Quantifying the Acidity of an Ammonium-based Fertilizer in Containerized Plant Production

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Abstract. In current horticultural practice, potential acidity or basicity of fertilizers is estimated using Pierre's method (PM) expressed in calcium carbonate equivalents (CCE) per unit weight of fertilizer. PM was developed using mineral field soil systems and may be inaccurate for quantifying fertilizer acidity in containerized plant production given the widespread use of soilless substrates and fertigation. The PM-predicted acidity of an ammonium-based fertilizer was compared against experimental data obtained when 'Ringo' geraniums [*Pelargonium ×hortorum* (Bailey, L.H.)] and 'Super Elfin' impatiens [*Impatiens wallerana* (Hook. F.)] were grown in 70% peat:30% perlite (v:v) limed with either hydrated limestone only (HL) or a combination of carbonate and hydrated limestone (CHL). Plants in 10-cm-diameter (0.35 L) containers were top-irrigated with a total of 2.0 L over 6 weeks using a 15.2N–1.9P–12.6K fertilizer [100% of nitrogen (N) as $\text{NH}_4\text{-N}$] applied with each irrigation at 100 mg N/L without leaching. According to PM, 61.8 meq of fertilizer acidity was applied per liter of substrate. During the experiment, the pH of the substrate decreased from 7.05 to 4.41 for the HL substrate and from 7.14 to 5.13 for the CHL substrate. A corresponding drop in substrate-pH was observed when 37.1 (HL) or 43.3 (CHL) meq of CCE from 0.5 N HCl was applied per liter of substrate in a laboratory titration of the same substrates without plants. Gasometric analysis of residual carbonate at Day 0 and at the end of the experiment quantified change in CHL substrate alkalinity with time, resulting in an estimated 30.7 meq of neutralized alkalinity. Using an electroneutrality approach that assumed anion uptake (NO_3^- , P_2O_5^-) was basic, and cations (NH_4^+ , K^+) were potentially acidic, nutrient analysis of the substrate at the beginning and end of the experiment estimated that an average 48.5 meq of acidity was contributed by the fertilizer. Experimentally measured acidity values were 13.1 to 31.1 meq·L⁻¹ of substrate lower for HL and CHL than those expected from PM, suggesting PM overestimated the amount of fertilizer acidity applied to the substrate. These results support the need for an alternative method to predict fertilizer acidity for plant production in soilless substrates.

Fertilizer type and concentration, plant species, water alkalinity, substrate components, and lime amendment dynamically affect substrate-pH during plant production. Fertilizer effect on substrate-pH occurs primarily through plant and microbial uptake of nutrients and the subsequent release of ions and/or root exudates along with other microbially induced

processes such as nitrification (Marschner, 1995). Using nitrogen as an example, uptake of $\text{NO}_3\text{-N}$ can result in the release of OH^- and HCO_3^- or coabsorption of a cation, whereas H^+ ions are released with uptake of $\text{NH}_4\text{-N}$. The microbial conversion of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ (nitrification) also produces H^+ .

Pierre's method ["PM," Pierre (1933)] is the standard used in the U.S. fertilizer industry to quantify the potential of a fertilizer to change soil acidity or alkalinity. The reported PM value for an acidic fertilizer, in units of calcium carbonate equivalents (CCE) of acidity per unit weight of fertilizer, refers to the CCE required to neutralize the acidity resulting from application of the fertilizer (Pierre, 1933). For basic reaction fertilizers, the CCE of basicity represents the basic residue in CCE left in the soil after application of the fertilizer.

Pierre's original methodology was modified and adopted by the Association of Official

Agricultural Chemists (AOAC) and is recognized as the official method to estimate the equivalent acidity/basicity of complete fertilizers (Tisdale and Nelson, 1966). The final official procedure was published by AOAC in 1970 with a minor revision in 1999 (AOAC, 1970, 1999). In brief, the fertilizer mixture is ground and a 0.25- to 1.0-g dried sample is mixed with a sodium carbonate–sucrose solution and ashed in a furnace (at 575 to 600 °C) to remove carbon and nitrogen compounds. After cooling, HCl is added for lime digestion (AOAC, 1970; Hignett, 1985). Once digested, the sample is titrated to pH 4.3 using 0.5 N NaOH and compared with a similar titration of a blank sample of sodium carbonate–sucrose solution only (AOAC, 1970). The titrated difference between the blank sample and the fertilizer sample is the acidity or basicity of the fertilizer other than that contributed by nitrogen (Hignett, 1985). Table 1 shows the equivalent acidity or basicity factors for individual salt elements (Hignett, 1985), in which a positive value indicates the fertilizer sample is basic (non-acid-forming) and a negative value indicates the sample is acidic (Horat, 1939). For elements other than nitrogen or phosphorus, therefore, the acidity or basicity of a fertilizer salt is a direct measurement of its inorganic acid/base reaction in this titration and is independent of the soil or plant system.

The acidity or basicity factors of elements (Table 1), with the exception of nitrogen and phosphorus, is based on stoichiometry calculated by dividing the molecular weight of CaCO_3 (100 g·mol⁻¹) by the equivalent weight of the element. The equivalent weight of the element is equal to its atomic weight (mw) for divalent elements and twice the atomic weight for monovalent elements. For example, the factor for potassium is determined as follows:

$$\frac{\text{mw CaCO}_3}{2 \times \text{mw K}^+} = \frac{100}{2 \times 39.1} = +1.28$$

Factors for nitrogen and phosphorus were based on empirical field studies by Pierre in the 1920s and 1930s that measured soil pH changes after fertilizer application, primarily using Cecil clay loam with an initial pH of 6 (Hignett, 1985). Pierre assumed that: 1) the acidifying effect is caused by all the sulfur and chlorine, one-third of the phosphorus, and one-half of the nitrogen contained in the fertilizer; 2) calcium, magnesium, sodium, and potassium are base-forming elements; and 3) ammonium nitrogen is completely nitrified; nitrate nitrogen combined with bases such as sodium or calcium will have a net basic effect (Pierre, 1933; Tisdale et al., 1999; Tisdale and Nelson, 1966).

These assumptions merit critical evaluation when applied to use of water-soluble fertilizers in soilless container crop production. Pierre's method assumes nitrogen in fertilizers is provided as nitrate or is converted to nitrate through nitrification (Pierre, 1933). Rapid nitrification does indeed occur in container substrate above pH 5.5, which is the typical growing range for most container crops (Argo and Biernbaum, 1997; Lang and Elliott, 1991). However, PM does not take into consideration acidification resulting from plant NH_4^+ uptake

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Table 1. Equivalent acidity (negative) or basicity (positive) values in units of kg of CaCO₃ per kilogram of element using Pierre's method (Hignett, 1985).

Element	Molecular wt (g)	Charge	Equivalent acidity (–) or basicity (+)
<i>Acid-forming elements</i>			
Sulfur	32.07	–2	–3.12
Chlorine	35.45	–1	–1.41
Nitrogen	14.00	±1	–1.79
Phosphorus	30.97	–1	–1.61
<i>Base-forming elements</i>			
Calcium	40.08	+2	+2.50
Magnesium	24.31	+2	+4.12
Sodium	22.99	+1	+2.18
Potassium	39.10	+1	+1.28

or acidity from nitrification, and therefore it underestimates the lime-equivalent values required to neutralize the acid formed by the various nutrient salts in the fertilizer (Tisdale et al., 1999; Tisdale and Nelson, 1966).

Andrews (1954) maintained that all ammonium converted to nitrate creates acidity equivalent to 3.57 kg CCE per kilogram of nitrogen (N) [calculated as mw of CaCO₃/(2 × mw of N) to correct for valence differences]. Andrews also argued that 3.57 kg CCE base is leached from the soil along with every kg of NO₃-N leached, and his analysis included multiple years of field trials and re-evaluation of Pierre's data. Andrews' assumptions result in differing acidity and basicity potentials for fertilizer salts than those of Pierre; he considered anhydrous ammonia to be twice as acidic as Pierre's estimate. Andrews' calculations indicate calcium nitrate is slightly acidic and potassium nitrate neutral, whereas Pierre's calculations indicate that they are both basic (Andrews, 1954; Tisdale and Nelson, 1966).

Pierre considered that NH₄⁺ uptake was possible but the amount was insignificant under normal agricultural conditions (Pierre, 1933). However, ammonium uptake is energetically favored over nitrate uptake when both N forms are supplied (Engels and Marschner, 1995; von Wiren et al., 2001). Plant species is an important factor to consider in N preference. For instance, plant species adapted to soils that are acidic or with low redox potential tend to have a greater rate of uptake of ammonium, whereas plant species adapted to calcareous soils have greater uptake of nitrate–nitrogen (Marschner, 1995, p. 247). Ammonium follows an electrochemical gradient from apoplasm to symplasm without the requirement of metabolic energy. The exact path of NH₄⁺ uptake is still unclear. It is believed that ammonium is taken up through an NH₄⁺ uniport, H⁺-NH₄⁺ symporter, diffusion, or ion channels through the plasma membrane (Engels and Marschner, 1995; von Wiren et al., 2001). In contrast to NH₄⁺, NO₃[–] requires active transport from the apoplasm into the symplasm in association with H⁺ fluxes through H⁺-NO₃[–] symporters and H⁺-ATPase stimulation that maintains membrane electrical potential (Engels and Marschner, 1995). It is estimated that the absorption of 1 mol of NO₃[–] consumes 1 to 3 mol of ATP (Touraine et al., 2001). For that 1 mol of NO₃[–] to be used by the plant, it must first be reduced to NH₄⁺ in a process requiring 347 kJ of energy (Lewis,

1986). Low NO₃[–] concentration in the soil solution, low soil pH, and low soil temperature have been shown to favor NH₄⁺ uptake over NO₃[–] (Engels and Marschner, 1995).

The relative balance among nitrification, ammonium and nitrate uptake, and nutrient leaching, which in turn affect substrate acidity, is affected by factors such as species, irrigation method, soil microbial activity rate, plant evapotranspiration rate, and relative size of the plant and substrate volume. Pierre's assumption that only half of the N is actually acid-forming is therefore an approximation based on the experimental conditions under which his model was calibrated.

Although on a strict inorganic chemistry basis using PM, cations such as calcium, magnesium, sodium, and potassium have a basic residue (Table 1), these cations can also have acidic behavior in a soil/crop system. Displacement of protons on exchange sites by cations causes a decrease in substrate-pH (Rippy and Nelson, 2005). Cation uptake by plants is an acidic or neutral process accompanied by anion uptake, base uptake, or in association with a proton pump (Marschner, 1995). Similarly, anion uptake by plants is a basic reaction despite the acidic factors for sulfur and chlorine in Table 1. Overall, the substrate-pH effect of a fertilizer salt is a balance between inorganic chemistry and the dynamic plant/microbial/soil system.

The objectives of this study were 1) to evaluate protocols to quantify fertilizer acidity or basicity in soilless substrates; and 2) to use these protocols to compare the reported fertilizer acidity from PM with the experimentally measured acidity when plants were grown with an ammonium-based, water-soluble fertilizer in a peat/perlite substrate.

Materials and Methods

Greenhouse substrate experiments

In Spring 2007, a 70%:30% (v:v) peat:perlite substrate was mixed with dolomitic hydrated limestone [97% Ca(OH)₂·MgO, 92% of which passed through a 45-μm screen; National Lime and Stone, Findlay, OH; reported acid-neutralizing value of 161% CCE] at a rate of 2.8 kg·m^{–3} to raise substrate-pH to 7.04. One week later, the substrate was divided with half remaining amended with hydrated lime only (HL) and half amended with additional dolomitic carbonate limestone (CHL) [CaMg(CO₃)₂, Lawn &

Garden limestone™; Oldcastle Stone Products®, Thomasville, PA] at a rate of 2.22 kg·m^{–3}. The additional dolomitic carbonate lime in the CHL substrate was added to provide residual carbonate and substrate-pH buffering throughout the experiment. The peat source used in the research substrates was Canadian Sphagnum peat (Sun Gro Horticulture, Vancouver, Canada) with long fibers and little dust (von Post scale 1 to 2; Puustjarvi and Robertson, 1975). The HL and CHL substrates were placed in 10-cm, 350-mL containers. Container capacity was 255 mL or 73.0% of container volume. Plugs of 'Ringo Scarlet' and 'Ringo Coral' geraniums [*Pelargonium ×hortorum* (Bailey, L.H.)] and 'Super Elfin White' and 'Super Elfin Salmon' impatiens [*Impatiens wallerana* (Hook. F.)] were transplanted into the containers. The geraniums had been seed-propagated in 105-celled plug trays and the impatiens in 162-celled plug trays.

The containers received a total of 20 irrigations in 6 weeks applied to the substrate surface. They were irrigated each time with 100 mL of an acidic fertilizer solution consisting of 100N–12.8P–83.3K–107.8S–75.8Cl mg·L^{–1} (100% total N as NH₄-N) and an Fe-EDDHA-chelate micronutrient blend of 1Fe–0.25B–0.25Cu–0.5Mn–0.1Mo–0.5Zn mg·L^{–1} (Greencare Fertilizers, Inc., Kankakee, IL) in deionized water. Saucers were placed under each container to allow reabsorption of any leachate. The plants were grown in a polycarbonate-covered greenhouse for 6 weeks with average temperatures of 22.4 ± 4.3 °C and average photosynthetically active radiation light of 10.9 ± 3.0 mol·m^{–2}·d^{–1} (daily mean ± SD).

The greenhouse experiment was a randomized complete block design with a factorial of two substrates (HL and CHL) × two species (geraniums and impatiens) × two cultivars (for each species). There were three blocks (greenhouse benches). Each block included one replicate (or container) of all substrate, species, and cultivar combinations for a total of three replicates (containers) per variable measured each sample date. Data were collected for all measurement variables over the course of 6 weeks from destructively sampled containers (i.e., there were no repeated measurements on the same plants). Substrate-pH and electrical conductivity (EC) were measured weekly (Weeks 0 to 6) using saturated media extraction (SME) (Rippy and Nelson, 2005; Warncke, 1986). SME solution samples were also analyzed for nutrient content by Quality Analytical Laboratories (Panama City, FL) using inductively coupled plasma (for phosphorus and potassium) and Lachat® (for NH₄⁺ and NO₃[–]). Changes in residual carbonate concentration were measured biweekly (Weeks 0, 2, 4, 6) using a gasometric analysis method (Huang et al., 2007). The acid drench experiment was conducted in a laboratory using the same HL and CHL substrates used in the greenhouse experiment. There were six drench rates (treatments) with four replicates each. Substrate-pH data were collected immediately before and 7 d after drenching for regression analysis. All data were analyzed using SAS PROC GLM (SAS

Institute, 2001) and means were separated using Tukey's honestly significant difference ($\alpha = 0.05$).

Methods for measuring fertilizer acidity or alkalinity

Pierre's method. The acidity of each salt that comprised the ammonium fertilizer was computed and summed using the factors shown in Table 1. The fertilizer blend consisted of 7.26% monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), 68.16% ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$], and 24.56% potassium chloride (KCl) by weight. To calculate the acidity of the individual salts, the following equations were used:

$$(A) \frac{\text{mw of element}}{\text{mw of salt}} \times \text{equivalent acidity or basicity for element in Table 1} \times 1000 \text{ kg} = \text{kg of CaCO}_3 \text{ acidity or basicity for element per 1000 kg (metric tonne) of fertilizer salt.}$$

(B) (A) $\times$ percent mass of fertilizer salt in fertilizer blend = kg of CaCO_3 acidity or basicity per metric tonne of nutrient in fertilizer blend.

$\text{NH}_4\text{H}_2\text{PO}_4$:

$$N : \frac{14.01[N]}{115.01} \times (-1.79) \times 1000 \text{ kg} = -217.89 \text{ kg CCE}$$

$$P : \frac{30.97[P]}{115.01} \times (-1.61) \times 1000 \text{ kg} = -433.58 \text{ kg CCE}$$

The negative CCE values indicate that the elements of N and phosphorus in $\text{NH}_4\text{H}_2\text{PO}_4$ are acidic. Total calculated acidity from 1000 kg (metric tonne) of $\text{NH}_4\text{H}_2\text{PO}_4$ was equivalent to 651.47 kg CaCO_3 (217.89 kg + 433.58 kg = 651.47 kg), which contributed 47.28 kg CaCO_3 acidity per tonne of 15.2N-1.9P-12.6K fertilizer ($7.26\% \times 651.47 \text{ kg of CaCO}_3 = 47.28 \text{ kg}$).

$(\text{NH}_4)_2\text{SO}_4$:

$$N : \frac{14.01 \times 2[N]}{132.12} \times (-1.79) \times 1000 \text{ kg} = -379.56 \text{ kg CCE}$$

$$S : \frac{32.07[S]}{132.12} \times (-3.12) \times 1000 \text{ kg} = -757.25 \text{ kg CCE}$$

The negative CCE values indicate that the elements of N and sulfur in $(\text{NH}_4)_2\text{SO}_4$ are acidic. Total calculated acidity was equivalent to 1136.61 kg CaCO_3 per tonne of $(\text{NH}_4)_2\text{SO}_4$ (379.56 kg + 757.25 kg = 1136.61 kg), which

accounted for 774.92 kg acidity per tonne of 15.2N-1.9P-12.6K fertilizer ($68.16\% \times 1136.61 \text{ kg} = 774.92 \text{ kg}$).

KCl:

$$K : \frac{39.09[K]}{74.55} \times (+1.28) \times 1000 \text{ kg} = 671.34 \text{ kg CCE}$$

$$Cl : \frac{35.45[Cl]}{74.55} \times (-1.41) \times 1000 \text{ kg} = -670.48 \text{ kg CCE}$$

The net effect of KCl is therefore $\approx 0 \text{ kg CaCO}_3$ acidity according to PM assumptions.

Based on previous calculation, the 15.2N-1.9P-12.6K fertilizer had a net acidity of 822.20 kg CaCO_3 [47.28 kg from $\text{NH}_4\text{H}_2\text{PO}_4$ + 774.92 kg from $(\text{NH}_4)_2\text{SO}_4$ + 0 kg from KCl] per tonne of fertilizer. To convert kilograms CaCO_3 acidity per tonne of fertilizer to pounds CaCO_3 acidity per U.S. ton of fertilizer, as typically reported on fertilizer labels, the following conversion is made:

$$\frac{822.2 \text{ kg CaCO}_3 \text{ acidity}}{\text{metric tonne fertilizer}} \times \frac{1 \text{ metric tonne}}{1.1 \text{ U.S. ton}} \times \frac{2.2 \text{ lbs}}{1 \text{ kg}} = 1644.39 \text{ lbs acidity/U.S. ton}$$

Milliequivalents CaCO_3 (CCE) acidity applied per liter of substrate during each irrigation were calculated as:

$$(A) \frac{1}{0.152 \%N} \times 100 = 6.58 \text{ g fertilizer for every 1 g N.}$$

(B) 100 mg-L⁻¹ N applied $\times$ 0.1 L of fertilizer applied = 10.0 mg N applied per irrigation.

$$(C) \frac{(A) \times (B)}{1000 \text{ mg}} = 0.066 \text{ g fertilizer applied.}$$

$$(D) \frac{822.2 \text{ kg CaCO}_3 \text{ calculated}}{1000 \text{ kg (metric ton)}} \times (C) = 0.054 \text{ g of CaCO}_3 \text{ acidity applied.}$$

$$(E) (D) \times 2.86 \text{ containers per L of substrate} \times 20 \text{ meq per g CaCO}_3 = 3.09 \text{ meq CCE}$$

acidity applied per liter substrate per irrigation. The molecular weight of CaCO_3 is 100.08 g-mol⁻¹. One mole of CaCO_3 neutralizes 2 mol of acid. To neutralize 1 mole of acid, half the weight of CaCO_3 (50.04 g) is needed. The milliequivalent of CCE in 1 g of CaCO_3 is determined as: 1000 mg/50.04 = 20 meq CCE.

Because 20 applications (2.0 L) of the 100 mg-L⁻¹ N 15.2N-1.9P-12.6K ammonium fertilizer solution was made, a total of 61.8 meq of acidity was applied per liter of substrate during the 6-week experiment. Of this total acidity (N, phosphorus, sulfur, and chlorine = 2458.76 kg CCE), the relative percentage contribution to acidity estimated using PM for each nutrient was 24% N, 18% phosphorus, 31% sulfur, and 27% chlorine, whereas all of the basicity was contributed by potassium.

Gasometric method. Reduction in carbonate alkalinity in the substrate with time was used to quantify acidification during the experiment period. The gasometric procedure described by Huang et al. (2007) measures carbonates and bicarbonates but not other sources of substrate alkalinity such as phosphates and cation exchange capacity that are present in substrates. In this procedure, the addition of HCl to substrate containing carbonate-based limestones releases CO_2 gas as a byproduct, causing a volume displacement of solution in the gasometric system apparatus. This displacement by CO_2 can be measured and related to moles of CaCO_3 using the Ideal Gas Law. This procedure was shown to yield reliable estimations of CCE by Huang et al. (2007) for recovery of incorporated CaCO_3 . The gasometric procedure was used to measure initial and final residual carbonate lime present in the substrate. In the procedure, a 50-mL sample of substrate was placed in a 1-L flask with 75 mL deionized water. A stir bar was placed inside the flask that was then connected to a closed gasometric system. Twenty-five milliliters of 6 M HCl was then dispensed into the flask and the resulting CO_2 gas released from the reaction of HCl with carbonates and bicarbonates was measured by volume displacement of a solution. Temperature and pressure readings were recorded before and after testing a sample. The total reaction time for each sample was 30 min or when CO_2 volume readings were steady for at least 5 min, after which the final CO_2 volume was measured. The volume of CO_2 displacement was used to determine the amount of CaCO_3 present using the Ideal Gas Law (Huang et al., 2007). The change in CaCO_3 , or the amount of carbonate neutralized, was assumed to be the amount of acidity that had been added to the substrate using the equation:

$$\left[\frac{\text{g CaCO}_3}{\text{L}_{(\text{initial})}} - \frac{\text{g CaCO}_3}{\text{L}_{(\text{final})}} \right] \times 20 \text{ meq per g CaCO}_3 = \text{milliequivalent CCE per L of substrate.}$$

Acid drench method. Water alkalinity is normally calculated by titrating with mineral acid to a target pH of 4.5 (Bailey, 1996). The same principle was adapted in an acid drench method to measure alkalinity in the substrate (Huang et al., 2009). Samples of 350 mL of the HL and CHL substrates were placed in plastic bags and kept at container capacity for 7 d (without plants), and substrate-pH was measured. Hydrochloric acid (0.5 N) was then

added at volumes of 0, 14, 28, 42, 56, and 70 mL, resulting in 0, 20, 40, 60, 80, or 100 meq of acid per L of substrate, respectively. Substrate-pH was measured 7 d after acid application with four replicates. The change in substrate-pH (Δ pH) was analyzed using quadratic regression to generate Δ pH–milliequivalent relationships for each substrate. The Δ pH–milliequivalent regression curves were then used to estimate the equivalent milliequivalent of acidity from fertilizer in the greenhouse trial with geranium and impatiens using the measured change in substrate-pH from the beginning to the end of the crop.

Charge balance method. One approach to quantify acidity or basicity of a fertilizer is based on the principle of electroneutrality, whereby plant uptake of positively or negatively charged nutrient ions is counterbalanced with the exchange between plant and substrate of protons (H^+), hydroxyl (OH^-), carbonate (CO_3^{2-}), or other root exudates (Marschner, 1995). In this context, the milliequivalent of cations taken up by plant roots causes an equal milliequivalent of acidity to be added to the substrate, whereas anion uptake causes an equivalent basic reaction.

Soil processes should also be considered in the context of charge balance, particularly nitrification. The oxidation of 1 meq of NH_4^+ will produce a net acidity of 1 meq as long as the end product NO_3^- is also taken up by a plant with a net charge balance equal to direct plant uptake of NH_4^+ :

When determining the net milliequivalent of acidity created from application and uptake of fertilizer using charge balance, the acidity estimate of total nutrients applied must be corrected for those applied nutrients that are not taken up by the plant (accumulating in the substrate) or that change form (such as the NO_3^- product of nitrification).

For the charge balance method used in this study, acidity estimates were based only on N, phosphorus, and potassium because these three macronutrients comprised the bulk of the experimental fertilizer, are among the elements taken up in the greatest quantity by plants, and thus would be expected to have the greatest influence on acidity (Epstein and Bloom, 2005). Calcium (Ca) and magnesium (Mg) were not included in the acidity estimates because for each milliequivalent of H^+ released by a milliequivalent of Ca and Mg, a milliequivalent of acid neutralizing HCO_3^- or CO_3 was applied, thus neutralizing the Ca and Mg addition. Milliequivalents of acidity or basicity derived from the portion of nutrients applied but not taken up or nitrified can be determined using the change in nutrient concentration in the substrate. Substrate analysis has a key advantage over tissue analysis because total N uptake by plant tissue does not differentiate between nitrate and ammonium forms. These estimations include the

assumption that no leaching, volatilization, or other loss of nutrients occurred. To calculate the net milliequivalent of acidity (or basicity) of fertilizer nutrients applied and taken up or nitrified (as determined by nutrient change in the substrate), the following series of calculations were made:

1. Calculate total milliequivalent of acidity/basicity of nutrient applied:

$$(a) \frac{\% \text{ nutrient}}{\% \text{ Total N}} \times 100 = \text{mg} \cdot \text{L}^{-1} \text{ of fertilizer applied.}$$

(b) $(a) \times L$ of fertilizer solution applied per container = mg applied per container.

(c) $(b) \times 2.86$ containers $\cdot \text{L}^{-1}$ substrate = mg applied/L substrate.

$$(d) \frac{(c)}{\text{atomic wt. of nutrient}} = \text{millimoles per L of substrate.}$$

(e) $(d) \times \text{valence of nutrient salt} = \text{milliequivalent of acid (or base)/L substrate.}$

2. Subtract milliequivalent of potential acidity/basicity of nutrient not taken up (or nitrified) based on measured substrate nutrient concentration. There was no nitrate–nitrogen applied in the fertilizer, so all nitrate measured in the substrate was assumed to be equivalent to the amount of ammonium nitrogen nitrified and not taken up.

(a) $\text{mg} \cdot \text{L}^{-1} \text{ nutrient}_{(\text{final})} - \text{mg} \cdot \text{L}^{-1} \text{ nutrient}_{(\text{initial})} = \text{mg} \cdot \text{L}^{-1} \text{ change in nutrient per container.}$

(b) $(a) \times 2.86$ containers/L substrate = mg change in nutrient/L substrate.

$$(c) \frac{(b)}{\text{atomic wt. of nutrient}} = \text{millimoles not take up per L of substrate.}$$

(d) $(c) \times \text{valence of nutrient ion} = \text{milliequivalent of potential acid (or base)/L}$

substrate from nutrient not taken up or nitrified.

(e) milliequivalent of acid (base) applied – milliequivalent of acid (base) not taken up = milliequivalent of acid (base) from nutrient taken up.

Statistical analysis

Fertilizer acidity data estimated from all the methods were subject to analysis of variance analysis using SAS PROC GLM (SAS Institute, 2001). Means were separated using 95% confidence interval by substrate types (for gasometric and acid drench methods) or by species (for charge balance methods).

Results and Discussion

With respect to all data measured in the greenhouse experiment, cultivar within each of the two species did not affect any treatment comparisons. Data of cultivars within each species were therefore combined within species and further analyzed for species and/or substrate influences.

Substrate-pH and electrical conductivity

Substrate-pH did not differ between species with time ($P = 0.1706$). As expected, residual carbonate limestone in the CHL substrate resulted in less pH change (i.e., greater pH buffering) than the HL substrate ($P = 0.0001$) (Fig. 1). After 6 weeks, substrate-pH decreased by 2.01 units from the starting pH of 7.14 in the CHL substrate, compared with 2.64 units below the initial pH of 7.05 in the HL substrate. Although the additional carbonate limestone in the CHL substrate provided some buffering against decreasing pH, the pH of both the CHL and HL substrates dropped low enough to result in visual micronutrient toxicity symptoms in the geraniums, which commonly occurs below pH 6 (Argo and Fisher, 2002).

Substrate EC differed between species ($P = 0.0011$) but not substrate type ($P = 0.2714$). Substrate EC increased with time from an average 1.7 to 3.5 $\text{dS} \cdot \text{m}^{-1}$. It finished 0.5

Fig. 1. Substrate-pH change with time in the CHL substrate (containing hydrated and carbonate lime) and HL (hydrated lime only) in the greenhouse trial with data averaged across geranium and impatiens plants. Error bar represents pooled 95% confidence interval and symbols represent the mean of 12 replicates.

dS·m⁻¹ higher for geranium than impatiens. EC levels remained within acceptable to optimum values for container plants reported by Warncke (1995).

Substrate nitrogen–phosphorus–potassium

Substrate nutrient data differed between species for NO₃, NH₄, and phosphorus (P) ($P \leq 0.0003$) but not potassium (K) ($P = 0.3531$). The residual and non-residual substrates differed only in NO₃ concentration ($P = 0.0047$). There was also a species $\times$ substrate interaction for NO₃ ($P = 0.0250$), but substrate nutrient data for both substrates were combined for each species in the charge balance method results and calculations shown in Table 2 for a simpler illustration of the method.

Pierre's method. Using the previously shown calculations, 3.1 meq CCE of acidity per liter of substrate was introduced into the substrates with each fertigation event. During the course of 6 weeks, an estimated 61.8 meq CCE of acidity was contributed by the fertilizer per liter of substrate (Fig. 2A).

Gasometric method. Because the gasometric method measures residual carbonate, only the CHL substrate (which included carbonate limestone) was analyzed. There were no statistically significant differences between species ($P > 0.05$) at any week, so data were combined within each measurement date. Residual calcium carbonate lime measured in the substrate decreased with time (Fig. 2B). Residual carbonate CCE decreased to 27.1 meq/L of substrate from the initial 57.8 meq CCE of carbonate measured.

Fig. 2. (A) Milliequivalents (meq) of calcium carbonate (CCE) of acidity from 15.2N–1.9P–12.6K (100% N as NH₄-N) fertilizer applied per liter of substrate determined by Pierre's method (PM) and meq of CCE of carbonate neutralized with time as determined by change in residual carbonate using the gasometric method. (B) Milliequivalents of residual CCE in CHL (carbonate and hydrated lime) substrate measured with time using the gasometric method used to calculate the gasometric curve in A. With each fertigation, 100 mL of 100 mg·L⁻¹ N ammonium fertilizer was applied 20 times per 10-cm-diameter container, which according to PM provided a total of 61.8 of CCE per liter of substrate (3.09 meq per irrigation). Error bar represents 95% confidence interval of each data point and symbols represent the mean of 12 replicates.

Table 2. Fertilizer acidity calculated by the charge balance method which assumes cations (+) are acidic and anions (–) are basic.^z

	Geraniums				Impatiens			
	NO ₃ -N (–)	NH ₄ -N (+)	P (–)	K (+)	NO ₃ -N (–)	NH ₄ -N (+)	P (–)	K (+)
Total acidity applied from N–P–K								
Fertilizer analysis (%)	0.0	15.2	1.9	12.6	0.0	15.2	1.9	12.6
mg nutrient per L solution applied (a):	0.0	100.0	12.5	83.0	0.0	100.0	12.5	83.0
(a) $\times$ 2 L applied per container (b) = mg	0.0	200.0	25.0	165.9	0.0	200.0	25.0	165.9
nutrient applied per container (c):								
1 L/350 mL per container = 2.9 containers	0.0	571.4	71.4	474.1	0.0	571.4	71.4	474.1
per L substrate (d) (c) $\times$ (d) = mg nutrient								
applied per L substrate (e):								
atomic weight of element (f):	14.0	14.0	31.0	39.1	14.0	14.0	31.0	39.1
(e) $\div$ (f) = millimoles nutrient applied per L	0.0	40.8	2.3	12.1	0.0	40.8	2.3	12.1
substrate (g):								
cationic (anionic) charge of nutrient ion (h)	–1.0	1.0	–1.0	1.0	–1.0	1.0	–1.0	1.0
(g) $\times$ (h) = milliequivalent acid (base) from	0.0	40.8	–2.3	12.1	0.0	40.8	–2.3	12.1
nutrient per L substrate (i)								
Net N–P–K acidity =				50.6				50.6
Acidity corrected for substrate charge balance	NO ₃ -N	NH ₄ -N	P	K	NO ₃ -N	NH ₄ -N	P	K
initial mg nutrient per L of SME (Day 0,	8.2	11.1	1.8	9.8	8.2	11.1	1.8	9.8
before fertigation) (j)								
final mg nutrient per L SME (after 6 weeks	33.0	55.3	11.5	99.6	3.1	15.5	6.5	93.9
of fertigation) (k)								
(k) – (j) = change in mg nutrient per L of	24.8	44.2	9.7	89.8	–5.1	4.4	4.7	84.1
SME (l)								
(l) $\times$ (0.73 L SME per L of substrate) = change	18.1	32.3	7.1	65.5	–3.7	3.2	3.5	61.4
in mg nutrient per L of substrate (m)								
[(m) $\div$ (f)] $\times$ (h) = milliequivalent of nutrient	–1.3	2.3	–0.2	1.7	0.3	0.2	–0.1	1.6
not taken up per liter of substrate (n)								
(i) – (n) = milliequivalent nutrient assumed	1.3	38.5	–2.1	10.5	–0.3	40.6	–2.3	10.6
taken up or nitrified								
Net N–P–K acidity =				48.2				48.7

^zNutrient concentrations in substrate for geraniums and impatiens were means across the two substrates within species. N = nitrogen; P = phosphorus; K = potassium.

By difference, fertilizer applications were therefore estimated to contribute 30.7 meq CCE of acidity into the substrate (Fig. 2A).

Acid drench method. Substrate-pH decreased with increasing milliequivalent of HCl applied. Substrate-pH decreased as much as 3.49 units in the CHL substrate and 4.32 units in the HL substrate 7 d after applying the HCl acid drench (Fig. 3). Using the acidity and pH response curves shown in Figure 3, the estimated acidity required for similar pH drops observed in the greenhouse experiment were 43 and 37 meq for the CHL (2.01 units) and HL (2.64 units) substrates, respectively.

Charge balance method. Species resulted in different N and P (but not K) concentrations in the substrate at Week 6. The acidity estimate using the charge balance method was therefore calculated separately by species in Table 2. There was 3.5 times more $\text{NH}_4\text{-N}$ ($55.3 \text{ mg}\cdot\text{L}^{-1}$ SME) and nearly twice as much P ($11.5 \text{ mg}\cdot\text{L}^{-1}$) remaining in the geranium substrate compared with the impatiens substrate ($15.5 \text{ mg NH}_4\text{-N/L}$ and 6.5 mg P/L) (Table 2). There was also 10 times more $\text{NO}_3\text{-N}$ remaining in the geranium substrate ($33.0 \text{ mg NH}_4\text{-N/L}$) than in the impatiens substrate ($3.1 \text{ mg NH}_4\text{-N/L}$). There was no nitrate applied through fertigation, so the presence of nitrate in the substrate was assumed to be the result of nitrification. Nitrification has been shown to occur rapidly in container substrates above pH 5.5 (Argo and Biernbaum, 1997; Lang and Elliott, 1991). The lower concentration of nitrate in the impatiens substrate indicates there was either less nitrification or faster nitrate uptake compared with geraniums.

The net estimated acidity applied from N, P, and K fertilizer was calculated as 50.6 meq ($\text{NO}_3^- = 0.0$, $\text{NH}_4^+ = 40.8$, $\text{P} = -2.3$, $\text{K} = 12.1$ meq) with 40.8 meq (80.6%) from $\text{NH}_4\text{-N}$ alone (Table 2). The charge balance method used measured substrate nutrient data to account for nutrients that were applied but not taken up by the plant. Using data collected from the geranium substrate, N–P–K acidity was 48.2 meq CCE ($\text{NO}_3^- = 1.3$, $\text{NH}_4^+ = 38.5$, $\text{P} = -2.1$, $\text{K} = 10.5$ meq) with 80.1% from $\text{NH}_4\text{-N}$ uptake alone (Table 2). Using data collected from the impatiens substrate, N–P–K acidity was calculated at 48.7 meq CCE ($\text{NO}_3^- = -0.3$, $\text{NH}_4^+ = 40.6$, $\text{P} = -2.3$, $\text{K} = 10.6$ meq) with 83.4% from $\text{NH}_4\text{-N}$ uptake.

Comparisons between Pierre's method and other methods

Experimental estimates (summarized in Table 3) indicate that PM overpredicted the potential acidity of the ammonium-based fertilizer used in this experiment. Results of the gasometric, acid drench, and charge balance methods varied by 18 meq between each method. After 20 100-mL, 100-mg·L⁻¹ N applications of ammonium (100% $\text{NH}_4\text{-N}$) fertilizer, a total 61.8 meq of CCE (acid) per liter of substrate was applied during the course of the 6-week experiment using PM (Table 3). Using other methods, measured CCE acidity values ranged from 30.7 to 48.7

Fig. 3. Change in substrate-pH 7 d after a single application of 0.5 N HCl acid to CHL (containing hydrated and carbonate lime) and HL (hydrated lime only) substrates using the acid drench method. A quadratic curve was fit separately to each substrate type: Change in pH of CHL = $0.0002 \text{ meq}^2 - 0.0574 \text{ meq} + 0.0821$, $R^2 = 0.8907$; change in pH of HL = $0.0004 \text{ meq}^2 - 0.0839 \text{ meq} - 0.0812$, $R^2 = 0.9626$. Each symbol represents a single replicate.

Table 3. Comparison of milliequivalents (meq) of calcium carbonate equivalent (CCE) acidity per liter of substrate estimated using different fertilizer acidity methods when a 10-cm, 350-mL container received a total of 2 L of 15.2N–1.9P–2.68K fertilizer at an N rate of $100 \text{ mg}\cdot\text{L}^{-1}$.

Fertilizer acidity method	meq of CCE/L of substrate	
Pierre's method	61.8	
Charge balance substrate	Geranium 48.2 (± 2.12) ^z CHL ^y	Impatiens 48.7 (± 0.45) ^z HL ^y
Gasometric	30.7 (± 3.04) ^z	—
HCl acid drench	43.3 (± 2.65) ^x	37.1 (± 3.15) ^x

^zMeans $\pm 95\%$ confidence interval ($n = 12$).

^yCHL = substrate containing hydrated and carbonate lime; HL = substrate with hydrated lime only.

^xMeans $\pm 95\%$ confidence interval ($n = 12$) using pH measurements collected in a greenhouse experiment.

per L of substrate. Pierre's method, therefore, overestimated the acidity of the ammonium fertilizer by as much as 31.1 meq compared with other methods.

Conclusions

Three experimental methods were compared with PM. The charge balance method illustrates how the valence of nutrient ions can be used to estimate acidity. However, a weakness of this method was in our calculation of changes in substrate nutrient concentrations during the experiment, because an SME test with deionized water does not measure total nutrients, but only nutrients in the substrate solution. A more complete analysis using the charge balance approach could be applied to other nutrients in addition to N, P, and K, and indeed that would represent a completely new model that would require further validation. Ions contributed by the substrate itself, Ca and Mg from the lime sources, micronutrients and other ions in the fertilizer, irrigation water quality, or other contaminant sources would have some influence on pH dynamics.

The concept of measuring change in substrate alkalinity was achieved using two approaches. The gasometric method requires a carbonate source (typically limestone) in the substrate and is therefore not appropriate for all substrates (Huang et al., 2007). In addition, once all available carbonate is neutralized, the alkalinity measured with

the gasometric method will remain zero even if additional acid continues to be added by fertilizer. The acid drench method would be useful across a wider range of experimental conditions than the gasometric method, and the laboratory-generated pH response curve means that only pH measurement is required in subsequent plant experiments for a particular substrate.

We conclude that an alternative estimation of fertilizer acidity or basicity to PM could be developed that more closely represents plant, microbial, and soil chemical processes in soilless substrates with the potential to improve pH management. To develop such an equation, research and validation would be required. The charge balance–plant uptake and microbial components are particularly sensitive to N, which would therefore be a focus of future research and integration of the wealth of knowledge on cation–anion preference and the N cycle. An emphasis on N is also appropriate in terms of expected importance of N in contributing to pH effects of fertilizer. Epstein and Bloom (2005) indicate that on average, crop plants take up 1000 N atoms for every 250 K, 50 P, 30 sulfur, and three chlorine atoms. This ratio differs greatly from the relative importance of ions estimated using PM for the ammonium fertilizer in this study, whereby contribution to acidity was estimated in the proportions of 24% N, 18% P, 31% sulfur, and 27% chlorine, and 100% of basicity was

estimated to result from K. We did not observe differences in pH response between *Pelargonium* [an iron-efficient species (Argo and Fisher, 2002)] and *Impatiens*. However, differences between species in their total nutrient uptake ratios, cation–anion uptake ratio, and iron efficiency may mean that either species-specific parameters would need to be developed for fertilizers or, more realistically, assumptions would be needed to average across multiple species.

There are limits to the accuracy in predicting the pH effect of a fertilizer based on its chemical formulation only, because multiple factors interact once a fertilizer is applied in plant production (for example, plant species, initial soil pH, residual lime, and so on). By necessity, a series of assumptions would be needed for any estimation. However, an equation could include 1) a charge balance–plant uptake component that considers nutrient ionic charge and valence and relative proportion of uptake; 2) a microbial component, which takes into account the N cycle process such as nitrification and urea hydrolysis; and 3) a pure chemical component that accounts for pH reaction of fertilizer and other salts (for example, bicarbonate) in solution. By basing the acidity or basicity on concentration of ions in a nutrient solution rather than a dry fertilizer weight basis, such an equation would more closely represent the pH dynamics of production in soilless media or with hydroponics. Working on a solution basis would also facilitate balancing alkalinity of an irrigation water source with the acidity of the fertilizer to develop an overall neutral pH response of the overall nutrient solution. However, the same equation could also be adapted for controlled-release, slow-release, and granular fertilizers applied as solids to soilless substrates.

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