to nitrate (zero nitrite accumulates and negligible amounts of nitrogen is used to produce bacterial biomass):

$$V \frac{d[NO_3^-]}{dt} = r_{NH_4^+}^B - r_{NO_3^-}^P \quad (1)$$

Where, $[NO_3^-]$ is the concentration of nitrate in solution (mM), $r_{NH_4^+}^B$ is the ammonium oxidation rate by the bacteria which is assumed equal to the nitrate excretion rate by the bacteria (mmol day^{-1}), $r_{NO_3^-}^P$ is the nitrate uptake rate by the plant (mmol day^{-1}) and V is the solution volume (L).

The ammonium balance over the solution at constant volume:

$$V \frac{d[\text{NH}_4^+]}{dt} = r_{\text{NH}_4^+}^D - r_{\text{NH}_4^+}^B - r_{\text{NH}_4^+}^P \quad (2)$$

Where, $[\text{NH}_4^+]$ is the concentration of ammonium in solution, $r_{\text{NH}_4^+}^D$ is the rate of digestate ammonium dosed to the solution (mmol day^{-1}), $r_{\text{NH}_4^+}^B$ is the ammonium oxidation rate by the bacteria (mmol day^{-1}) and $r_{\text{NH}_4^+}^P$ is the ammonium consumption rate by the plant (mmol day^{-1}).

The proton balance becomes:

$$\frac{d\text{H}^+}{dt} = -\delta r_{\text{NH}_4^+}^D - \eta_1 r_{\text{NO}_3^-}^P + \eta_2 r_{\text{NH}_4^+}^P + \eta_3 r_{\text{NH}_4^+}^B \quad (3)$$

The total nitrogen uptake rate by the plant (r_N^P) in mmol day^{-1} :

$$r_N^P = r_{\text{NO}_3^-}^P + r_{\text{NH}_4^+}^P \quad (4)$$

The total nitrogen content of the plants in run 1 (nitrate only) was equal to the nitrogen content of the plants from run 2 (ammonium only), which was shown in Fig. 7. This result shows that r_N^P is constant (at a specific plant size) and independent of the nitrogen source (nitrate or ammonium). Therefore, nitrate and ammonium uptake cannot be modelled separately since the total amount of

nitrogen absorbed is constant. Although an affinity often exists for a particular nitrogen source (which is dependent on plant species and environmental conditions), the uptake rates of each nitrogen source will depend on its availability relative to the other (ammonium-to-nitrate ratio). As a preliminary assumption, a linear relationship is assumed between the nitrate uptake rate and the concentration fraction of nitrate-to-ammonium in solution (no affinity). When an affinity exists, a non-linearity is introduced, α , which is the affinity of the plant to absorb ammonium over nitrate. Assuming $\alpha = 1$, i.e., the plant has equal affinity for both nitrogen sources:

$$r_{NO_3^-}^P = r_N^P \left(\frac{[NO_3^-]}{[NO_3^-] + [NH_4^+]} \right)^\alpha \quad (5)$$

With the pH controlled, $dH^+ \approx 0$. Also, assuming all the ammonium dosed is immediately consumed, $d[NH_4^+] \approx 0$ (and letting $\alpha = 1$), substitution of equations 2, 3, 4 and 5 into 1 followed by algebraic manipulation yields:

$$V \frac{d[NO_3^-]}{dt} = -r_N^P \frac{(\delta + \eta_1 - \eta_3)[NO_3^-] + (\delta - \eta_2)[NH_4^+]}{(\delta - \eta_3)([NO_3^-] + [NH_4^+])} \quad (6)$$

Let, $\delta = 1.25$ (allowing for nitrate depletion in solution), $\eta_1 = 0.5$, $\eta_2 = 1$, $\eta_3 = 2$ (from results shown in Fig. 3), $r_N^P = 1$ (unit nitrogen uptake, at specific

plant size), $V = 1$, $\text{NH}_4^+ = 0.1$ mM (assuming the ammonium concentrations remain low and constant). With an initial nitrate concentration of 1 mM and 0 mM, integration of equation 6 yields the two profiles shown in Fig. S1 (b), for each of the initial nitrate concentrations. Fig. S1 (b) conveys a decrease in the nitrate depletion rate as the nitrate concentration approaches that of ammonium from a higher concentration, as observed in run 5, effectively inhibiting nitrate extinction. Also, a steady state nitrate concentration is predicted.

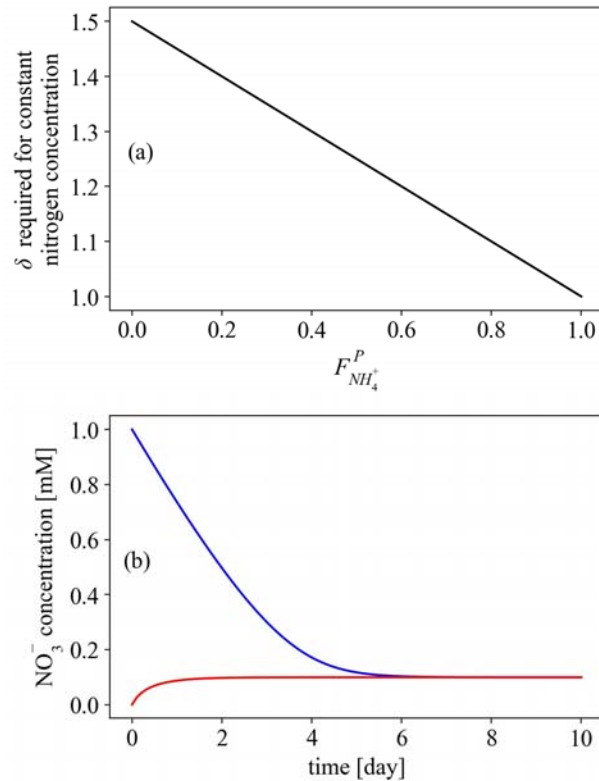


Fig. S1: Mathematical predictions of the flux model shown in Fig. 2. Subplot (a) shows the relationship between the hydroxide-to-ammonium ratio (δ) in the digestate (which is dosed to control the pH) required maintain the nitrate

concentration at a constant value, versus the fraction of the dosed ammonium which is absorbed by the plant (the rest being absorbed by the bacteria). When this fraction ($r_{NH_4^+}^P / r_{NH_4^+}^D$) is equal to zero (high nitrate concentrations), $\delta = 1.5$ as discussed in Section 3.2. As the nitrate concentration decreases and approaches that of ammonium, a higher fraction of ammonium is absorbed by the plant and δ decreases as seen in (a). If this δ is lower than the actual δ being dosed, nitrate will accumulate in solution and vice versa. This is demonstrated in Subplot (b) in which equation 6 was integrated at a constant $\delta = 1.25$ (actual being dosed).