Optimizing the Physical and Nutritional Environment of Unleached Root-Zones

Curtis B. Adams

Utah State University

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OPTIMIZING THE PHYSICAL AND NUTRITIONAL ENVIRONMENT
OF UNLEACHED ROOT-ZONES

by

Curtis B. Adams

A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Plant Science
(Crop Physiology)

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ABSTRACT

Optimizing the Physical and Nutritional Environment of Unleached Root-Zones

by

Curtis B. Adams, Master of Science
Utah State University, 2010

Major Professor: Dr. Bruce Bugbee
Department: Plants, Soils, and Climate

Unleached root-zones represent an environmental ideal by eliminating wasteful leaching of nutrients and water. NASA grows plants in space in unleached root-zones, incorporating polymer-coated fertilizer (PCF) into a ceramic media (Turface or Profile). However, lack of growth productivity in space has led to the need for research to improve the nutritional and physical environment of the root-zone, which is the objective of this research. PCF types are diverse in release characteristics and the effects of temperature and substrate water content have not been well characterized. In spite of widespread use, studies on chemical properties and applied studies to verify soil physical models of ceramic media have been limited.

We quantified the release rate of three widely-used types of PCF (Polyon, Nutricote, and Osmocote) in water and in sand over a wide range of temperature (5, 15, 20, 30, and 40°C). Results indicated that substrate water content had a minimal effect on release rates. Nutricote fertilizers were the most consistent in releasing individual
nutrients with temperature and over time. Polyon fertilizers had the slowest release rates relative to the manufacturer’s specifications, but a relatively linear response to temperature. Osmocote fertilizers rapidly released nutrients at all temperatures. For more efficient PCF use, we present a comprehensive model that couples models to predict plant growth and PCF nutrient release rates. This model is based on phosphorus release, the nutrient found to be limiting to PCF-fertilized plants. The efficacy of the model to accurately predict PCF application rates was verified with a growth trial.

In ceramic media, relative media-sorbed nutrient concentrations were highly variable from bag to bag. Excesses of manganese, boron, magnesium, and sulfur in the media induced nutrient imbalances in plant tissues. Rinsing and soaking procedures on the media helped mitigate these nutrient imbalances. Ceramic media also interacted with added fertilizer ions. Copper, phosphorus, and zinc ions were largely removed from solution by these interactions. We also used plants to extract water from root-zones of ceramic media to characterize plant-available water and water supply dynamics. The results suggest that soil physical models may be used to predict plant-available water in ceramic media.
ACKNOWLEDGMENTS

Since my time as an undergraduate worker in the Crop Physiology Lab at Utah State University until now, as I complete my master’s degree, I have continually learned and gained understanding on what it takes to be a scientist. This is, to no small degree, due to the direction I have received from Dr. Bruce Bugbee. I appreciate his tutelage and patience, and for inviting me into his lab. Julie Chard and Alec Hay have been tremendous mentors in the lab from the beginning to end. I appreciate the input of my committee members, Drs. Scott Jones, Bill Doucette, and Astrid Jacobson, enhancing my research projects and aiding my understanding.

Thank you to my parents, Alma and Marie Adams, for always promoting the value of an education, encouraging me, and being a support as I have continued in educational pursuits. Thank you Jodi for the encouragement over the past year and, in advance, for the encouragement that will be needed in the years to come with more schooling.

Thank you to NASA for funding this research; and to the people at the Space Dynamics Lab for their collaboration to make this research impact the cultural practices for plant growth in space.

Curtis B. Adams
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USEFUL UNIT CONVERSIONS

Electrical Conductivity Unit Conversions

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<th>Common Salt Solutions</th>
<th>--------------- per cm ---------------</th>
<th>------------------ per m ------------------</th>
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<td>Tap Water</td>
<td>0.35 mS cm⁻¹ 0.35 mmho* cm⁻¹ 350 µS cm⁻¹</td>
<td>0.035 S m⁻¹ 0.35 dS m⁻¹ 35 mS m⁻¹</td>
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<tr>
<td>Optimal Nutrient Solution</td>
<td>1.0 mS cm⁻¹ 1.0 mmho* cm⁻¹ 1000 µS cm⁻¹</td>
<td>0.1 S m⁻¹ 1.0 dS m⁻¹ 100 mS m⁻¹</td>
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*S = Siemen, the SI unit for electrical conductance.

**mho = ohm spelled backward, an older unit of electrical conductance.

**mmho = millimho = 1 x 10⁻³ mhos

USEFUL ACRONYMS AND ABBREVIATIONS

SRF – Slow-Release Fertilizer(s)
An improvement over water soluble fertilizers, however greatly affected by environmental conditions (ex. inorganic materials of low solubility).

CRF – Controlled-Release Fertilizer(s)
A term often used synonymously with SRF; and equally often used to indicate that a fertilizer is an improvement over SRF, providing more actual “control” over nutrient release (ex. sulfur-coated urea).

PCF – Polymer-Coated Fertilizer(s)
The most technically advanced form of CRF in terms of controlling nutrient release (ex. Osmocote, Nutricote, and Polyon).

EC – Electrical Conductivity

PVC – Polyvinyl Chloride Pipe

ICP-OES – Inductively Coupled Plasma Optical Emission Spectroscopy

PPF – Photosynthetic Photon Flux

NO₃⁻ – Nitrate

NH₄⁺ – Ammonium

P – Phosphorus

K – Potassium

Ca – Calcium

Mg – Magnesium

S – Sulfur

B – Boron

Cu – Copper

Fe – Iron

Mn – Manganese

Zn – Zinc
CHAPTER 1
INTRODUCTION

Unleached root-zones represent an environmental ideal by eliminating wasteful leaching of nutrients and water. However, without leaching, nutrient excesses cannot be flushed out, making it necessary to precisely control the concentrations of each of the 14 plant-essential nutrients in the root-zone. In this pursuit, both fertilizer inputs and media characteristics must be optimized, which is the objective of this research (Figure 1 – 1).

![Diagram of leached versus unleached root-zones]

Figure 1 – 1: An illustration showing the fate of nutrients and water in leached versus unleached root-zones. Proper water and nutrient balance is more important in an unleached system, because imbalances cannot be flushed out of the pot.

Unleached root-zones are used in spaceflight applications where water and nutrient conservation are essential----an ideal model for unleached systems on Earth. The
colonization of space and long-term space travel will depend on our ability to provide for
the metabolic needs (oxygen, water, and food) of a crew, with minimal re-supply from
Earth. Currently, controlled-release fertilizer (CRF) is used to supply nutrients and
ceramic aggregates are the media for spaceflight root-zones.

Controlled-release fertilizers (CRF) are a class of fertilizers designed to provide
regulated availability of nutrients over time, increasing fertilizer use efficiency. The
subset of CRF that were investigated in these studies were polymer-coated fertilizers
(PCF), which are the most technically advanced form of CRF in terms of controlling
product longevity (Goertz, 1993).

Ceramic media is commercially sold as Turface or Profile and is often called
arcillite. Beyond use in spaceflight root-zones, ceramic media is a medium of choice for
research applications because it can easily be removed from root surfaces at harvest.
Ceramic media has been intensively modeled for physical and hydraulic properties
(Blonquist et al., 2006; Heinse et al. 2007; Monje et al. 2003; Steinberg et al. 2005), but
plant growth studies are necessary to provide verification of the soil physical models.
The chemical/nutritional interaction of ceramic media with growing plants is also poorly
categorized.

**Polymer-Coated Fertilizer Literature Review**

**Introduction**

Providing predictable, prolonged availability of nutrients has long been a goal of
fertilizer manufacturers. In response, options classified as slow-release fertilizers (SRF)
and controlled-release fertilizers (CRF) have been developed. Potential agronomic and
physiologic benefits include decreased fertilizer loss by leaching, increased nutrient recovery by plants, decreased labor inputs, and increased control of substrate nutrient levels (Shaviv and Mikkelsen, 1993).

The terms SRF and CRF are often used synonymously; however, CRF is also often meant to denote an improvement over more rudimentary SRF, exhibiting more “control” over the nutrient release profile (Shaviv, 2001). SRF include options such as inorganic materials of low solubility and relatively soluble materials that gradually decompose in the soil, the release rates of which are highly affected by environmental conditions (Shaviv and Mikkelsen, 1993). CRF options are most commonly fertilizer materials coated with a physical barrier that mediates release. While coated materials are generally an improvement over the SRF options described above, they do not come without drawbacks. CRF options, such as sulfur-coated fertilizers, may have undesirable characteristics such as large, initial “bursts” of fertilizer release and prolonged unavailability of nutrients that are “locked-off” and insoluble (Shaviv, 2001). Polymer-coated fertilizers (PCF) are the most technically advanced form of CRF in terms of controlling product longevity and providing nutrient-use efficiency, attempting to minimize the undesirable characteristics of other CRF, such as sensitivity in release to environmental conditions (Goertz, 1993).

PCF use polymer-coating technologies for regulation of fertilizer release. Fertilizer release is mediated by movement of nutrients through a semi-permeable, organic polymer membrane. Nutrient salts attract water through the polymer coating, which condenses, dissolves nutrients, and creates pressure within the polymer coating that drives the diffusion of nutrients outward. Due to relatively high coating costs, PCF
are generally used in higher value applications, such as in containerized nursery plant propagation (Goertz, 1993). PCF are the most viable option for providing successful, prolonged, controlled release of nutrients in unleached root-zone environments.

**Descriptions of Osmocote, Nutricote, and Polyon**

Osmocote, Nutricote, and Polyon are widely used types of PCF that represent three of the primary controlled-release polymer coating technologies that are available. Polymer coatings can be categorized as thermoset resins or thermoplastics, but technologies vary greatly among manufacturers (Goertz, 1993). The following descriptions of PCF technologies are adaptations on Goertz (1993).

Osmocote is produced by the Grace Sierra Horticultural Products Co, Marysville, Ohio, USA. A soluble fertilizer core is coated with a thermoset copolymer of dicyclopentadiene and a glycerol ester (linseed oil) dissolved in an aliphatic hydrocarbon solvent. Coating weights vary from 10 to 20% of total fertilizer weight, depending on the release duration. Nutrient release patterns vary simply with coating thickness and the composition of the fertilizer core.

Nutricote is produced by the Chisso-Asahi Fertilizer Company, LTD., Tokyo, Japan. A soluble fertilizer core is coated with thermoplastic resins, such as polyolefins, poly(vinylidene chloride), and copolymers. Thermoplastic polymers are highly impermeable to water, so release controlling agents such as ethylene-vinyl acetate and surfactants are added to the coating to obtain the desired diffusion characteristics. Coating thicknesses are uniform among all fertilizers, with release being dependent only on the amount of release-controlling agents that are added. A designation of T-180 means the product releases 80% of its nutrients within 180 days of the time that the
fertilizer is placed in water at room temperature (25°C). Like all PCF, release rate is a
function of temperature; however, the manufacturer attempts to minimize this effect by
dispersing mineral fillers into the coating.

Polyon is produced by Pursell Industries, Sylacauga, Alabama, USA. Nutrient
salts are coated by a process known as reactive layer coating. The fertilizer substrate is
coated with an excess of liquid diphenylmethane diisocyanate, which is then treated with
liquid polyesters; the two react, polymerizing in situ to form a polyurethane coating that
is chemically bonded to the fertilizer core. The resultant ultra-thin membrane coating has
lower production costs than other types of PCF. Coating weights vary from 1.5 to 15%
of total fertilizer weight, depending on the release duration. Nutrient release patterns
vary simply with coating thickness and the composition of the fertilizer core, similar to
Osmocote.

Factors Affecting Release

Only a few factors significantly affect PCF nutrient release rates. Factors such as
soil pH and soil type have a negligible effect on the release of nutrients, and substrate
water content only has a small effect (Broschat, 2005; Gambash et al., 1990; Kochba et
al., 1990; Oertli and Lunt, 1962b; Richards and Reed, 2004; Shibata et al., 1980).

Broschat (2005) reported small differences in PCF nutrient release with substrate
water content: nutrient release was fastest when placed in pure water, slower when
incorporated into a moist substrate, even slower when applied to the surface of a moist
substrate, and stopped completely when dry. In Nutricote fertilizers, Shibata et al. (1980)
claimed that nutrient release rate was approximately 1.2 to 1.5 times faster in pure water
than in soil. Work by Kochba et al. (1990) found that CRF release in substrates with
moisture contents from 50% to 100% of field capacity were not significantly different, and only at moisture contents below 50% of field capacity were release rates slowed.

To explain the weak dependence of PCF nutrient release on water content, Kochba et al. (1990) and Gambash et al. (1990) suggested that the vapor pressure of water in the soil is the limiting step in nutrient release. This theory suggests that the onset of nutrient release from PCF is limited by the migration of water vapor into fertilizer prills, the rate of which is determined by the vapor pressure of water in the environment surrounding the fertilizer prills. Kochba claims that PCF polymer coatings are not initially permeable to liquid water. After vapor migration into the prill, condensation occurs, fertilizer salts are dissolved, pressure is generated within the prill which changes prill permeability to liquid water, and fertilizer solution is driven out of pores in the polymer coating. Only when substrate water contents descend to low enough levels for the water vapor pressure to decrease will fertilizer released be slowed. Given that relative humidity is approximately 100% within even moderately wet soil substrates at all times, release would only be slowed in dry soil conditions according to this theory. However, this theory fails to consider the contribution of osmotic potential in driving fertilizer release. The concentrated fertilizer cores of PCF prills have a tremendously negative osmotic potential, which draws in water, creating a high positive pressure within PCF polymer coatings. This positive pressure would be in the mega-Pascal range, the exact value of which would depend on the core ion composition and the temperature (according to the Morse equation). This theory also fails to consider the individual physical characteristics of PCF polymer coatings related to permeability as a function of environmental parameters.
Richards and Reed (2004) also found a weak dependence of PCF release rate on substrate moisture content. Because moisture content varies within plant-growth substrates, especially on the surface, the location and method of PCF application within substrates can have an effect on nutrient release and, as a result, plant growth. To determine the PCF placement that would give rise to the greatest plant percent dry mass, Richards and Reed (2004) applied Osmocote prills to media by incorporation, topdressing, placing on bottom, and placing by dibble. They found that incorporated placement increased dry weight percentages slightly from other application methods. They assumed that an increase in percent dry mass was representative of an increase in fertilizer release.

The Effect of Temperature

The environmental factor that imposes the most significant effect on PCF nutrient release rates is temperature (Goertz, 1993; Huett and Gogel, 2000; Husby et al., 2003; Kochba et al., 1994; Oertli and Lunt, 1962a). The nutrient release longevities of the three brands of PCF included in these studies are based on different temperatures: Nutricote 25°C, Osmocote 21°C, Polyon 27°C. Use of PCF at temperatures higher than prescribed can cause considerable reduction in product longevity, overloading nutrient supply early and leaving plants without sufficient nutrients later; and likewise, use of PCF at temperatures lower than prescribed can extend product longevity beyond what is desired, leaving plants without sufficient nutrients. Adjustments to PCF application rate and release formulation may be made based on the temperature at which the PCF will be used to better match plant demand with nutrient supply.
An early study on the effects of temperature by Oertli and Lunt (1962a) showed that temperature has long been a concern in the use of CRF. The study, on an undisclosed CRF, claimed almost a doubling (~10% increase in release rate per °C) in initial release rate with an increase in temperature from 10 to 20°C. However, given more time, past the initial stages of release, the effect of temperature on release decreased drastically in this study. Table 1 – 1 presents calculations from the original data of Oertli and Lunt (1962a). Based on the percent nutrient released, Table 1 – 1 shows that the effect of temperature was less than 10% (increase in release rate per °C) after five and ten weeks in the case of every nutrient. However, it is our opinion that there may be significant experimental or labeling error in this experiment, since at the conclusion of the experiment, percent release at 23°C exceed that at 27°C in the case of every nutrient other than ammonium. Excluding the high percent increases from 21 to 23°C and the decreases from 23 to 27°C (with the assumption of experimental error invalidating these values), percent increases per degree Celsius were in the range of 0.2 to 3.

Table 1 – 1: Calculations made from data in Oertli and Lunt (1962a). The data points are the percent increase or decrease per degree Celsius for NO$_3$, NH$_4$, P and K release from a slow-release fertilizer as the temperature was raised in four increments from 10 to 27°C.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Time (weeks)</th>
<th>10°C - 16°C (% °C$^{-1}$)</th>
<th>16°C - 21°C (% °C$^{-1}$)</th>
<th>21°C - 23°C (% °C$^{-1}$)</th>
<th>23°C - 27°C (% °C$^{-1}$)</th>
<th>(10°C - 27°C) (% °C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3$</td>
<td>0 - 5</td>
<td>1.2</td>
<td>0.4</td>
<td>7.5</td>
<td>-2.0</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>0 - 10</td>
<td>1.0</td>
<td>0.2</td>
<td>7.5</td>
<td>-3.0</td>
<td>2.4</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>0 - 5</td>
<td>1.2</td>
<td>1.4</td>
<td>1.5</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0 - 10</td>
<td>0.7</td>
<td>1.4</td>
<td>0.5</td>
<td>0.3</td>
<td>2.1</td>
</tr>
<tr>
<td>K</td>
<td>0 - 5</td>
<td>0.8</td>
<td>1.6</td>
<td>6.0</td>
<td>0.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0 - 10</td>
<td>1.7</td>
<td>2.2</td>
<td>7.0</td>
<td>-0.3</td>
<td>2.4</td>
</tr>
<tr>
<td>P</td>
<td>0 - 5</td>
<td>1.0</td>
<td>1.6</td>
<td>3.0</td>
<td>0.0</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>0 - 8</td>
<td>1.8</td>
<td>1.8</td>
<td>3.0</td>
<td>-0.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>
In a steady-state temperature study by Huett and Gogel (2000), the nutrient release rate of 17 PCF formulations of Nutricote, Apex Gold (Polyon), Osmocote, and Macrocrete were measured at 30°C and 40°C, higher than the prescribed temperatures for use of any of these PCF. The mean reduction in longevity for these products with an increase in incubation temperature from 30°C to 40°C was 19-21% for nitrogen, 13-14% for phosphorus, and 14-15% for potassium. Nutricote showed the overall lowest reduction in longevity, with 19% mean reduction for nitrogen, 13% for phosphorus, and 14% for potassium. The Nutricote and Polyon products had release periods that were up to 10 weeks longer than comparable Osmocote products. However, considerable variation was found among products of the same brand. For example, the nitrogen release period of red and blue Nutricotes (type 140) was 56 to 63 days, while Nutricote Plus (type 140) was 110 days in this study. Table 1 – 2 below summarizes the effect of temperature on the release of nitrogen, phosphorus, and potassium in each fertilizer (in terms of percent increase in release rate per °C, for comparison among other studies).
Table 1 – 2: Calculations made from data in Huett and Gogel (2000). The data points are the reduction in time per degree Celsius for 17 fertilizers to release 90% of their N, P, and K when held at 40°C relative to their release rates at 30°C.

<table>
<thead>
<tr>
<th>Fertilizers</th>
<th>N (°C⁻¹)</th>
<th>P (°C⁻¹)</th>
<th>K (°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nutricote 140 d plus</td>
<td>2.2</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Nutricote 140 d blue</td>
<td>2.3</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Nutricote 140 d red</td>
<td>1.6</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Nutricote 270 d black</td>
<td>1.5</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Nutricote 270 d green</td>
<td>2.3</td>
<td>0.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Nutricote 360 d brown</td>
<td>1.2</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Polyon high N 5-6 m</td>
<td>1.8</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Polyon high N 8-9 m</td>
<td>1.9</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Polyon 8-9 m</td>
<td>3.5</td>
<td>0.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Polyon high N 10-12 m</td>
<td>1.2</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Polyon 10-12 m</td>
<td>1.9</td>
<td>2.4</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>2.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Osmocote 5-6 m plus</td>
<td>2.5</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Osmocote 5-6 m</td>
<td>1.5</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Osmocote 8-9 m plus</td>
<td>0.6</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Osmocote 12-14 m plus</td>
<td>1.9</td>
<td>1.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Osmocote 12-14 m</td>
<td>3.0</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>avg</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Macrocote plus 9 m</td>
<td>2.5</td>
<td>0.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Kochba et al. (1994) studied the effect of temperature on PCF (Multicote) release rate as a function of time by incubating Multicote KNO₃ granules at 30 and 40°C for 110 days. Calculations on the percent increase in release rate per degree Celsius are presented in Table 1 – 3. Except for the final value at 110 days, the percent increase is relatively invariant over time with an average of ~6% per degree Celsius.
Table 1 – 3: Calculations made from data presented by Kochba et al. (1994). The table shows the percent increase in release rate from Multicote polymer-coated fertilizer incubated at 40ºC from those incubated at 30ºC as a function of time.

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>% ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>5.7</td>
</tr>
<tr>
<td>40</td>
<td>5.1</td>
</tr>
<tr>
<td>60</td>
<td>6.7</td>
</tr>
<tr>
<td>80</td>
<td>6.4</td>
</tr>
<tr>
<td>110</td>
<td>3.7</td>
</tr>
</tbody>
</table>

In contrast to steady-state temperature effects, to understand the effect of a simulated, diurnal temperature change on nutrient release rate, Husby et al. (2003) measured nutrient release from PCF as the temperature was raised from 20ºC to 40ºC and again lowered to 20ºC over the course of a 20 hour period. Three PCF were studied, all with an 8-9 month release period: Osmocote Plus 15-9-12, Polyon 18-6-12, and Nutricote 18-6-8. The results, as shown in Table 1 – 4, suggest that PCF nutrient release was extremely affected by a diurnal temperature fluctuation, creating percent increases per degree Celsius in nutrient release an order of magnitude or more greater than those found in steady-state temperature studies. One factor that may have contributed to the higher percent increases in nutrient release in their study was the continuous flow-through method used to gain instantaneous nutrient concentration measurements over the 20 hour period, perhaps increasing the driving gradient for nutrient release over more typical, steady-state conditions. It is also possible that the integrity of the fertilizers’ coating was compromised in the process of transferring the prills from water into sand, creating artificial results.
Table 1 – 4: Calculations made from data presented by Husby et al (2003). The values are the percent increase in nitrate release per degree Celsius as the temperature was raised from 20°C to 40°C and lowered back to 20°C over a 20 hour time period.

<table>
<thead>
<tr>
<th>Osmocote</th>
<th>Nutricote</th>
<th>Polyon</th>
</tr>
</thead>
<tbody>
<tr>
<td>206.2</td>
<td>63.9</td>
<td>79.6</td>
</tr>
</tbody>
</table>

**Release as a Function of Time**

With all environmental factors constant, at a given temperature, unique nutrient release profiles may exist for each nutrient in each PCF. Effective use of PCF requires knowledge of these release profiles so accommodation can be made for the increases and decreases in nutrient release rates that are unique to each PCF with time.

Research on individual prill release characteristics and prill population heterogeneity suggests that some or all PCF may achieve slow release by the combined effect of heterogeneously releasing prills, rather than by uniform delay and prolongation of release by each prill over time. Given this heterogeneity, the unique release profile of each PCF as a function of time would therefore be the result of the distribution of release heterogeneity among the population. A study of individual Macrocote (release timetable unspecified) prill behavior by Kochba et al. (1994) showed extreme variation from prill to prill, with some prills releasing all of their nutrient contents rapidly, while others had released less than half of their nutrient contents after 110 days. Kochba et al. (1994) noted that individual prills differed in the time after exposure to moisture needed to start their release process and in their duration of release. Gambash et al. (1990) found the same heterogeneity in prill populations of unspecified, commercially available CRF.
Husby (2000) studied nutrient release as a function of time for Osmocote Plus 15-9-12, Polyon 18-6-12, and Nutricote 18-6-8 at 40°C, a temperature higher than prescribed for use of all these fertilizers. He found that Osmocote released a large amount of nutrients quickly and subsequently showed a declining release rate over time, while Nutricote and Polyon had relatively more consistent nutrient release patterns over time.

**Relative Nutrient Release Rates and Recovery**

It appears that 100% release of nutrients from PCF rarely occurs. In a study of seven PCF in which nutrient release was measured until release ceased, Broschat and Moore (2007) found that the percent release of phosphorus ranged from 50 to 80%, while over 90% of potassium was released, and nearly 100% of nitrogen was released. The release of magnesium, manganese, and iron was poor, with less than 50% these elements released from Osmocote and Plantacote, while Nutricote products released iron and manganese more effectively. The nutrient release of Nutricote and Polyon continued long after the manufacturers’ stated product longevity (the study was conducted at temperatures 2°C and 3.5°C lower than the temperature correlated with Nutricote and Polyon’s stated longevities, respectively).

In another study where nutrient release was tracked just over the timeframe for which the fertilizers are rated by their manufacturers, Broschat (2005) compared the relative nutrient release of 8-9 month Osmocote and Nutricote type 180 at 23°C (Figures 1 – 2 and 1 – 3). Broschat reported that Osmocote released more of its nutrients than Nutricote over this timeframe. At 7 months, Osmocote prills retained 8% of their original NO$_3$, 11% of NH$_4$, 25% of K, and 46% of their P, whereas Nutricote prills retained 21% of their original NO$_3$, 28% of NH$_4$, 51% of K, and 65% of P. Although absolute nutrient
release rates differed among fertilizers, trends in relative nutrient release were the same with the release of nitrogen to be the fastest, followed by potassium, and finally phosphorus (Figures 1 – 2 and 1 – 3). Other researchers (Du et al., 2006; Huett and Gogel, 2000) have observed the same trend across a wide range of PCF (Osmocote, Nutricote, Macrocote, and Polyon). Both the unique physical characteristics of each nutrient that affect their diffusion characteristics and the unique characteristics of each PCF’s polymer coating technology contribute to this shortcoming. These differences in relative release rates are a cause for concern, as they may lead to nutrient ratios that are out of balance and not ideal for plant growth. For example, Huett and Gogel (2000) reported phosphorus being released at 60-80% the rate of nitrogen and potassium, creating phosphorus:nitrogen ratios low enough to cause phosphorus deficiency.

![Nutricote T-180 (6 month)](image)

Figure 1 – 2: The relative rate of nutrient release from Nutricote 18 – 6 – 8 (T-180) fertilizer incubated at 23°C (adapted from Broschat (2005)). Graph points represent the nutrient average relative release in several substrate environments.
Figure 1 – 3: The relative rate of nutrient release from Osmocote 15 – 9 – 12 (8-9 month) fertilizer incubated at 23°C (adapted from data in Broschat (2005)). Graph points represent the nutrient average relative release in several substrate environments.

PCF Nutrient Movement Depending on Irrigation Scheme

In pots and other plant-growth containers, the method of irrigation affects the movement of nutrients released from PCF prills within the container. A study by Richards and Reed (2004) was done to track the movement of nutrients in a recirculating sub-irrigation system and a top-watering system. The results showed that the amounts of nutrients found in each zone (top, middle, and bottom) of the pots was greatly affected by the irrigation system. In the sub-irrigated pots, the nutrients were mostly concentrated in the top and middle zones; whereas in the top-watered pots, the nutrients were more evenly distributed. It was found that, at the end of the experiment, more total nutrients had accumulated in the media of the sub-irrigated pots than the top-watered pots. For example, 23% of applied K remained in the media of the sub-irrigated pots, whereas 9%
of applied K remained in the media of the top-watered pots. This difference in nutrient accumulation was caused by the leaching of nutrients in the top-watering system and lack of leaching in the sub-irrigated pots; and to the greater accumulation of nutrients in the top layer in the sub-irrigation system where fewer plant roots exist. However, no significant difference in the rate of nutrient uptake by the plants in either of the irrigation systems was observed in this study. Thus, in an unleached, sub-irrigated system, less PCF can be added without loss of growth, with less waste of nutrients.

**PCF Rate Modeling**

In attempts to describe the processes determining PCF nutrient release, physical principals and empirical tests have been used to develop models of release. Kochba *et al.* (1990) and Gambash *et al.* (1990) developed a simple model based on the proposition that the vapor pressure of water surrounding PCF prills is the factor limiting release rate, and included constants specific for each PCF that must be empirically determined. Fujinuma *et al.* (2009) is an example of semi-empirical model that was developed for the special case in which PCF is surface-applied, a case in which the effect of substrate water content cannot be ignored. Fully mechanistic, mathematically intensive models have extended understanding of the physical principals and processes underlying release for single-nutrient PCF (Al-Zahrani, 1999; Du *et al.*, 2004; Du *et al.*, 2008; Shaviv *et al.*, 2003a; Shaviv *et al.*, 2003b); however, these models may be most effectively used by the manufacturers of PCF products and not by PCF users. These models are generally based on designating three distinct stages of the release process (lag period, constant release stage, and gradual decay stage) and include parameters for prill characteristics such as coating permeability, coating thickness, prill diameter, and chemical properties of the
fertilizer. The precise modeling of mixed-nutrient PCF is a more complex problem due to the individual chemical properties of each nutrient ion and the interactions among nutrients.

Ceramic Media Literature Review

Introduction

Ceramic aggregates (Turface or Profile) have long been used as media for plant growth, especially in scientific settings, because root growth in baked ceramics is regular and it may be washed out of roots with relative ease for root analysis. More recently, baked ceramics have found popularity as a plant growth substrate for space flight applications. Conventionally, however, ceramic media is used as an amendment to sports fields and golf courses. The manufacturer of Turface and Profile (Profile Products LLC, Buffalo Grove Illinois) claims that the two products are derived from a common parent, clay material, and that they only differ in particle size distribution. Turface (Pro League and MVP) has a relatively large particle-size distribution, with roughly 50% of media mass containing particles having diameters < 2 mm, and 50% > 2 mm (up to ~ 4 mm). Profile has a smaller particle-size distribution, with virtually all particles having diameters between 0.25 and 0.5 mm.

Physical and Hydraulic Properties

Steinberg et al. (2005) preformed a comprehensive review of the physical and hydraulic properties of ceramic media. Table 1 – 5 below, taken directly from Steinberg et al. (2005), lists the values of eight physical and hydraulic parameters or properties of ceramic media of two aggregate size distributions. Note the difference between the total
porosity and the saturated water content, $\theta_s$, which is likely due to the trapping of air upon wetting from a dry state. Complete saturation (porosity = $\theta_s$) is possible with a vacuum or other techniques that remove trapped air.

Table 1 – 5: The values of eight physical and hydraulic parameters and properties of ceramic media of two particle size distributions (from Steinberg et al., 2005).

<table>
<thead>
<tr>
<th>Parameter/property</th>
<th>0.25 – 1 mm</th>
<th>1 – 2 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g·cm$^{-3}$)$^\dagger$</td>
<td>0.68</td>
<td>0.64</td>
</tr>
<tr>
<td>Particle density (g·cm$^{-3}$)</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>BET surface area (m$^2$·g$^{-1}$)</td>
<td>83 ± 0.75</td>
<td>93.5 ± 1</td>
</tr>
<tr>
<td>Total porosity (%)$^i$</td>
<td>72.8</td>
<td>74.4</td>
</tr>
<tr>
<td>Air filled porosity (%)$^§$</td>
<td>≈8 – 9</td>
<td>≈6 – 8</td>
</tr>
<tr>
<td>$\theta_s$ (cm$^3$·cm$^{-3}$)$^¶$</td>
<td>0.65</td>
<td>0.665</td>
</tr>
<tr>
<td>$\theta_r$ (cm$^3$·cm$^{-3}$)$#$</td>
<td>0.374</td>
<td>0.371</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity (cm·s$^{-1}$)$^#$</td>
<td>0.12 ± 0.06</td>
<td>0.941 ± 0.5</td>
</tr>
</tbody>
</table>

$^\dagger$Oven dry basis.
$^i$Total porosity as calculated from: 1 – (bulk density/particle density).
$^§$Similar results also obtained by mercury porosimetry.
$^¶$Calculated from: total porosity – saturated water content ($\theta_s$).
$^#$Saturated water content ($\theta_s$).
$^\#$Residual water content for inter-aggregate pore space.

The soil water retention curve or soil water characteristic is a unique soil or medium property that describes the relationship between soil water content and the matric potential. Matric potential is a descriptor of the energy by which water is held in a substrate, including the adhesive forces among solid substrate surfaces and water, and the cohesive forces among water molecules. Matric potential can be measured in situ by a tensiometer or, in disturbed samples, by other methods that apply suction to saturated substrate (Raviv et al., 2004). Heinse et al. (2007), Blonquist et al. (2006), Steinberg and Portiz (2005), and Steinberg et al. (2005) have done work to establish the water retention characteristics of ceramic media of three particle size distributions (Figure 1 – 4).
The application of orders of magnitude more suction beyond the matric potential suction ranges shown in Figure 1 – 4, reveals that ceramic media has a bimodal pore size distribution, which includes both inter-aggregate pores and intra-aggregate micropores. Total porosity of the material $\approx 74\%$ for both 0.25 – 1 mm and 1 – 2 mm aggregates, $\sim 50\%$ of which is intra-aggregate micropores and $\sim 50\%$ is inter-aggregate pores (Steinberg et al., 2005). Steinberg et al. (2005) suggested in their research that water held within intra-aggregate micropore spaces was mostly tightly bound and unavailable to support plant growth. Of the total water extractable by plants, which was found to be $\sim 45\%$ (v/v *100), $\sim 22\%$ was found to be within intra-aggregate micropores and $\sim 78\%$ in inter-aggregate pores. The value of 45% available water directly aligns with observations.
of a 45% change in water content over a relatively small matric potential suction range in both Profile and sieved Turface.

In practice, the unavailability of water in the intra-aggregate micropores and the readily available water within the inter-aggregate pores, creates a media that generously supplies water for plant growth, until the water content in the inter-aggregate pores is depleted. Hydraulic conductivity drops by several orders of magnitude as the water-filled pore size transitions across pore domains. However, negative effects of this characteristic may be mitigated to some extent by altering particle-size distribution, watering method and frequency, and growth container height.

High water holding capacity coupled with good aeration is a requirement for good plant growth medium. The particle-size distribution of a medium dictates the pore size distribution, and thus determines the water (and consequently air) retention properties of the media (Steinberg et al., 2005). Particle-size distribution, in addition to watering frequency and plant-growth container height, are factors that may be adjusted for air/water level optimization (Richards et al., 1986). With great structural integrity (low potential for structural breakdown) and availability in diameter from 0.25 to ~4 mm, ceramic media may be sieved and/or mixed to provide a wide range of particle size distributions (Steinberg et al., 2005).

The soil water characteristic curves shown in Figure 1 – 4 graphically illustrate how optimizing particle size distribution can provide a more ideal physical condition within the root-zone environment. In Figure 1 – 4, the lines representing the widest range of aggregate sizes (0.25 – 2 mm diameters), exhibits a larger change in the matric potential for a given change in water content, while the narrower particle size
distributions shown (i.e., 0.25 – 1 mm and 1 – 2 mm diameters) exhibit less change in matric potential for a unit change in water content. This can lead to too much water and insufficient air below a point in the root-zone related to particle size distribution and too much air and insufficient water above that point. The narrow particle size distribution results in a reduced factor of safety when trying to manage water based on an imposed matric potential. A broader particle size distribution potentially provides a more ideal air to water ratio across a broader range of the root-zone, depending on root-zone height and water retention property of the medium in question.

**Ceramic Media as a Media Amendment**

Several studies report the use of ceramic media as amendments to various plant growth media. Desirable properties that ceramic aggregates may add to media include increased water holding capacity and the capacity for nutrient exchange.

Warren and Bilderback (1992) carried out an experiment to test the chemical and physical effects of amending a pine bark plant growth substrate with ceramic aggregates. In this study, container capacity water content, plant-available water, and substrate bulk density increased with increasing ceramic media rate. Substrate NH$_4^+$, P, and K concentrations increased with increasing ceramic aggregate rate, suggesting that the ion exchange capacity of ceramic aggregates improved the retention of nutrients within the root-zone. As a result of these effects, Cotoneaster ‘Skogholm’ shoot dry weight increased linearly with increasing ceramic aggregate rate; and Azalea ‘Sunglow’ shoot dry weight increased curvilinearly with increasing ceramic aggregate rate.

Jaeger and Hellmers (1981) compared the growth of three plant species (soybean, tomato, and marigold) in a 1:1 gravel-vermiculite medium (a standard Duke University
medium) to a 1:1:1 gravel-vermiculite-ceramic aggregate medium. The growth response of each species differed for another, but growth was improved with the amendment of ceramic media across all species. Dry weight increases with ceramic media amendment were 21% for soybeans, 19% for tomatoes, and 8% for marigolds. The authors suggested that these increases in dry matter production were due to increased water holding and ion exchange capacities that resulted from the addition of ceramic aggregates.

REFERENCES


CHAPTER 2

EFFECTS OF SUBSTRATE WATER CONTENT AND TEMPERATURE ON THE NUTRIENT RELEASE OF THREE TYPES OF POLYMER-COATED FERTILIZERS

ABSTRACT

Polymer-coated fertilizers (PCF) are designed to provide a regulated supply of nutrients over specified time intervals. The release rate is known to fluctuate with temperature, but the effect of temperature on the release of individual nutrient ions has not been well characterized. In addition, the effect of substrate water content has not been consistent among studies. We quantified the release rate of three widely-used types of PCF (Polyon, Nutricote, and Osmocote) in water and in sand over a wide range of temperature (5, 15, 20, 30, and 40ºC). Release rate formulations of each type ranging from one to 14 months were studied. Electrical conductivity and individual nutrient concentrations were measured at weekly intervals. There were no statistically significant differences in nutrient release rates between PCF placed in water and incorporated into sand for any PCF type, indicating that substrate water content has a minimal effect on release rates. There was a nonlinear effect of temperature on the release rates of Nutricote and Polyon PCF. The effect of temperature was less evident in Osmocote fertilizers, because they rapidly released nutrients at all temperatures. Nutricote fertilizers were the most consistent in releasing individual nutrients with temperature and over time. Polyon fertilizers had the slowest release rate relative to the manufacturer’s
specifications. This study provides a quantitative basis for more precise determination of PCF application in containerized plant production.

**INTRODUCTION**

Providing predictable, prolonged availability of nutrients has long been a goal of fertilizer manufacturers. Potential agronomic, physiological, and economic benefits include decreased fertilizer loss by leaching, increased nutrient recovery by plants, reduced frequency of fertilizer application, and increased control of substrate nutrient levels (Shaviv and Mikkelsen, 1993). In response, slow-release fertilizer (SRF) and controlled-release fertilizer (CRF) options have been developed. The terms SRF and CRF are often used synonymously; however, CRF denotes an improvement over more rudimentary SRF, because of increased “control” over nutrient release rates (Shaviv, 2001). Polymer-coated fertilizers (PCF) are the most technically advanced form of CRF and are widely used for high value containerized plants (Goertz, 1993). PCF are also used by NASA in the unleached root-zones of spaceflight plant-growth (Monje *et al.*, 2003) and may be used in newly popular systems such as green roofs.

Ideally, controlled-release fertilizer should have uniform, steady release rates that match the longevity specifications of the manufacturer for all primary plant-essential nutrients over biologically relevant environmental conditions. PCF do not meet this ideal (Broschat and Moore, 2007), but are an improvement over other controlled-release options in that they are largely insensitive to environmental conditions such as soil pH, biological activity, and soil type or texture, and are only mildly dependent on substrate water content. In an early CRF study, Oertli and Lunt (1962), found insensitivity to soil
pH. Broschat (2005) and Shibata et al. (1980) found slight, if any, PCF sensitivity to soil type or texture; however, several studies have reported a mild dependence of PCF on substrate moisture content. Some reports claim that PCF nutrient release is faster when placed in water than when incorporated into solid media or soil substrates, although there is no mechanistic basis for this being the case. Broschat (2005) found PCF release rates to be slower when surface-applied, intermediate when incorporated into a moist substrate, and slightly faster when placed pure water. In an applied study, Richards and Reed (2004) found that incorporated PCF placement increased dry masses slightly over other application methods, indicating increased fertilizer release with incorporated placement over other methods such as top dressing. Shibata et al. (1980) found PCF release to be 1.2 to 1.5 times faster when placed in pure water than when incorporated into a solid substrate. However, Kochba et al. (1990) found PCF release to be indistinguishable when moisture contents were greater than 50% of field capacity.

Although affected little by most environmental conditions, temperature does have a significant effect on PCF nutrient release. The dependence of nutrient release on temperature in all forms of CRF has been long known, since Oertli and Lunt (1962a) tested release of an unspecified CRF over a range of five temperatures. High temperatures can reduce product longevity, overloading nutrient supply during early growth; while cool temperatures extend product longevity, causing release rate to be insufficient to sustain optimal plant growth. Huett and Gogel (2000), Kochba et al. (1994), and Husby et al. (2003) each studied the effect of temperature on PCF, finding different results. Kochba et al. (1994) found the effect of temperature on PCF to be greater than Huett and Gogel (2000) (~5.5 % average increase in release per degree
Celsius versus an average of ~1.7 % per degree Celsius). However, Kochba et al. (1994) studied a single PCF, while Huett and Gogel (2000) was a more comprehensive study testing 17 PCF. Husby et al. (2003) claimed that the effect of a diurnal temperature fluctuation was a sensational 63.9 to 206.2 % per degree Celsius, depending on the PCF, when temperature was varied between 20 and 40ºC.

In spite of these studies, it is not yet possible to make general conclusions about the effect of temperature on PCF nutrient release. There is also no mechanistic basis for the claims that release rates are faster when placed in pure water than when incorporated into moist, solid substrates. We sought to quantify the effect of temperature and substrate moisture content on specific-ion release rates for long- and short-term release rate formulations of three widely used PCF types.

**METHODS AND MATERIALS**

Three PCF types were investigated: Osmocote (Grace Sierra Horticultural Products Co, Marysville, Ohio, USA.), Nutricote (Chisso-Asahi Fertilizer Company, LTD., Tokyo, Japan), and Polyon (Pursell Industries, Sylacauga, Alabama, USA). Seven distinct fertilizers, representing short-, mid-, and long-term PCF, were studied (Table 2 – 1). These are widely used types of PCF that represent three of the primary controlled-release polymer coating technologies that are available.

Table 2 – 1: The fertilizers investigated in these studies, representing three PCF types and a range of specified release longevities.

<table>
<thead>
<tr>
<th>Brand Name &amp; NPK Ratio</th>
<th>Short-term</th>
<th>Mid-term</th>
<th>Long-term</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmocote (15 - 9 - 12)</td>
<td>3 to 4 month</td>
<td>12 to 14 month</td>
<td></td>
</tr>
<tr>
<td>Nutricote (18 - 6 - 8)</td>
<td>3 to 4 month</td>
<td>9 month</td>
<td>12 month</td>
</tr>
<tr>
<td>Polyon (15 - 6 - 11)</td>
<td>1 to 2 month*</td>
<td>10 to 12 month</td>
<td></td>
</tr>
</tbody>
</table>

*NPK ratio is 16 – 6 – 13 in this PCF.
PCF Release in Sand (Ottawa)

To test PCF release in when incorporated into a soil substrate, the fertilizers were placed in columns of a sand (Ottawa) known to be virtually inert (Figure 2 – 1). This data was also used for comparison with the “water” data (described below), to test the effect of substrate water content.

Release at Room Temperature

One and a half inch. (3.81 cm) diameter PVC columns were cut to contain 500 cm³ medium Ottawa sand (Appendix A, Figures A – 18 and A – 19) with an additional 2.5 in. (6.35 cm) of open space above the sand surface. The bottom of the columns were fitted with PVC slip couplers, which held a section of solid landscape fabric tight to the bottom of the columns, to contain the media while allowing free percolation of water and solutes. To prevent evaporation, a slip cap was put on the top of each column, and a water-impermeable plug of closed-cell foam was inserted into the bottom (Figure 2 – 1).

Figure 2 – 1: Columns used to study release of PCF in Ottawa sand.
Six and one-half grams of the “long-term” rated PCF listed in Table 2 – 1 were tested in this study. Each fertilizer sample was weighed individually, completely incorporated into individually measured allotments of sand, and placed into the columns (filled to a height of ~44 cm). Three replicate columns for each PCF were made.

Water retention measurements of Ottawa sand (Appendix A, Figure A – 19) showed that after drainage (container capacity), from a height of 0 to 44 cm, volumetric water contents ranged from ~0.33 cm$^3$ cm$^{-3}$ at the bottom to ~0.04 cm$^3$ cm$^{-3}$ at the top; the average volumetric water content was found to be ~0.13 cm$^3$ cm$^{-3}$, with a total water volume of ~65 ml.

To start the PCF nutrient release process and to flush any residual salts off the sand, 500 ml of deionized water (electrical conductivity ~0.0002 S m$^{-1}$) were added to each column and the leachate discarded. To provide the same ratio of fertilizer to water as in the water release test (described below), each week 200 ml of water was added to the top of each column and the leachate was collected. The volume of the leachate was measured for the first several weeks of the experiment and was found to consistently be between 195 and 200 ml. The electrical conductivity of the leachate was measured each week. The study was conducted at 23°C ± 1.4 °C.

**Release from 5 to 40°C**

Four replicate columns of Ottawa sand with 6.5 g of incorporated PCF were made for each of the “long-term” rated PCF listed in Table 2 – 1, following the same procedure outline above. The columns were randomly assigned to four temperature treatments: 15°C ± 1.44, 20°C ± 0.59, 30°C ± 0.72, and 40°C ± 1.11. The columns were leached with
200 ml of deionized water once a week and the leachate electrical conductivities were measured after the solutions had reached room-temperature.

**PCF Release in Water**

In order to obtain simplified summaries of PCF release profiles, without the interactions of soil/media, the fertilizers were tested for release rate in deionized water (Figure 2 – 2). This data was also used for comparison with the “sand” data, to test the effect of substrate.

![Figure 2 – 2: Examples of flasks of water holding polymer-coated fertilizers (6.5 g PCF to 200 ml water): Polyon, Nutricote, Osmocote (left to right).](image)

**Release at Room Temperature**

Thirteen replicate samples of 6.5 g of the “long-term” rated PCF listed in Table 2 – 1 were placed in 250-ml flasks with 200 ml of deionized water (electrical conductivity ~0.0002 S m$^{-1}$). The electrical conductivity of the water was measured once each week with a Hanna Instruments HI 8733 conductivity meter with temperature compensation. The water was replaced each week by placing nylon
mesh over each flask to hold in fertilizer prills, decanting the nutrient-full water, and adding 200 ml water with a volumetric flask. The study was conducted at 23°C ± 1.4°C.

**Release at from 5 to 40°C**

Six and a half gram samples of all seven PCF listed in Table 2 – 1 were prepared and processed as described above and kept at five temperatures: 5°C, 15°C ± 1.44, 20°C ± 0.59, 30°C ± 0.72, and 40°C ± 1.11. Three replicate samples were made for each combination of levels of fertilizer and temperature, totaling 84 samples. Plexiglass chambers with temperature control and circulating fans were employed to carry out the test. Chamber temperatures were maintained 24 hours per day, and the fertilizers were removed from the chambers only for a 2-3 hour period once a week in which data was collected and water was renewed. Before electrical conductivity measurement, the fertilizer solutions were allowed to come within 5°C of room temperature in order to minimize measurement error, despite meter temperature compensation. Periodic water samples were sent for nutrient analysis by ICP-OES speciation analysis (Thermo IRIS Intrepid II, Thermo Scientific Inc., Waltham, MA), and nitrogen concentrations were measured using colorimetric nitrate and ammonium tests (LaMotte Smart Colorimeter, Chestertown MD).

At the conclusion of the experiment, after 105 days of incubation in water, the fertilizers were dried at 105°C for seven days in order to quantify the amount (by mass) of nutrients that had been expended from the fertilizers at each temperature. 105°C was the temperature chosen in order to remove all water, with the exception of waters of hydration (Methods of Soil Analysis, Part 3—Chemical Methods. Soil Science Society
of America). Estimation of the mass of the polymer coatings was necessary. In order to quantify the coatings, 30 g of each fertilizer was ground in a blender with 2 L of water, dissolving as much nutrient salt as possible. A beaker and a piece of solid nylon mesh were pre-weighed. The fertilizer mixture was poured through the mesh, capturing the coating while allowing all water and soluble fertilizer to flow through. Any fertilizer that was not in solution was left in the blender, additional water was added, and the procedure was repeated until all fertilizer was in solution and all coating material was recovered in the mesh. The mesh was placed in its pre-weighed beaker, dried for 2 days at 80°C, and weighed again. Because Nutricote fertilizers are designed to have a uniformly thick polymer coating, the results of this procedure were averaged for all Nutricote fertilizers to yield a value of 11% ± 0.73 polymer coating, by mass. Polyon 1 to 2 month was determined to have 7% polymer coating, and a value of 14% was determined for 10 to 12 month. Due to the nature of the polymer coating of Osmocote products, once pulverized, recovering all of the polymer coating was impossible; as a result, values of polymer coating percentage were calculated from information obtained from Osmocote bag labels (10% polymer coating for Osmocote 3 to 4 month; and 15% for 12 to 14 month).

RESULTS AND DISCUSSION

The Effect of Substrate on PCF Nutrient Release and General Nutrient Release Profiles

The Effect of Substrate

For the three “long-term” rated PCF (Table 2 – 1) that were tested for release in water and sand, the release in both substrates were not statistically different over the
entire duration of the study (Figure 2 – 3). This result provides evidence that substrate water content has a minimal effect on PCF nutrient release and that PCF release is not faster in pure water than when incorporated into a moist, solid substrate. That PCF nutrient release is the same in solid substrates as in pure water simplifies the quantification of PCF nutrient release greatly, as water tests exclude many of the complicating factors present in solid substrates, such as adsorption/desorption chemistry, and are less expensive and simpler to carry out.

Figure 2 – 3: Left: Nutrient release profiles of three PCF as measured by weekly solution electrical conductivity in flasks of water and in columns of medium Ottawa sand. The solution was renewed each week. Right: The absolute difference in solution electrical conductivity measured between fertilizer release in water and columns of Ottawa sand, which shows no consistent or significant difference.
In order to test for potential interactions between temperature and substrate in PCF nutrient release, longer-term rated PCF types were tested for release from 5 to 40ºC in sand and water. Calculations relating the weekly leachate electrical conductivities of the columns to the water data can be seen in Figure 2 – 4. On an absolute basis, the water and sand electrical conductivity data of Nutricote and Polyon were in close alignment, with slight deviation was seen at 40ºC, the cause of which is unknown. In the case of Osmocote, there was significant discrepancy between the water and sand data; however, no consistent trend over time or temperature was observed. This data shows no definitive evidence of an interaction between temperature and substrate, or temperature and substrate water content in PCF nutrient release rate.
Comparisons of PCF Release in Sand and Water at Four Temperatures

Osmocote 12-14 month

Nutricote 9 month (T-270)

Polyon 10-12 month

Electrical Conductivity ($S \ m^{-1} \ \text{week}^{-1}$), Absolute difference (Water EC - Sand EC)

Temperature (C)

Figure 2 – 4: Comparisons of the weekly electrical conductivity of seven formulations of Osmocote, Nutricote, and Polyon in water and sand columns at four temperatures expressed as an absolute difference. Three-way interactions are shown between substrate, temperature, and fertilizer.
General Release Profiles

The data in Figure 2 – 3 also reveals general patterns of PCF nutrient release as a function of time, showing the unique release profile of each PCF. Osmocote released a relatively large amount of nutrients immediately and had a relatively sharply decreasing trend in nutrient release over time. Practically, a trend such as this would lead to an overload in root-zone nutrients early after PCF application and a deficiency of nutrients later, with only a narrow window of time in which nutrient release would be at optimal levels.

Nutricote quickly reached its peak release rate, but released a relatively small amount of nutrients and maintained a more flat release profile over time. No significant decreasing trend in nutrient release rate was apparent until about 100 days of nutrient release; and the decline was more gradual relative to Osmocote. Due to its relatively stable release profile, the window in which nutrient release would be at optimal levels is greatly extended by this fertilizer.

In contrast to the other PCF, Polyon did not immediately reach its peak release rate; rather, the nutrient release of Polyon ramped up to its peak rate over the course of about 40 days. After reaching the peak, this PCF maintained a relatively stable release profile over time, appearing much like the release profile of Nutricote.

Effect of Temperature on General Nutrient Release Profiles

The results of this study showed that the effect of temperature on PCF was generally nonlinear with temperature and time (Figures 2 – 5 and 2 – 6). Osmocote fertilizers had highly nonlinear nutrient release trends with time, tending to rapidly
release nutrients at all temperatures, with decreasing nutrient release rates after an initial pulse. This characteristic made the effect of temperature on Osmocote less evident. Nutricote and Polyon fertilizers tended to release slower at lower temperatures and faster at higher temperatures, with the greatest effect observed between 30 to 40°C.

These graphs summarize the effect of temperature through measurements of electrical conductivity. In salt solutions, as a function of ion species in solution and increasing ion concentrations, ion pairing (a weak, transient bonding between ions of opposite charge) may diminish measured electrical conductivities, creating an understated relative measurement of ions in solution. However, a simple dilution test on our most concentrated PCF nutrient solutions showed that the effect of ion pairing was minimal in this study.
Figure 2 – 5: The weekly electrical conductivity of water solutions containing formulations of Osmocote, Nutricote, and Polyon at four temperatures over time.
Figure 2 – 6: The weekly electrical conductivity of water solutions containing PCF over time as a function of five temperatures (different graphical form of the data presented in Figure 2 – 5). This data shows how Osmocote products have rapid initial nutrient release and the striking effect of temperature on Polyon and Nutricote products between 30 and 40°C.
The Effect of Temperature on the Release of Individual Nutrients

Nutrient concentrations in the water solutions were measured every-other week in order to understand the effect of temperature on the release of individual ions from PCF. Graphs of the biweekly nutrient release of 12 plant-essential nutrients as a function of temperature and as a function of time are presented in this text for select, longer-term rate PCF (Figures 2 – 7 to 2 – 12). These graphs were made for the remaining PCF and can be found in Appendix A, Figures A – 1 to A – 8. A discussion follows of the trends that were observed for all PCF.

The most notable, overall trend for Osmocote PCF was the immediate peak in nutrient release with a subsequent decreasing trend over time that dropped nutrient release rates to low levels before the time the products were specified to last. There was little effect of temperature on nutrient release evident in the 3-4 month product, because nutrient release was rapid at all temperatures. In the 12-14 month product, peak release was delayed for several weeks in the case of most nutrients, rather than being immediate. In both Osmocote products, copper and zinc were immediately purged at all temperatures, with release of these nutrients nearly ceasing after the first week.

Macronutrient release rate in Polyon 1-2 month were more consistent over time than micronutrient release, which tended to drastically diminish in rate. More consistent nutrient release, among micro- and macronutrients, was observed in Polyon 10-12 month. The effect of temperature was very evident in Polyon 10-12 month, with a nearly linear increase in release of all nutrients as a function of increasing temperature. Peak release rates for most nutrients were delayed 20 to 40 days, with no “purge” of nutrients evident,
with the exception of boron which shot to its peak rate and then nearly ceased release for
the duration of the study.

Among all three Nutricote PCF, release trends as a function of temperature
appeared to be the exponential due to the striking increase in nutrient release between 30
and 40°C for all nutrients. However, the consistency of the effect of temperature (15 to
40°C) across all nutrients in all Nutricote PCF was striking. This characteristic of
Nutricote gives it a measure of predictability in nutrient release that is not apparent
among the other PCF tested.
Figure 2 – 7: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Osmocote 12 – 14 month (15 – 9 – 12), graphed as a function of time. It can be seen that Cu and Zn supplies are immediately released.
Figure 2 – 8: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Osmocote 12 – 14 month (15 – 9 – 12), graphed as a function of temperature.
Figure 2 – 9: The release of 12 plant-essential nutrients from 15 to 40ºC for ~80 days from Nutricote T-360 (18 – 6 – 8), graphed as a function of time.
Figure 2 – 10: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Nutricote T-360 (18 – 6 – 8), graphed as a function of temperature. The effect of temperature between 30 and 40°C is very apparent.
Figure 2 – 11: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Polyon 10 – 12 month (15 – 6 – 11), graphed as a function of time.
Figure 2 – 12: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Polyon 10 – 12 month (15 – 6 – 11), graphed as a function of temperature.
Relative Release among Nutrients

Oertli and Lunt (1962a), Huett and Gogel (2000), Broschat (2005), and Du et al. (2006) have all found that nutrients are not released at the same relative rates from PCF. Among macronutrients, each study reported a pattern of nutrient release rates such that: \( \text{NH}_4^+ > \text{NO}_3^- > K > P \), across all PCF studied. We have found the same trend in our studies. Extending this principal, we compared PCF nutrient release relative to specified release rates and compared the results among PCF (Figure 2 – 13). This analysis showed that, although relative nutrient release rates differ, the patterns of release of each nutrient with temperature, for a given PCF, are remarkably similar with temperature and nonlinear. In Nutricote, the patterns of nutrient release are remarkably similar with temperature and time regardless of the specified release longevity (ie. 3 to 4 month or 12 month Nutricote), while this is not the case in Osmocote and Polyon PCF.

Graphs of the biweekly percent release of PCF nutrients on a molar basis as a function of temperature (moles of ions of a specific type released / total moles of ions released over the same time period * 100) are shown in Appendix A, Figures A – 9 to A – 15. These graphs more definitively show that individual nutrient release rates are affected by the same, nonlinear temperature effect.
Figure 2 – 13: Nutrient release as a fraction of the release rate specified by manufacturers for 77 days for seven PCF. The relative release of nutrients, across all PCF, is such that: \(\text{NH}_4^+ > \text{NO}_3^- > \text{K} > \text{P}\). The patterns of release across nutrients from each PCF are remarkably similar with temperature. In Nutricote, the patterns of nutrient release across nutrients from all PCF are remarkably similar with temperature and time.
Physical Principles Determining PCF Release Rates

In modeling PCF nutrient release, Shaviv et al. (2003) proposed that nutrient release occurs in a three phase process. The first phase is a short lag phase in which there is no nutrient release; a time in which water diffuses into PCF prills, hydrating fertilizer salts. Second, a period of linear release in which the driving gradient for nutrient release remains constant due to the presence of undissolved fertilizer salts. Finally, a decay phase in which the nutrient release rate declines due to a diminishing driving gradient for release as the concentration of fertilizer in solution decreases within the prills. Extending this model, as varied by the concentration of fertilizer in solution within the prills, the physical principal of water potential is the driving force for nutrient release from PCF prills. The component parameters of water potential (Table 2 – 2 and Figure 2 – 14) tend toward equilibrium through permeable membranes. Within PCF prills, highly negative osmotic potentials must be offset by highly positive pressure potentials in order to be in equilibrium with the water potential of the environment surrounding the prills (slightly negative, under common circumstances, due to the presence of substrate salts). This pressure drives nutrients outward and changes with changes in nutrient concentrations in solution.

The data collected in this study seems to substantiate the validity of the release process proposed by Shaviv et al. (2003). The three phases are visible in the nutrient release profiles of longer-term release rated Nutricote and Polyon PCF, however appear to be absent in Osmocote (Figure 2 – 3). It is important to note, however, that the relative length (and visibility) of the phases would be dependent on the permeability and elasticity of the polymer coating. For example, shorter-term rated PCF with more
permeable polymer coatings may have rapid or no linear release phases, as the concentrations of nutrients may rapidly begin to decrease in solution within the prills. Also, a PCF with a highly elastic polymer coating, such as Osmocote (Appendix A, Figure A – 17), that tends to expand in response to internal pressure, effectively increases its coating permeability upon expansion and its internal water to nutrient ratio due to increased size.

Table 2 – 2: Water potential dynamics within and without PCF prills. Highly negative solute potentials within PCF prills must be offset by highly positive pressure potentials to equal the total water potential outside the prills.

\[
\psi = \text{Water Potential}
\]

\[
\psi_{\text{Total Outside Prill}} = \psi_{\text{Total Inside Prill}}
\]

\[
\psi_{\text{Total}} = \psi_{\text{Solute}} + \psi_{\text{Pressure}}
\]

\[
\psi_{\text{Total Outside Prill}} = 0 + 0 \text{ MPa}
\]

\[
\psi_{\text{Total Inside Prill}} = <<0 + >>0 \text{ MPa}
\]

Figure 2 – 14: An illustration showing water and nutrient movement in PCF prills.
Quantifying the Temperature Effect

The general nonlinearity of PCF nutrient release over time at all temperatures makes quantification of the effect of temperature challenging. Calculating the effect of temperature on an instantaneous basis is not useful, as the value continually changes with time. Cumulative quantification of the temperature effect, in an expression such as the change in product longevity per unit temperature change (from a reference temperature), may be the most useful method, but says nothing about release dynamics with time. In our analysis, we hoped to find consistent patterns in the effect of temperature among fertilizers of the same brand. Figure 2 – 13 above shows that the effect of temperature is remarkably consistent across all Nutricote fertilizers with time; however, this was not found to be in the case in Osmocote and Polyon fertilizers. An empirical expression of \((-0.127) + (0.0213 \times \text{Temp }[^\circ C])\) was found to describe the cumulative percent release of phosphorus (most limiting macronutrient) from all Nutricote fertilizers as a function of temperature. No such expression can be developed collectively for Osmocote or Polyon fertilizers, based on the data collected in this study.

Weighing the fertilizers at the conclusion of the temperature experiment showed the effect of temperature after 3.5 months of release for seven PCF (Table 2 – 3 and Figure 2 – 15). In Figure 2 – 15, the flattening slopes of the trend lines between 30 and 40°C for the “short-term” rated PCF indicate that nutrient release was creasing at these temperatures (seen in Osmocote and Nutricote). The graph shows, however, that 15 to 20% of nutrients remained in PCF prills while, after 3.5 months, these PCF would have ideally released all or nearly all of their nutrients. This result is in alignment with other studies that report less than complete PCF nutrient release. This data concisely shows
that Polyon had a remarkably linear and dramatic response in nutrient release to
temperature. We see how dramatically nutrient release is slowed by low temperatures in
Nutricote and Polyon PCF. We also see how quickly nutrients are depleted in Osmocote
at all temperatures, regardless of specified release longevity (Osmocote 12 – 14 month or
3 – 4 month).

Figure 2 – 15: The percent of nutrient salts expended, based on loss of mass, from
formulations of Osmocote, Nutricote, and Polyon incubated in water from 5 to 40°C for 3.5
months.
Table 2 – 3: The percent increase per degree Celsius in polymer-coated fertilizer nutrient release from 15 to 40°C, over the course of 105 days.

<table>
<thead>
<tr>
<th>Fertilizer</th>
<th>% °C⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmocote 3 - 4 m</td>
<td>0.92</td>
</tr>
<tr>
<td>Osmocote 12 - 14 m</td>
<td>1.6</td>
</tr>
<tr>
<td>Nutricote 3 - 4 m (T-100)</td>
<td>1.4</td>
</tr>
<tr>
<td>Nutricote 9 m (T-270)</td>
<td>2.16</td>
</tr>
<tr>
<td>Nutricote 12 m (T-360)</td>
<td>2.4</td>
</tr>
<tr>
<td>Polyon 1 - 2 m</td>
<td>1.52</td>
</tr>
<tr>
<td>Polyon 10 - 12 m</td>
<td>2.16</td>
</tr>
</tbody>
</table>

**Release Variability**

Tracking the variability in the “water” data shown in Figure 2 – 3 showed that variability in release among PCF is dynamic with time, and differs among PCF types (Figure 2 – 16).

In the case of Polyon, variability was extreme in the initial stages of release, with a sharp decline in variability after ~30 days of release to become the least variable PCF of the three tested. The source of variability in the initial release of Polyon appeared to be, at least in part, due to incompletely coated fertilizer prills, which were infrequent but white and readily visible among completely coated green prills. A simple test showed that these uncoated, white fertilizer prills were approximately 200 times more soluble than fully coated prills after one day in water (Appendix A, Figure A – 16). However, the absolute release rate of all replicate Polyon samples was low relative to the other PCF in the initial stages of release.

Nutricote had more variability in the early stages of its release relative to the later stages. Variability declined over the course of about 50 days, and then maintained a low level of variability for the duration of the study.
In the early stages of its release, Osmocote showed the least variability relative to its mean release rate among the PCF tested. A source of variability in the release of Osmocote may have been cracked or broken prills. Some cracked and broken Osmocote prills were observed directly out of the bag. Osmocote had inconsistent, erratic inclining and declining trends in variability and, unlike Nutricote and Polyon, generally increased in variability over time.

Figure 2 – 16: The coefficient of variation (standard deviation / mean * 100), for the electrical conductivity of 13 replicate, 6.5 g samples of Osmocote, Nutricote, and Polyon in water. This gives an indication of the relative variation among the fertilizers over time.
REFERENCES


CHAPTER 3

BALANCING SUPPLY AN DEMAND: A MASS BALANCE APPROACH TO OPTIMIZING POLYMER-COATED FERTILIZER APPLICATION RATES

ABSTRACT

Polymer-coated fertilizers (PCF) are designed to increase nutrient use efficiency by coating nutrients to provide a regulated availability. No comprehensive model has been developed that couples models to predict plant growth and PCF nutrient release rates. We present a plant growth model based on incoming photosynthetic photon flux (PPF) and the efficiency of four plant-growth determinants. We also present a model to predict PCF ion release rates. This model is based on the finding that, among macronutrients, phosphorus is released at the slowest relative rate from PCF, and is thus the limiting nutrient to plant growth. PCF application rates are adjusted by empirically derived equations that describe the cumulative release of phosphorus as a function of temperature relative to the prescribed release for a given PCF. The efficacy of the model to accurately predict PCF application rates was verified with a growth trial. Plant growth, in the growth trial, matched the growth predicted by the model; and peak growth occurred at a PCF application rate that matched the predicted application rate. This result suggests that this modeling approach has potential to provide a basis for determining optimum PCF application rates when the fertilizer release rate has been characterized.
INTRODUCTION

Ideally, in supplying nutrient to growing plants, nutrient supply and demand would be matched, producing optimal plant growth and increasing fertilizer use efficiency. This ideal is complicated by the many patterns of plant growth that are possible, varying by plant type, light level, and harvest regimes. Figures 3 – 1 and 3 – 2 graphically demonstrate two of these patterns. Polymer-coated fertilizers (PCF) are the most technically advanced fertilizers in controlled-release granule fertilizer technology, designed to provide regulated availability of a large stock of nutrients (Goertz, 1993). PCF are a great improvement over soluble fertilizers and more rudimentary controlled-release fertilizers, getting closer to the ideal of matching nutrient supply and demand. However, for efficient use, the release characteristics of polymer-coated fertilizers (PCF) must be understood and modeled.

Figure 3 – 1: Plant growth rate and nutrient uptake rate over time. A plant biomass production scenario in which plants are repeatedly harvested and/or a root-zone is repeatedly planted.
Several empirical studies have contributed to our understanding of PCF nutrient release and helped to define the effects of environmental parameters, such as temperature and water potential, on release (Broschat, 2005; Broschat and Moore, 2007; Gambash et al., 1990; Huett and Gogel, 2000; Kochba et al., 1990; Kochba et al., 1994; Oertli and Lunt, 1962; Richards and Reed, 2004; Shibata et al., 1980). In attempts to describe the processes determining PCF nutrient release, physical principals and empirical tests have been used to develop models. Kochba et al. (1990) and Gambash et al. (1990) developed a simple model based on the proposition that the vapor pressure of water surrounding PCF prills is the factor limiting release rate, and included constants specific for each PCF that must be empirically determined. Fujinuma et al. (2009) is an example of a semi-empirical model that was developed for the special case in which PCF is surface-applied, a case in which the effect of substrate water content cannot be ignored. Fully mechanistic, mathematically intensive models have extended understanding of the
physical principals and processes underlying release for single-nutrient PCF (Al-Zahrani, 1999; Du et al., 2008; Du et al., 2004; Shaviv et al., 2003a; Shaviv et al., 2003b); however, these models may be most effectively used by the manufacturers of PCF products and not by users of PCF. These models are generally based on designating three distinct stages of the release process (lag period, constant release stage, and gradual decay stage) and include parameters for prill characteristics such as coating permeability, coating thickness, prill diameter, and chemical properties of the fertilizer.

The modeling of mixed-nutrient PCF is a more complex problem due to the individual chemical properties of each nutrient ion and the interactions among nutrients. However, several empirical studies have noted a consistent pattern in relative macronutrient release among all PCF: $\text{NH}_4^+ > \text{NO}_3^- > \text{K} > \text{P}$ (Broschat, 2005; Du et al., 2006; Huett and Gogel, 2000). Since the macronutrients are taken up by plants in concentrations orders of magnitude greater than the micronutrients, this pattern of deficient phosphorus release makes PCF-fertilized plants limited in growth by phosphorus. As the limiting nutrient, knowledge of phosphorus release patterns for a given PCF lends itself to being the basis of a model for prediction of the optimal application rate for that PCF. This concept is the basis of our modeling approach.

No comprehensive model has been developed for users of PCF that couples models to predict plant growth and to predict the PCF nutrient release. Such a model would be useful to provide a basis for determining optimum PCF application rates.
A model, based on the determinants of plant growth and photosynthetic photon flux (PPF), was used to predict growth of mizuna (*Brassica juncea*) (Table 3–1).

Table 3–1: A model for prediction of plant growth based on PPF and plant growth determinants. “Parameters specific to this research” relate to model verification.

<table>
<thead>
<tr>
<th>PPF Input</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PPF Input (µmol photons m⁻² s⁻¹)</td>
<td>100</td>
</tr>
<tr>
<td>Photoperiod (h d⁻¹)</td>
<td>x 16</td>
</tr>
<tr>
<td>Total PPF (mol_{photon} m⁻² d⁻¹) = 5.8</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Determinants of Plant Growth</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PPF Capture</td>
<td>0.85</td>
</tr>
<tr>
<td>Quantum Yield</td>
<td>x 0.07</td>
</tr>
<tr>
<td>Respiration Efficiency</td>
<td>x 0.6</td>
</tr>
<tr>
<td>mol_{Carbon} mol_{photon}⁻¹ = 0.036</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon Fixed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total PPF (mol_{photon} m⁻² d⁻¹)</td>
<td>5.8</td>
</tr>
<tr>
<td>mol_{Carbon} mol_{photon}⁻¹ x 0.036</td>
<td></td>
</tr>
<tr>
<td>Carbon Fixed (mol_{carbon} m⁻² d⁻¹) = 0.21</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biomass Production</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Fixed (mol_{carbon} m⁻² d⁻¹)</td>
<td>0.21</td>
</tr>
<tr>
<td>g_{dry mass} mol_{carbon}⁻¹ x 30.0</td>
<td></td>
</tr>
<tr>
<td>Biomass Production (g_{dry mass} m⁻² d⁻¹) = 6.2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters Specific to This Research</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Production (g_{dry mass} m⁻² d⁻¹)</td>
<td>6.2</td>
</tr>
<tr>
<td>Trial Length (d)</td>
<td>x 60</td>
</tr>
<tr>
<td>Root-Zone Surface Area (m²)</td>
<td>x 0.030</td>
</tr>
<tr>
<td>Adjustment for Actual PPF (212/100)*</td>
<td>x 2.12</td>
</tr>
<tr>
<td>Total Biomass (g_{dry mass}) = 23.9</td>
<td></td>
</tr>
<tr>
<td>Coefficient for Unmeasured Biomass**</td>
<td>x 0.95</td>
</tr>
<tr>
<td>Measured Biomass Prediction (g_{dry mass}) = 22.7</td>
<td></td>
</tr>
</tbody>
</table>

*Actual PPF Input (µmol photons m⁻² s⁻¹) = 212.0
**Accounts for Unmeasured Roots for Model Verification
The parameters of the model must be adjusted individually for specific applications. The growth period, daily photoperiod, and average daily PPF must be measured or estimated. Quantum yield quantifies the moles of carbon that are fixed per mole of incident photons. Quantum yield ranges from \( \sim 0.04 \) to \( 0.08 \text{ mol mol}^{-1} \), and depends on light intensity and optimality of environmental conditions: higher light intensity and optimal environmental conditions increase quantum yield, closer to \( 0.08 \text{ mol mol}^{-1} \). Respiration efficiency is relatively constant at a value of 0.6. The parameter, \( g_{\text{dry mass mol carbon}^{-1}} \), is a constant value of 30. PPF capture describes the average interception of light by the plant canopy over a growth period as a fraction of a given surface area, on a scale from 0 to 1. The root-zone surface area can easily be measured and provides an estimate of the area over which light may be intercepted, but may provide only a crude estimate of the surface area over which the actual plant is intercepting light. In determining the most appropriate value for this parameter, the known growth pattern and predicted size of the plant should be considered. For example, when dealing with individual plants or pots, the surface area of geometric shapes that approximate the size and shape of a given plant may provide more accurate estimates of the light interception area. We added a “coefficient for unmeasured biomass” only for model verification, to eliminate the portion of total biomass production that went into roots.

Once a prediction of biomass production has been made, a PCF application rate can be modeled (Table 3 – 2). The variables in the model are the optimum phosphorus concentrations, the stated PCF phosphorus content (taken directly from the bag), and the average daily temperature. Optimum plant tissue phosphorus concentrations are
generally within the range of 3.0 to 5.0 mg P g\text{dry mass}^{-1}, for most plants. In verification of our model we grew mizuna, which has an abnormally high optimum phosphorus concentration of 8.0 g P g\text{dry mass}^{-1}. The time over which the fertilizer will be used relative to its specified time of use must also be known. For example, Nutricote T-100 is specified for 100 days of use, but may be used for a lesser amount of time.

Table 3 – 2: A model for prediction of optimal Nutricote application rates. The current inputs to the model are the biomass production modeled in Table 3 – 1 and optimal phosphorus concentrations for mizuna. The model is based on patterns of phosphorus release found to be consistent in Nutricote PCF.

<table>
<thead>
<tr>
<th>Nutrient Demand</th>
<th>Predicted Dry Mass (g\text{dry mass})</th>
<th>22.7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimum Phosphorus Concentrations (mg P g\text{dry mass}^{-1})</td>
<td>x 8.0</td>
</tr>
<tr>
<td></td>
<td>Nutrient Demand (mg_{nutrient})</td>
<td>= 181.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nutrient Supply</th>
<th>Stated PCF Phosphorus Content ((g P_2O_5 g PCF^{-1} x100)</th>
<th>9.54</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg P g P_2O_5^{-1} x 436</td>
<td>mg P g PCF^{-1} = 41.59</td>
<td></td>
</tr>
<tr>
<td>C_{P/T}* x 0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{T}** x 0.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nutrient Supply (mg P g PCF^{-1})</td>
<td>= 9.08</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Predicted PCF Application Rate</th>
<th>Nutrient Demand (mg_{nutrient})</th>
<th>181.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nutrient Supply (mg P g PCF^{-1})</td>
<td>/ 9.08</td>
<td></td>
</tr>
<tr>
<td>PCF Required (g)</td>
<td>= 20.0</td>
<td></td>
</tr>
</tbody>
</table>

*(C_{P/T}) = Phosphorus/Temperature Release Coefficient 
= (-0.127) + (0.0213 x Temperature °C)

(C_{P/T}) = (-0.127) + (0.0213 x 23 °C) = 0.36

**(C_{T}) = Time Coefficient = Actual PCF Use (d) / Specified Release (d)

C_{T} = 60 d / 100 d = 0.60

The current inputs into the model in Figure 3 – 2 are specific to a growth trial in which mizuna was grown in order to verify the model. A custom Nutricote fertilizer
(Nutricote 13.6 – 9.5 – 13.6 (T-100)) was mixed from three distinct component fertilizers: 32.6% 18 – 6 – 8 (T-100), 58.4% 13 – 13 – 13 (T-100), and 9.0% 2 – 0 – 38 (T-100). The trial was conducted with 2.7-L plant-growth containers (19 x 16 x 9 cm (lwh) --- surface area of 0.030 m$^2$) with no leaching. Rate treatments were: 5, 10, 20, 40, and 80 g per container (1.9, 3.7, 7.4, 14.8, and 29.6 g L$^{-1}$). A single Osmocote 3 – 4 month 14 – 14 – 14 treatment, at a rate of 15 g per container (5.6 g L$^{-1}$) was included for comparison. The substrate was ceramic media with a 50/50 mix by volume of 0.25 – 1 mm ceramic aggregates and 1 – 2 mm aggregates. The ceramic medium was prepared by rinsing with tap water over a large screen with free drainage for approximately 3 minutes; and soaking the media in a complete nutrient solution (Appendix B, Table B – 1) over the course of five days in which the solution was changed daily. To test for media interactions, 10 and 20 g per container (3.7 and 7.4 g L$^{-1}$) Nutricote treatments in peat/vermiculite were also included. Watering was done with deionized water (electrical conductivity ~0.0002 S m$^{-1}$) by maintaining 1 cm of water in the bottom of each container that was wicked throughout the root-zone. Covers were made for the containers, with 2-cm wide openings that ran the length of the container in which the plants could grow, in order to prevent evaporation and wicking of nutrients to the media surface (Figure 3 – 3).

Mizuna was planted at an excess and thinned to 10 plants per container. Five sequential harvests were completed over the course of 60 days. From planting to first harvest was 20 days, while each subsequent harvest was done after nine or 10 days of growth. Harvest was done by selective removal of leaves, in which all of the mature
leaves were harvested, few of the juvenile leaves were taken, and at least two leaves of 4 – 6 cm height were left.

The light levels were 130 – 215 µmol m$^{-2}$ s$^{-1}$ (16 hour photoperiod) in a controlled environment system at a temperature of 23ºC ± 1.4 ºC. A light level was determined individually for each container by averaging measurements of light at the container surface and at a height of 8 cm above the surface. Across treatments, growth was normalized to a light level of 215 µmol m$^{-2}$ s$^{-1}$, based on the effect of light on growth that was determined in an analysis of growth in this study (Appendix A, Figure A – 20).

Nutrient analysis was done on the plant tissues in each harvest by ICP-OES speciation analysis (Thermo IRIS Intrepid II, Thermo Scientific Inc., Waltham, MA). Nitrogen content was measured by CHN combustion analysis (Perkin-Elmer 2400 Series, Perkin-Elmer Inc., Waltham, MA).

Figure 3 – 3: The system in which a growth trial was conducted to verify a model of optimal Nutricote application rates.
RESULTS AND DISCUSSION

In verification of our model, the intersection of predicted plant growth and the predicted PCF application rate occurred at actual peak growth (Figure 3 – 4). This result provided evidence that this model may be used as a mechanistic basis for predicting optimal PCF application rates.

Figure 3 – 4: The cumulative dry mass of mizuna for five sequential harvests with Nutricote rate treatments.

While the model matches the data, peak dry mass production and optimal PCF application rates were highly dynamic with time (Figure 3 – 5). In the first harvest, all treatments preformed virtually the same, with only the 5 g (per 0.03 m$^2$ root-zone) PCF treatment falling short. Over time, the 80 g treatment began to show symptoms of salt stress, until the plants completely died. Forty grams of PCF outperformed all other
treatments in harvests two and three, but then also overloaded the root-zone with nutrient salts, as shown by decreasing growth and physical symptoms of salt stress that were observed. After the third harvest, the 20 g treatment became the top performer, showing no signs of salt stress. The 10 g treatment steadily produced over time. These dynamic trends highlight the inability of Nutricote (or any PCF) to supply nutrients at rates that perfectly match plant uptake over time; but also the ability to optimize application rates for the best, overall, outcome.

Figure 3 – 5: Mizuna dry mass production as a function of time with Nutricote rate treatments. Each point on the graphs represents a harvest event. Peak growth with Nutricote treatment was dynamic with time.
Nutrient analysis was done on the plant tissues to determine the nutrient(s) that might be limiting growth in lower-yielding PCF treatments (Figure 3 – 6). None of the analyzed nutrients appeared to be limiting growth, with concentrations higher than traditionally accepted as adequate for optimal plant growth (Bennett, 1993; Marshner, 1995). Other, unpublished studies in our lab have shown mizuna to be prone to luxury uptake of nutrients. Select measurements of tissue nitrate concentrations from harvest three were made in order to reveal luxury nitrogen uptake in this study (Table 3 – 3). However, increasing trends in nitrogen and potassium concentrations with increasing PCF rate seen in Figure 3 – 6, suggest that these nutrients were limiting, despite their large values even at low PCF rates.

Table 3 – 3: Forms of nitrogen in mizuna tissues with different PCF treatments (5, 10, 40 g). High nitrate concentrations at high fertilizer application rates reveal heavy luxury uptake.

<table>
<thead>
<tr>
<th>Tissue Nitrogen</th>
<th>5 g (%)</th>
<th>10 g (%)</th>
<th>40 g (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total N</td>
<td>3.97</td>
<td>5.81</td>
<td>8.64</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.16</td>
<td>0.77</td>
<td>2.36</td>
</tr>
<tr>
<td>Assimilated N</td>
<td>3.81</td>
<td>5.04</td>
<td>6.28</td>
</tr>
</tbody>
</table>

As shown by differences in tissue nutrient concentrations between plants grown in ceramic media and peat/vermiculite, K, Ca, Mg, B, and Mn were taken up by the plants from ceramic media itself. Despite uptake of nutrients from ceramic media, growth was not significantly affected (Figure 3 – 4).
Figure 3 – 6: Nutrient concentrations of mizuna tissues grown in a Nutricote rate growth trial. The macronutrients were in concentrations greater than typically considered optimal, however nitrogen and potassium appeared to be limiting growth. Optimal nutrient range adapted from Bennett (1993) and Marshner (1995).
REFERENCES


CHAPTER 4

OPTIMIZATION OF CERAMIC MEDIA FOR PLANT GROWTH:

NUTRIENT BALANCE

ABSTRACT

Ceramic media (Turface or Profile) is commonly used in research applications because it easily washes off root surfaces. It is also used by NASA in the unleached root-zones of spaceflight plant growth. In spite of widespread use, studies on the chemical properties of ceramic media have been limited. This research sought to more thoroughly understand the plant-availability of nutrients from ceramic media, the origin of those nutrients, the efficacy of soaking and rising procedures to mitigate nutrient imbalances, and the chemical interactions of fertilizer ions added to ceramic media. Relative media-sorbed nutrient concentrations were highly variable from bag to bag. In many cases, ceramic media supplied an excess of manganese, boron, magnesium, and sulfur, which induced nutrient imbalances in plant tissue and reduced plant growth. Rinsing and soaking procedures on the media helped mitigate these nutrient imbalances. When media nutrient imbalances were absent or improved by rinsing/soaking, if imbalanced, growth was comparable to growth in a standard peat/vermiculite medium. Ceramic media also interacted with fertilizer ions added to it. Copper, phosphorus, and zinc ions were largely removed from solution by these interactions. However, despite the removal of most of these ions from the root-zone solution, only copper was ever found deficient in plant tissues. Copper supplementation may be necessary to replace the copper removed from solution. Despite some chemical complexity, ceramic media is a valuable plant-growth
substrate when accommodation is made for its chemical properties that negatively affect plant growth.

INTRODUCTION

Ceramic media, commercially sold as Turface or Profile (Profile Products LLC, Buffalo Grove Illinois) and often called arcillite, is often a media of choice for the root-zones of research applications because it can easily be removed from root surfaces at harvest. Ceramic media is also used by NASA in the unleached root-zones of spaceflight plant-growth (Monje et al., 2003). A number of studies have characterized the physical and hydraulic properties of ceramic media (Blonquist et al., 2006; Heinse et al., 2007; Steinberg et al. 2005; Steinberg and Portiz, 2005). Several applied studies, including Warren and Bilderback (1992) and Jaeger and Hellmers (1981), have characterized the effect of amending plant-growth media with ceramic aggregates. However, while the physical and hydraulic properties of ceramic media are well characterized, little has been done to characterize the chemical properties of the media.

METHODS AND MATERIALS

Quantification of Relative Ceramic Media-Sorbed Nutrients

Commercially Available Ceramic Media

Ceramic media samples were obtained from commercial retailers and represented newly produced and older Turface and Profile products. By volume, 50 ml samples of air-dry ceramic media were measured in a 50-ml graduated cylinder and placed in 125-ml Erlenmeyer flasks with 100 ml of deionized water (EC ~0.0002 S m⁻¹). The media and
water were initially swirled to thoroughly mix the contents and then allowed to sit still in a controlled temperature lab (23°C ± 1.4 °C) for five days. Previous tests showed that general equilibrium in nutrient concentrations was consistently reached within 5 days (Appendix B, Figure B – 3). At day five, the flasks were again swirled to mix the contents, allowed to settle for several minutes, and vacuum filtered with Whatman #5 filters. If the filtered solution appeared cloudy, a second filtration was performed. The filtered solutions were acidified with 0.7 ml 16 N nitric acid (HNO₃) per 13 ml solution and analyzed by ICP-OES speciation analysis (Thermo IRIS Intrepid II, Thermo Scientific Inc., Waltham, MA).

**Ceramic Media Directly from Profile**

Ceramic media samples were also obtained directly from the Profile company, including crude clay (unfired, Turface precursor), Turface cooled by water, and Turface cooled by air. The standard procedure for production of Profile ceramic media products is to fire aggregated clay and to cool it by applying locally available well water, which contains some dissolved nutrient ions. Media-sorbed nutrients were quantified following the procedure outlined for commercially available ceramic media. The crude clay was tested for soluble nutrients in a wet condition, directly from its source. Appropriate correction factors in calculations of nutrient concentrations were made to correct for the water content of the samples. A sample of the well water that is used for cooling the media was obtained from the Profile Company and also analyzed for nutrient contents.
Effects of Ceramic Media-Sorbed Nutrient Balance on Plant Growth and Nutrition

Imbalanced Nutrients

This trial used ceramic media with known nutrient imbalances in order to observe the effects on growth as compared to a standard peat/vermiculite media. The study included ceramic media of three particle size distributions (1 – 2 mm diameter, 0.25 – 1 mm, and a 50/50 mix by volume of 1 – 2 mm and 0.25 – 1.0 mm diameter particles), and a 50/50 mix by volume of peat/vermiculite. There were four replicate root-zones with no leaching per level of media.

The study was conducted in an indoor, controlled-environment system, supplying the plants with a light level of 350 – 450 µmol photons m$^{-2}$ s$^{-1}$, with a 16-hour photoperiod. 33 g of 12 to 14 month Osmocote Plus (15 – 9 – 12) polymer-release fertilizer was added to each container. The crop tested was mizuna, which was planted at an excess, and thinned to six plants per root-zone. A comparison was made between growth and tissue nutrient contents in each treatment for the first harvest. Tissue nutrients were measured by ICP-OES speciation analysis.

Proper Nutrient Balance

This trial used ceramic media (0.25 – 1 mm diameter) known to have no nutrient imbalances in order to compare tissue nutrient concentrations of plants grown in this media as compared to a standard peat/vermiculite media. The media were packed into containers with no leaching and the test was carried out in a greenhouse environment. Nutrients were supplied by liquid feed in irrigation water (Peatlite 17 – 4 – 17). Two crops were grown: mizuna and Cherry Belle radishes.
Three replicate pots per combination of levels of plant species and media were included. The plants were grown to a harvestable size, harvested, and analyzed for nutrient contents by ICP-OES speciation analysis. Nutrient contents were compared among treatments for similarities and differences.

**The Efficacy of Rinsing/Soaking Ceramic Media to Improve Nutrient Balance**

Rinsing ceramic media has been suggested as a method to remove nutrients that are sorbed to media surfaces that may be out of balance and detrimental for plant growth. Soaking ceramic media has been suggested as another method for removing these nutrients and also as a method for exchanging undesired media ions for desired ones. Theses studies sought to determine the relative merits of soaking and rinsing ceramic media as shown through plant growth, tissue nutrient concentration analysis, and media desorption.

**Soaking Ceramic Media (Nutrient Solution and Deionized Water)**

Soaking ceramic media with a nutrient solution was compared with soaking with deionized water. The nutrient solution used for soaking was a complete, dilute (EC ~0.12 S m\(^{-1}\)) greenhouse nutrient solution of Peatlite 17 – 4 – 17. Soaking was done simply by adding sufficient solution to cover the media in large tubs, allowing the media to soak overnight, draining the solution, and repeating the process each day for five days.

The efficacy of the soaking treatments was determined through plant growth and plant tissue nutrient concentrations. Plant growth in the media was tested with and without fertilizer, in order to gauge to ability of each media to supply plant-essential
nutrients to growing plants. Where fertilizer was present, 33 g of 12- to 14-month Osmocote Plus (15 – 9 – 12) was added to the treatments. The crop grown was Earligreen pea, which was planted at an excess and thinned to six plants per container. The plants were grown in containers with no leaching, where 1 cm of water was maintained in the bottom of each container and wicked throughout the root-zone. Three replicate containers were included per combination of soaking and fertilizer treatments. This trial is pictured in Figure 4 – 1.

Figure 4 – 1: Earligreen peas growing in ceramic media with rinsing/soaking and fertilizer treatments.

**Rinsing Ceramic Media**

The purpose of this test was to quantify the percent decrease in ceramic media-sorbed manganese that could be achieved by simply rinsing the media with tap water. Five samples of 0.25 – 1 mm diameter ceramic media were selected for analysis. The
samples were all distinct, originating from different bags and sources, and representing newly produced product and older product.

An approximate volume of 500 ml of each sample was collected and split into two parts. One part was rinsed with tap water over a screen with free drainage for approximately three minutes. The other part was left in its “out of bag” condition. All samples, including rinsed and unrinsed parts, were put into a drying oven at 80°C for 2 days, and stirred after one day in order to ensure complete drying.

After drying and cooling, two 50 ml sub-samples of each treatment were measured in a 50-ml graduated cylinder and placed in 125-ml Erlenmeyer flasks with 100 ml of deionized water. The media and water were initially swirled to thoroughly mix the contents and then allowed to sit still in a controlled temperature lab (23°C ± 1.4 ºC) for five days. At day five, the flasks were again swirled to mix the contents and were allowed to sit until suspended material dropped out of solution. Colorimetric manganese tests (LaMotte Smart Colorimeter, Chestertown, MD) were performed on the solutions.

Interactions of Fertilizer Ions with Ceramic Media and Peat/Vermiculite

Three media (0.25 – 2 mm diameter ceramic media, peat/vermiculite, and medium Ottawa sand) were selected. Five hundred milliliter samples of these media were measured in a graduated cylinder and placed in 1 ½ in. PVC columns. Two replicate columns were made per media type. Care was taken to achieve the same packing density among replicate columns. A large quantity (100 L) of a stock nutrient solution was prepared with elemental concentrations shown in Table 4 – 1, to pour through the media.
To begin the experiment, 400 ml of nutrient solution were added to each column in order to wet the media, bringing the each column to a water content at “container capacity.” After the initial input of nutrient solution, 200 ml of the solution was added to the columns daily and allowed to percolate through for approximately ½ hour (this amount of time allowed for 97.5 to 100% recovery of the solution volume). The electrical conductivity and pH of the leachate solutions were measured each day, while nutrient concentrations were measured every three days for the first 43 days of the experiment and every 7 days thereafter. The same parameters were measured on the stock nutrient solution. For nutrient analysis, leachate solutions were acidified with 0.7 ml 16 N nitric acid (HNO$_3$) per 13 ml solution and analyzed by ICP-OES speciation analysis. Nitrate and ammonium concentrations in the solutions were measured using colorimetric nutrient tests. This study was conducted in a controlled-temperature lab (23ºC +/- 1.4 ºC).

Table 4 – 1: Elemental nutrient concentrations (mM) in a solution that was poured through peat/vermiculite and ceramic media.

<table>
<thead>
<tr>
<th>NO$_3$ (mM)</th>
<th>NH$_4$</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>S</th>
<th>B</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Mo</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>4.0</td>
<td>0.5</td>
<td>2.5</td>
<td>1.0</td>
<td>1.0</td>
<td>3.0</td>
<td>0.008</td>
<td>0.01</td>
<td>0.004</td>
<td>0.009</td>
<td>0.004</td>
<td>0.0001</td>
<td>0.06</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Quantification of Relative Ceramic Media-Sorbed Nutrients

Comparing the media-sorbed nutrient concentrations of commercially available bags of Turface and Profile (Tables 4 – 2 and 4 – 3), higher average nutrient concentrations were found in Profile than Turface for every nutrient considered other
than phosphorus. The standard deviations of the nutrient concentrations for both products show that there was considerable variation in media-sorbed nutrient concentrations from bag to bag. Depending on the ratios of these media-sorbed nutrients one to another, there is potential for the induction of plant nutrient imbalances, which will be seen later in this chapter. Given the great variability in media-sorbed nutrients that has been measured from bag to bag, there are no guarantees that a particular bag of Profile or Turface will or will not have sorbed nutrient concentrations that are out of balance for optimal plant nutrition.

Table 4 – 2: Media-desorbed nutrient concentrations of 0.25 – 1 mm ceramic media (Profile). Great variation was found bag to bag among nutrient concentrations. For a micronutrient, Mn concentrations were extremely high.

<table>
<thead>
<tr>
<th>Lot #</th>
<th>P (mmol kg⁻¹)</th>
<th>K (µmol kg⁻¹)</th>
<th>Ca (mmol kg⁻¹)</th>
<th>Mg (µmol kg⁻¹)</th>
<th>S (µmol kg⁻¹)</th>
<th>B (µmol kg⁻¹)</th>
<th>Cu (µmol kg⁻¹)</th>
<th>Fe (µmol kg⁻¹)</th>
<th>Mn (µmol kg⁻¹)</th>
<th>Zn (µmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>2.1</td>
<td>1.3</td>
<td>0.4</td>
<td>7.7</td>
<td>163</td>
<td>1.88</td>
<td>6.6</td>
<td>195</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>0.011</td>
<td>1.2</td>
<td>0.4</td>
<td>0.2</td>
<td>7.3</td>
<td>113</td>
<td>1.64</td>
<td>2.5</td>
<td>79</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>0.031</td>
<td>4.6</td>
<td>2.3</td>
<td>0.9</td>
<td>7.9</td>
<td>188</td>
<td>0.00</td>
<td>4.4</td>
<td>317</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.029</td>
<td>3.7</td>
<td>1.7</td>
<td>0.6</td>
<td>7.1</td>
<td>170</td>
<td>0.00</td>
<td>5.2</td>
<td>234</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>0.045</td>
<td>3.2</td>
<td>8.1</td>
<td>1.6</td>
<td>11.5</td>
<td>119</td>
<td>0.00</td>
<td>6.1</td>
<td>33</td>
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</tr>
<tr>
<td>6</td>
<td>0.009</td>
<td>2.4</td>
<td>2.8</td>
<td>0.9</td>
<td>5.6</td>
<td>82</td>
<td>0.00</td>
<td>1.7</td>
<td>169</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>0.016</td>
<td>4.9</td>
<td>5.3</td>
<td>2.2</td>
<td>10.7</td>
<td>147</td>
<td>0.62</td>
<td>4.2</td>
<td>393</td>
<td>3.5</td>
</tr>
<tr>
<td>avg</td>
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<td>3.1</td>
<td>3.1</td>
<td>1.0</td>
<td>8.3</td>
<td>140</td>
<td>0.59</td>
<td>4.4</td>
<td>203</td>
<td>1.6</td>
</tr>
<tr>
<td>SD</td>
<td>0.013</td>
<td>1.3</td>
<td>2.7</td>
<td>0.7</td>
<td>2.1</td>
<td>37</td>
<td>0.83</td>
<td>1.8</td>
<td>126</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 4 – 3: Media-desorbed nutrient concentrations of 1 – 2 mm ceramic media (Turface). Great variation was found bag to bag among nutrient concentrations, as in Profile; however, generally concentrations were lower than in Profile.

<table>
<thead>
<tr>
<th>Lot #</th>
<th>P (mmol kg⁻¹)</th>
<th>K (µmol kg⁻¹)</th>
<th>Ca (mmol kg⁻¹)</th>
<th>Mg (µmol kg⁻¹)</th>
<th>S (µmol kg⁻¹)</th>
<th>B (µmol kg⁻¹)</th>
<th>Cu (µmol kg⁻¹)</th>
<th>Fe (µmol kg⁻¹)</th>
<th>Mn (µmol kg⁻¹)</th>
<th>Zn (µmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.032</td>
<td>1.6</td>
<td>0.42</td>
<td>0.22</td>
<td>1.8</td>
<td>92</td>
<td>0.00</td>
<td>0.6</td>
<td>10.5</td>
<td>0.40</td>
</tr>
<tr>
<td>9</td>
<td>0.031</td>
<td>1.5</td>
<td>0.41</td>
<td>0.22</td>
<td>1.7</td>
<td>84</td>
<td>0.00</td>
<td>1.0</td>
<td>8.5</td>
<td>0.19</td>
</tr>
<tr>
<td>10</td>
<td>0.029</td>
<td>1.6</td>
<td>0.43</td>
<td>0.21</td>
<td>1.8</td>
<td>83</td>
<td>0.00</td>
<td>0.0</td>
<td>10.2</td>
<td>0.00</td>
</tr>
<tr>
<td>11</td>
<td>0.256</td>
<td>0.8</td>
<td>0.06</td>
<td>0.04</td>
<td>0.5</td>
<td>153</td>
<td>0.00</td>
<td>0.0</td>
<td>0.4</td>
<td>0.00</td>
</tr>
<tr>
<td>12</td>
<td>0.036</td>
<td>2.0</td>
<td>0.51</td>
<td>0.51</td>
<td>3.4</td>
<td>93</td>
<td>0.00</td>
<td>2.4</td>
<td>4.9</td>
<td>0.00</td>
</tr>
<tr>
<td>13</td>
<td>0.040</td>
<td>3.2</td>
<td>1.25</td>
<td>0.73</td>
<td>4.4</td>
<td>142</td>
<td>0.34</td>
<td>13.7</td>
<td>3.8</td>
<td>1.60</td>
</tr>
<tr>
<td>avg</td>
<td>0.071</td>
<td>1.8</td>
<td>0.65</td>
<td>0.32</td>
<td>2.3</td>
<td>108</td>
<td>0.06</td>
<td>2.9</td>
<td>6.4</td>
<td>0.37</td>
</tr>
<tr>
<td>SD</td>
<td>0.091</td>
<td>0.8</td>
<td>0.52</td>
<td>0.25</td>
<td>1.4</td>
<td>31</td>
<td>0.14</td>
<td>5.4</td>
<td>4.0</td>
<td>0.63</td>
</tr>
</tbody>
</table>
The Origin of Ceramic Media-Sorbed Nutrients

We had three main hypotheses for the origin of the nutrients that are found adsorbed to ceramic media. The first hypothesis is that these nutrients may be the product of dissolution from the ceramic mineralogical structure itself, perhaps as a result of the firing process. The second hypothesis is that the nutrients, which are dissolved in the well water which is used to cool ceramic media after firing, adsorb to ceramic media exchange sites, becoming plant-available. The third hypothesis is that the origin is a combination of mineralogical dissolution and well water sources.

To partially test these hypotheses, samples of crude clay (unfired, Turface precursor), Turface cooled by air, and Turface cooled by water (the product that may be purchased commercially) were obtained directly from the Profile company and desorption of soluble nutrients was done. The nutrient concentrations of this desorption analysis are found in Figure 4 – 2. A sample of the well water that is used for cooling the fired clay was also obtained, and its nutrient concentrations are found in Figure 4 – 3. The well water analysis showed that all micronutrient concentrations are 5 µM or less, with the exception of boron which was measured to be 15 µM; and all macronutrient concentrations are around 1.0 mM, with the exception of sulfur which was measured at 2.5 mM.

Little deviation was observed between the “air-cooled” and “water-cooled” concentrations of all nutrients that were analyzed, with the exception of zinc. Zinc was found to be in approximately 300% higher concentration in air-cooled Turface than in water-cooled Turface. The results indicate that adsorption on exchange sites of nutrient ions dissolved in the well water during cooling has little or no effect on the
concentrations of ceramic media plant-available nutrients. Comparing the concentrations of desorbed nutrients in the crude clay material and fired Turface indicate increases in nutrient solubility with firing for some nutrients and decreases for others. According to the Turface MVP spec sheet on the Profile Company’s website (Turface.com, January 2010), Turface is fired in a rotary kiln at temperatures no less than 1200ºF, a temperature at which changes in clay mineral composition may take place.
Figure 4 – 2: Nutrients desorbed from ceramic media obtained directly from the Profile Company. “Crude Material” is the unfired clay used to make Turface. “Air-cooled Turface” samples were not cooled by well water, which the standard procedure in Turface production.
Effects of Ceramic Media Nutrient Balance on Plant Growth and Nutrition

Imbalanced Nutrients

In this trial, growth was deficient in all ceramic media, especially those containing 0.25 – 1 mm diameter ceramic aggregates (Figure 4 – 4). In addition, white spots were observed on the leaves of those plants grown in 0.25 – 1 mm ceramic media (Figure 4 – 5), indicating toxic nutrient uptake.
Figure 4 – 4: Growth of mizuna grown in four media. Growth was negatively affected as compared to a standard peat/vermiculite media, especially in ceramic (0.25 – 1 mm) and ceramic (0.25 – 2 mm), due to toxic nutrient uptake (Figure 4 – 6).

Figure 4 – 5: An image of the visual symptoms of toxic manganese uptake by mizuna. These leaves contained ~750 mg/kg manganese, approximately 15x the optimal level for healthy plant leaves.
Tissue nutrient levels were measured (Figure 4 – 6). Manganese levels in the plant tissue reached 730 mg kg$^{-1}$, whereas manganese levels in plants grown in a peat/vermiculite media under the same conditions were only 37 mg kg$^{-1}$. In addition to manganese, potassium, magnesium and sulfur were found to be in excess in plants grown in ceramic media. The ceramic media that was used to grow these plants was desorbed for measurement of relative nutrient concentrations (Table 4 – 4).
Nutrients Concentrations of Mizuna

Table 4–6: Mizuna tissue nutrient concentrations, from plants grown in peat/vermiculite and ceramic media. Manganese was taken up in toxic levels from ceramic media, and magnesium, sulfur, and potassium were taken up in excess. Optimal nutrient ranges adapted from Bennett (1993) and Marshner (1995).
Proper Nutrient Balance

In this study, radish and mizuna tissue nutrient concentrations differed little between those grown in ceramic media and peat/vermiculite (Figures 4 – 7 and 4 – 8). Plant growth between media treatments was also comparable. The ceramic media was used without rinsing or soaking of any kind, suggesting that the particular bag of ceramic media used in this study had nutrition balanced for optimal plant growth. When free of nutrient imbalances, ceramic media may grow plants with growth and tissue nutrient concentrations comparable to those grown in a standard peat/vermiculite media.

Table 4 – 4: Nutrients desorbed from the ceramic media in which plants were grown that accumulated ~750 mg kg\(^{-1}\) Mn, a toxic level.

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>S</th>
<th>B</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mg kg(^{-1}) media)</td>
<td>0.70</td>
<td>97.9</td>
<td>52.0</td>
<td>29.0</td>
<td>77.0</td>
<td>0.79</td>
<td>0.30</td>
<td>0.01</td>
<td>2.48</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figure 4 – 7: A comparison of radish root and leaf nutrient concentrations when grown in peat/vermiculite 0.25 – 1 mm diameter ceramic media. This is a case in which ceramic media nutrient levels directly out of the bag were not out of balance.
The Efficacy of Rinsing/Soaking Ceramic Media to Improve Nutrient Balance

Soaking Ceramic Media (Nutrient Solution and Deionized Water)

Given that ceramic media-sorbed nutrients are out of balance for plant nutrition, soaking the media in a nutrient solution may wash away nutrients in excess and exchange undesired nutrients for desired ones. Figure 4 – 9 displays the concentrations of media-sorbed nutrients desorbed from a bag of 0.25 – 1 mm diameter ceramic media before and after soaking with a complete nutrient solution (Table 4 – 1). This particular bag of ceramic media contained high levels of many nutrients, and soaking was effective in reducing the concentrations. For example, manganese concentrations decreased by approximately 85% with soaking.
Figure 4 – 9: Media-sorbed nutrients desorbed from 0.25 – 1 mm diameter ceramic media, before and after washing with nutrient solution. In this particular bag, most media-sorbed nutrients were reduced in concentration.
Another study tested the efficacy of the soaking ceramic media, comparing media soaked with a complete nutrient solution and media soaked with deionized water, through measuring plant growth and tissue nutrient concentrations. Plant growth in the media was tested with and without fertilizer, in order to gauge the ability of each media to supply plant-essential nutrients. Figure 4–10 shows the plant growth results for this trial.

As expected, the treatments with added fertilizer had statistically higher growth than those with no added fertilizer; however, the treatments with added fertilizer were not statistically different from each other. Statistical differences were found in growth between the deionized water-soaked and nutrient solution-soaked media with no added fertilizer, with more growth in the media soaked with nutrient solution. The growth in ceramic media soaked with nutrient solution was ~70% the growth of the treatments with added fertilizer, while the growth in ceramic media soaked with deionized water was about 45%. In this case, the result suggested that soaking ceramic media with nutrient solution promoted productive plant growth, placing beneficial nutrients on media surfaces that were available for plant uptake.
Figure 4 – 10: Growth of Earligreen pea plants grown in ceramic media with media-soaking and fertilizer treatments. Soaking the media with nutrient solution provided nutrients available for plant growth, as shown by the increased growth in the “nutrient solution soaked” treatments, with and without Osmocote.

Figure 4 – 11 shows the tissue nutrient contents for this trial. Tissue nutrient concentrations in the treatments with no added fertilizer were limited by phosphorus, potassium, and copper (and potentially nitrogen, which was not measured), which were in significantly higher proportion in the treatments with added fertilizer. Tissue manganese concentrations were high in both soaking scenarios; however, deionized water appeared to have been more effective at removing the excess levels in the media, as shown by tissue manganese levels being roughly three times higher in plants grown in nutrient solution-soaked media.
Earligreen Pea Nutrient Concentrations

Figure 4 – 11: Earligreen pea tissue nutrient concentrations. The experiment included media soaking and fertilizer treatments. Optimal nutrient ranges adapted from Bennett (1993) and Marshner (1995).
Given the results of these studies, a combination of soaking with deionized water and a nutrient solution may provide the best results in terms of reducing the concentration of media ions in excess and replacing potentially detrimental ions with beneficial nutrients.

**Rinsing Ceramic Media**

A study was done to determine the percent reduction in ceramic media-sorbed manganese that could be achieved by simply rinsing with tap water. Five distinct samples of 0.25 – 1 mm diameter ceramic media, with varying concentrations of sorbed manganese, were included in the study. The result was an average of 54.3% reduction in manganese levels by rinsing with tap water, as shown by colorimetric manganese tests on solutions containing pre- and post-rinsing ceramic samples (Table 4 – 5).

<table>
<thead>
<tr>
<th>Lot #</th>
<th>% Mn Reduction</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-55.2</td>
<td>9.4</td>
</tr>
<tr>
<td>2</td>
<td>-69.4</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>-50.8</td>
<td>2.9</td>
</tr>
<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>-36.4</td>
<td>3.2</td>
</tr>
<tr>
<td>avg</td>
<td>-54.3</td>
<td>12.2</td>
</tr>
</tbody>
</table>

**Interactions of Nutrient Ions with Ceramic Media and Peat/Vermiculite**

Ceramic media was found to chemically interact with nutrients that were introduced to it. To show overall trends of chemical interaction, the electrical conductivities of media leachate solutions were measured after percolating a nutrient solution through. The media leachate electrical conductivities were initially lower than
that of the stock solution, but, over time, increased to exceed the electrical conductivity of the stock (Figure 4 – 12). Our hypothesis to explain these dynamic electrical conductivity trends was that chemical binding, nutrient exchange reactions, ions released into solution through media dissolution, and/or pH changes may have been responsible. See Appendix C for a more comprehensive discussion of these chemical interactions.

![Graph showing electrical conductivity and pH of a nutrient solution, before and after percolating through media](image)

Figure 4 – 12: The electrical conductivities of a stock nutrient solution before and after percolating through three solid substrates.

To test our hypotheses, stock and leachate nutrient concentrations were periodically measured and compared. Figure 4 – 13 displays the concentrations of leachate nutrients before and after percolating through the media columns. Each nutrient had a unique interaction with each media that was dynamic with time. Some general trends were observed, from which conclusions can be drawn.
Figure 4 – 13: Nutrient concentrations of a nutrient solution before and after percolating through columns of plant-growth media. Dynamic interactions and reactions of the nutrients with the media occur over time.
Ceramic media almost entirely removed phosphorus, copper, and zinc from solution. Over the course of ~60 days, both ceramic media and peat/vermiculite began to allow zinc to remain in solution; however, phosphorus and copper were almost entirely removed from solution over the entire scope of this study (~100 days). Figure 4 – 13a more clearly displays the concentrations of these specific nutrients.

Figure 4 – 13a: Rescaled versions of graphs from Figure 4 – 13 that more clearly show leachate nutrient concentrations that are largely removed from solution by ceramic media and/or peat/vermiculite.

Ammonium was consistently removed from solution, while nitrate was consistently higher in leachate solutions than in the stock. It is our opinion that these trends may be a dual function of nutrient exchange reactions and nitrification.
Nitrification is a biological process in which ammonium is converted to nitrate by nitrifying bacteria.

Potassium, calcium, magnesium, boron, manganese, and iron were in higher concentrations in ceramic leachate solutions than in the stock solution over the course of the study, suggesting that these nutrients are the product of ceramic dissolution and/or that they were exchanged from media exchange sites. The same trend was observed in peat/vermiculite for calcium and magnesium, and to a small extent for manganese and boron.

Only a single nutrient, sulfur, passed through both media with no observable interaction whatsoever. However, phosphorus, copper, and iron passed through peat/vermiculite without interaction.

In the attempt to attain optimal plant nutrition in these media, the trends discussed above should be considered. In order to achieve optimal plant uptake of phosphorus, copper, and zinc in ceramic media, over-fertilization or supplementation with these nutrients may be necessary. However, in our plant-growth studies in ceramic media with no manipulation of fertilizer treatments, copper is the only nutrient we have found to be consistently deficient in plant tissues. Given that certain nutrients are released into solution by ceramic media, it may be appropriate to decrease the concentrations of these nutrients in fertilizer treatments.
REFERENCES


CHAPTER 5

OPTIMIZATION OF CERAMIC MEDIA FOR PLANT GROWTH:

PARTICLE SIZE

ABSTRACT

Ceramic media (Turface or Profile) is commonly used in research applications because it easily washes off root surfaces. It is also used by NASA in the unleached root-zones of spaceflight plant growth research. Much research has been done to characterize and model the physical and hydraulic properties of ceramic media, but plant growth studies in the media to verify the models have been limited. We used plants to extract water from root-zones of ceramic media of three particle-size distributions, characterizing plant-available water and water supply dynamics in a system of practical height (9 cm). Plant-available water in ceramic media was intermediate between water retained in the macropore spaces of the wetting and drying curves determined in soil physical measurements presented by Heinse et al. (2007). This result suggests that the work of Heinse et al. (2007) may be used to predict plant-available water in ceramic media with varying root-zone height, with the margin of error being the values determined by wetting and draining curves. At best, at a 9 cm root-zone depth, depending on particle-size distribution, 37% of the root-zone volume contained plant-available water, showing that minimal internal, micropore water is plant-available. A linear decrease in plant-available water was observed with an increase in mean particle size distribution, even at a shallow root-zone height of 9 cm. In terms of water supply dynamics, a characteristic of ceramic media, regardless of particle size distribution, was steady supply of water to transpiring...
plants and, at points related to particle size distribution, abruptly stopping water supply. This characteristic would mandate meticulous watering management (ex. sensor-based irrigation) if plant wilting were to be avoided. Ceramic media may be successfully used as a plant-growth media with particle-size optimization for specific applications and meticulous watering management.

**INTRODUCTION**

Ceramic media, commercially sold as Turface or Profile (Profile Products LLC, Buffalo Grove Illinois) and often called arcillite, is often a media of choice for research applications because it can easily be removed from root surfaces at harvest. Ceramic media is also used by NASA in the unleached root-zones of spaceflight plant growth research (Monje *et al*., 2003).

Turface (Pro League and MVP) has a relatively large particle-size distribution, with roughly 50% of its mass containing aggregates having diameters < 2 mm, and 50% > 2 mm (up to ~ 4 mm). Profile has a smaller particle-size distribution, with virtually all of its aggregates having diameters between 0.25 and 0.5 mm. These media can be sieved and/or mixed to provide wide ranges of particle size distributions. Total porosity of the material ≈74% for both 0.25 – 1 mm and 1 – 2 mm aggregates, ~50% of which is intra-aggregate micropores and ~50% is inter-aggregate pores (Steinberg *et al*., 2005).

Ceramic media has been intensively modeled for physical and hydraulic properties (Blonquist *et al*., 2006; Heinse *et al*. 2007; Steinberg *et al*. 2005; Steinberg and Portiz, 2005). Soil physical models suggest retention of plant-available water in ceramic media up to heights of approximately 20 cm, with high water retention low in the root-
of 1 cm of water in the bottom of each container, allowing the media to come to a water content equilibrium. This watering method allowed for differences in plant-available water to be apparent based on the unique level of capillary rise active in each media, in a container of typical to shallow height for plant growth (9 cm). Once watered, the containers were drained, bringing them to “container capacity” water contents. Each container was placed on a balance which output to a Campbell’s Scientific CR1000 datalogger. A datalogger program was written which calculated a rate of transpiration
from changes in mass recorded by the balances over time \((\text{mass}_{\text{initial}} - \text{mass}_{\text{final}}) / (\text{time}_{\text{initial}} - \text{time}_{\text{final}})\). Assuming that all loss of mass could be attributed to loss of water through the plants by transpiration (with negligible evaporation rates), values of transpiration in units of g min\(^{-1}\) were converted to units of ml min\(^{-1}\) (1.0 g water = 1.0 ml). Plant-available water was determined by summing the water use by the plants until transpiration fell to 33% of its maximum rate during each dry down. 33% was chosen because this was a point observed to immediately precede plant wilting. The rate of transpiration was monitored instantaneously on a computer screen and the plants were removed from the balances and watered near their wilting points for a second dry-down, following the same procedure.

**RESULTS AND DISCUSSION**

**Plant-Available Water of Ceramic Media**

On a volume basis, the amount of plant-available water in all ceramic media ranged from approximately 18% to 61% (Figure 5 – 1), in the second dry-down. Among the ceramic media, there was a linear increase in plant-available water with decreasing particle size distribution: 1 – 2 mm, 18%; 0.25 – 2 mm, 29%; and 0.25 – 1 mm, 37%. However, all ceramic media supplied significantly less plant-available water than peat/vermiculite, with a value of 61%.
Figure 5–1: Plant-available water in four plant growth media on a second dry-down. The values were derived from the transpiration data of Figure 5–3, summing the water loss through transpiration from “container capacity” to the point at which transpiration reached 33% of its maximal rate.

Work by Heinse et al. (2007) shows the differences in water retention in ceramic media as particle size distribution is altered as a function of height or matric potential (Figure 5–2). Figure 5–2 shows how height is of central importance to the use of ceramic media for plant growth. Wet conditions exist at low heights in the media and rapid losses in water content occur at heights uniquely related to particle size distribution. As the height of the system is increased and water in the macropore network has drained away, it is increasingly difficult to sustain productive plant growth. Heinse’s data shows an approximately 37% decrease in water contents under the narrow matric potential ranges of 0 to 10 cm for 1–2 mm ceramic media, and 0 to 20 cm for 0.25 – 1 mm and 0.25 – 2 mm ceramic media. Matric potentials of 0 to 20 cm are far below the permanent wilting point (-1.5 MPa or -15,000 cm) at which plants cannot extract water. Since total media
porosity has been shown to be ~74%, 50% of which (37%) inter-aggregate macropores, this result suggests that plant-available water is only found in the inter-aggregate macropores, with minimal micropore water plant-available. The result found in this study of 37% plant-available water in 0.25 – 1 mm ceramic media seems to substantiate this conclusion and the results of Heinse’s work. The values found in this study of 19% plant-available water for 1 – 2 mm and 29% for 0.25 – 2 mm ceramic suggest that, even at the shallow root-zone height of 9 cm, plant-available water was diminished by limited capillary rise in these coarser media.

Figure 5 – 2: Water retention curves (van Genuchten, 1980) for ceramic media of three particle size distributions adapted from Heinse et al. (2007).

With the assumption that no intra-aggregate micropore water is plant-available, if the areas under the curves from Figure 5 – 2 (from saturation to the point at which matric potential rapidly increases with little change in volumetric water content) are integrated
over heights of interest, a value for plant-available water may be obtained. To compare with the results of our test, the curves were integrated from 0 to 9 cm heights (Table 5 – 1). In general, values of plant-available water determined in our procedure were intermediate between predicted values obtained from the wetting and draining water retention curves of Figure 5 – 2, the exception being 0.25 – 1 mm ceramic, which matched the water retention curve value for draining. This result suggests that Heinse’s water retention curves may be used to predict ceramic media plant-available water with varying root-zone height, with the margin of error being the values determined by wetting and draining curves.

Table 5 – 1: Ceramic media plant-available water determined in soil physical measurements (wetting and draining) by Heinse et al. (2007); and plant-available water determined by using plants as the water-extractant. Plant values are, in general, intermediate between wetting and draining values determined by Heinse et al. (2007).

<table>
<thead>
<tr>
<th>Media</th>
<th>Draining % (v/v)*100</th>
<th>Wetting % (v/v)*100</th>
<th>Plant Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 2 mm Ceramic</td>
<td>25.4</td>
<td>14.9</td>
<td>19</td>
</tr>
<tr>
<td>0.25 - 2 mm Ceramic</td>
<td>33.2</td>
<td>22.3</td>
<td>29</td>
</tr>
<tr>
<td>0.25 - 1 mm Ceramic</td>
<td>36.4</td>
<td>23.2</td>
<td>37</td>
</tr>
</tbody>
</table>

A characteristic of all the ceramic media was steady supply of water to transpiring plants and, at a point related to particle size distribution, abruptly stop supplying water (Figure 5 – 3). This characteristic would mandate meticulous watering management (i.e. sensor-based watering control) if plant wilting were to be avoided. Peat/vermiculite showed no sharp decline in water supply as in the ceramic media, but gradually declined in water supply over a more extended period of time, delaying plant wilting.
Figure 5 – 3: The transpiration rate of containerized radishes in two sequential drys-down, from container capacity to a water content at which moderate wilting symptoms were observed.

REFERENCES


CHAPTER 6

SUMMARY AND CONCLUSIONS

Effects of substrate water content and temperature on the nutrient release of three types of polymer-coated fertilizers

Polymer-coated fertilizer (PCF) release rates are known to fluctuate with temperature, but the effect of temperature on the release of individual nutrient ions has not been well characterized. In addition, the effect of substrate water content has not been consistent among studies. We quantified the release rate of three widely-used types of PCF (Polyon, Nutricote, and Osmocote) in water and in sand over a wide range of temperature (5, 15, 20, 30, and 40°C).

There were no statistically significant differences in nutrient release rates between PCF placed in water and incorporated into sand for any PCF type, indicating that substrate water content has a minimal effect on release rates. There was a nonlinear effect of temperature on the release rates of Nutricote and Polyon PCF. The effect of temperature was less evident in Osmocote fertilizers, because they rapidly released nutrients at all temperatures. Nutricote fertilizers were the most consistent in releasing individual nutrients with temperature and over time. Polyon fertilizers had the slowest release rate relative to the manufacturer’s specifications. This study provides a quantitative basis for more precise determination of PCF application in containerized plant production.
Balancing supply and demand: A mass balance approach to optimizing polymer-coated fertilizer application rates

No comprehensive model has been developed that couples models to predict plant growth and PCF nutrient release rates. We present a plant growth model based on incoming photosynthetic photon flux (PPF) and the efficiency of four plant-growth determinants. We also present a model to predict PCF ion release rates. This model is based on the finding that, among macronutrients, phosphorus is released at the slowest relative rate, and is thus the limiting nutrient to plant growth. PCF rates are adjusted by empirically derived equations that describe the cumulative release of phosphorus as a function of temperature relative to the prescribed release for a given PCF.

The efficacy of the model to accurately predict PCF application rates was verified with a growth trial. Plant growth, in the growth trial, matched the growth predicted by the model; and peak growth occurred at a PCF application rate that matched the predicted application rate. This result suggests that this modeling approach has potential to provide a basis for determining optimum PCF application rates when the fertilizer release rate has been characterized.

Optimization of ceramic media for plant growth: Nutrient balance

Ceramic media (Turface or Profile) is commonly used in research applications because it easily washes off root surfaces. It is also used by NASA in the unleached root-zones of spaceflight plant growth. In spite of widespread use, studies on the chemical properties of ceramic media have been limited. This research sought to more thoroughly understand the plant-availability of nutrients from ceramic media, the origin of those
nutrients, the efficacy of soaking and rising procedures to mitigate nutrient imbalances, and the chemical interactions of fertilizer ions added to ceramic media.

Relative media-sorbed nutrient concentrations were highly variable from bag to bag. In many cases, ceramic media supplied an excess of manganese, boron, magnesium, and sulfur, which induced nutrient imbalances in plant tissue and reduced plant growth. Rinsing and soaking procedures on the media helped mitigate these nutrient imbalances. When media-sorbed nutrient imbalances were absent or improved by rinsing/soaking, if imbalanced, growth was comparable to growth in a standard peat/vermiculite medium. Ceramic media also interacted with fertilizer ions added to it. Copper, phosphorus, and zinc ions were largely removed from solution by these interactions. However, despite the removal of most of these ions from the root-zone solution, only copper was ever found deficient in plant tissues. Copper supplementation may be necessary to replace the copper removed from solution. Despite some chemical complexity, ceramic media is a valuable plant-growth substrate when accommodation is made for its chemical properties that negatively affect plant growth.

**Optimization of ceramic media for plant growth:**

**Particle size**

Much research has been done to characterize and model the physical and hydraulic properties of ceramic media, but plant growth studies in the media to verify the models have been limited. We used plants to extract water from root-zones of ceramic media of three particle-size distributions, characterizing plant-available water and water supply dynamics in a system of practical height (9 cm). Plant-available water in ceramic media was intermediate between water retained in the macropore spaces of the wetting
and drying curves determined in soil physical measurements presented by Heinse et al. (2007). This result suggests that soil physical models may be used to predict plant-available water in ceramic media with varying root-zone height, with the margin of error being the values determined by wetting and draining curves. At best, at a 9 cm root-zone depth, depending on particle-size distribution, 37% of the root-zone volume contained plant-available water, showing that minimal internal, micropore water is plant-available. A linear decrease in plant-available water was observed with an increase in mean particle size distribution, even at a shallow root-zone height of 9 cm. In terms of water supply dynamics, a characteristic of ceramic media, regardless of particle size distribution, was steady supply of water to transpiring plants and, at points related to particle size distribution, abruptly stopping water supply. This characteristic would mandate meticulous watering management (ex. sensor-based irrigation) if plant wilting were to be avoided. Ceramic media may be successfully used as a plant-growth media with particle-size optimization for specific applications and meticulous watering management.
APPENDICES
APPENDIX A: Polymer-Coater Fertilizer Material
Figure A – 1: The release of 12 plant-essential nutrients from 15 to 40ºC for ~80 days from Osmocote 3 – 4 month (15 – 9 – 12), graphed as a function of time.
Figure A – 2: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Osmocote 3 – 4 month (15 – 9 – 12), graphed as a function of temperature.
Figure A – 3: The release of 12 plant-essential nutrients from 15 to 40ºC for ~80 days from Nutricote T-100 (18 – 6 – 8), graphed as a function of time.
Figure A – 4: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Nutricote T-100 (18 – 6 – 8), graphed as a function of temperature.
Figure A – 5: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Nutricote T-270 (18 – 6 – 8), graphed as a function of time.
Figure A – 6: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Nutricote T-270 (18 – 6 – 8), graphed as a function of temperature.
Figure A – 7: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Polyon 1 – 2 month (16 – 6 – 13), graphed as a function of time.
Figure A – 8: The release of 12 plant-essential nutrients from 15 to 40°C for ~80 days from Polyon 1 – 2 month (16 – 6 – 13), graphed as a function of temperature.
Percent Nutrient Release on a Molar Basis with Temperature

Figure A – 9: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Osmocote 3 – 4 month (15 – 9 – 12), graphed as a function of temperature.
Figure A – 10: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Osmocote 12 – 14 month (15 – 9 – 12), graphed as a function of temperature.
Figure A – 11: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Nutricote T-100 (18 – 6 – 8), graphed as a function of temperature.
Figure A – 12: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Nutricote T-270 (18 – 6 – 8), graphed as a function of temperature.
Figure A – 13: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Nutricote T-360 (18 – 6 – 8), graphed as a function of temperature.
Figure A – 14: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Polyon 1 – 2 month (16 – 6 – 13), graphed as a function of temperature.
Figure A – 15: The percent release of 12 plant-essential nutrients on a molar basis (moles of ions of a specific type released / total moles of ions released over the same time period * 100) from 15 to 40°C for ~80 days from Polyon 10 – 12 month (15 – 6 – 11), graphed as a function of temperature.
**Solubility of “Bald” Polyon Prills**

Among fully coated green Polyon prills, it was observed that a small percentage of prills were “bald” with little or no green coating (Figure A – 16). In order to test whether these bald prills were more soluble than regular, coated prills, a simple test was conducted. 10 “bald” Polyon 10 – 12 month prills were manually picked out from among regular, coated prills; and 10 regular, coated prills of comparable size were picked out. Each type of prill was placed in 200 ml of deionized water (electrical conductivity ~0.0002 S m\(^{-1}\)) and measured for electrical conductivity periodically over the course of two days. “Bald” Polyon prills were nearly 200 fold more soluble than regular, coated prills after a single day in water (Table A – 1)

![Figure A – 16: Uncoated, bald Polyon prills are seen among regular, coated prills.](image)
Table A – 1: The fold increase in solubility of “bald” Polyon prills over regular, coated prills.
**Osmocote Prill Expansion at 40°C**

During our studies it was observed that a portion of Osmocote prills that were held at higher temperatures experienced extreme expansion, appearing balloon like. No similar effect was observable by eye among prills of Polyon and Nutricote. The fertilizers shown in Figure A – 17 were held in flasks of water at 20 and 40°C for one month.

![Polyon, Osmocote, Nutricote](image)

Figure A – 17: The effect of temperature on PCF prill expansion. At higher temperatures, a portion of Osmocote prills expand like balloons, making fertilizer solution within readily visible. If Polyon and Nutricote prills expand due to temperature, it is not observable by eye.
Figure A – 18: Particle size distribution of medium Ottawa sand.
Figure A – 19: Water retention curves for Ottawa sand of differing particle size distributions (Heinse, 2009). The medium grained sand was used in our studies.
The Effect of PPF on Mizuna Growth

The Effect of PPF on Mizuna Yield in Unleached Root-Zones

Figure A – 20: The effect of PPF on the dry mass production of mizuna. This data was taken from a fertilizer rate study and the values have been normalized for fertilizer rate to show the effect of PPF.
APPENDIX B: Ceramic Media Material
Methods and Materials

It is a common practice to sieve ceramic media (Turface) to contain only particles of 1 – 2 mm diameter. Directly out of the bag Turface contains particles up to about 4 mm in diameter, creating a coarse media. This growth trial was designed to observe the necessity of sieving ceramic media (1 ~ 4 mm) to contain only particles of 1 – 2 mm. The study included four distinct media: peat/perlite, peat/vermiculite, ceramic (0.25 – 1 mm), and ceramic (1 ~ 4 mm). The peat/perlite and peat/vermiculite media were 50/50 mixes by volume, and both ceramic media were used directly in their out-of-bag condition.

The trial was carried out in an unleached root-zone system, where 1 cm of water was maintained in the bottom of each plant-growth container and moved throughout the root-zone by the hydraulic conductivity of each media. There were three replicate, 2.7 L plant-growth containers per level of media. 9.5 g of 3 to 4 month Osmocote Plus (15 – 9 – 12) controlled-release fertilizer was put into each container as a long-term nutrient source. Cherry Belle radishes were planted at an excess, thinned to five plants per container, and allowed to grow for 24 days. The study was conducted in a greenhouse setting, with the plant receiving a light level of 200 – 400 µmol photons m⁻² s⁻¹. Media comparison was done by a point measurement of radish fruit and leaf growth.
Figure B – 1 shows the growth of radishes grown in four media: peat/perlite, peat/vermiculite, ceramic (0.25 – 1 mm), and ceramic (1 – 4 mm). The result of growing plants in coarse ceramic media directly out of the bag was moderate to severe water stress, as reflected by the decreased radish root growth in this treatment as compared to the other treatments.

Figure B – 1: Dry mass of radish leaves and roots grown in four media. These results showed that not removing particles above 2 mm from ceramic media (1 – 4 mm) was detrimental to radish growth, due to the limited capillary rise of water with a larger particle size distribution.
Figure B – 2 shows bottom and side views of the root growth from the trial above. Due to high water content, root growth was suppressed in the bottom of the fine ceramic (0.25 – 1 mm) root-zone and concentrated higher in the root-zone. Due to its coarse nature, water could not be wicked to the highest points of the root-zone in the coarse ceramic (1 ~ 4 mm) media, limiting the area where root growth could take place. Root growth was more uniform from the top to bottom of the root-zones of the peat-based media.

![Bottom View](image)

![Side View](image)

Figure B – 2: Bottom and side images of the root growth in four media. Root growth was suppressed on the bottom of the root-zone in the fine ceramic media due to excessive water. Root growth was suppressed in the upper part of the root-zone of the coarse ceramic media due to the presence of particles above 2 mm diameter limiting capillary rise of water.
Manganese Desorption Equilibrium from Ceramic Media in Deionized Water

Manganese Desorption from Ceramic Media
(Profile: 99328 707, Turface: 97469 507)

Figure B – 3: Establishment of manganese equilibrium in solution with a 2:1 water to media ratio.
Nutrient Solution Elemental Composition

Table B – 1: Elemental nutrient concentrations in a solution that was poured through peat/vermiculite and ceramic media. Nutrient concentrations were measured before and after percolating through the media.

<table>
<thead>
<tr>
<th>NO$_3$ (mM)</th>
<th>NH$_4$</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>S</th>
<th>B</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Mo</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>4.0</td>
<td>0.5</td>
<td>2.5</td>
<td>1.0</td>
<td>1.0</td>
<td>3.0</td>
<td>0.008</td>
<td>0.01</td>
<td>0.004</td>
<td>0.009</td>
<td>0.004</td>
<td>0.0001</td>
<td>0.06</td>
</tr>
</tbody>
</table>
APPENDIX C: Ceramic and Peat/Vermiculite Media
Chemically and Biologically Interact with Fertilizer Ions
Interaction of Nutrient Ions
with Ceramic Media and Peat/Vermiculite

Introduction

In studying the nutrient release of polymer-coated fertilizers (PCF) in water and inert Ottawa sand, another study was done that tracked the electrical conductivity of leachate solutions from columns containing Osmocote, Nutricote, or Polyon in two plant-growth media, peat/vermiculite and ceramic media. The baffling results of this study seemed to indicate that PCF release rates were faster in media than in water or Ottawa sand. No prior experimentation on PCF presented in the literature had ever shown PCF release rates to be faster in plant-growth media than in water. As a result, some further investigation was done in order to determine the fate of nutrients released from PCF into peat/vermiculite and ceramic media.

Methods and Materials

PCF Nutrient Release Profiles in Media

Three replicate samples of 6.5 g of three PCF (Osmocote 12-14 month (15 – 9 – 12), Nutricote type 270 (18 – 6 – 8), and Polyon 10-12 month (15 – 6 – 11)) were incorporated into 500 cm$^3$ of two media, ceramic media (0.25 – 2 mm) and peat/vermiculite, and placed into 1 ½ in. PVC columns. An initial 500 ml of deionized water (EC ~0.0002 S/m) was added to each column in order to wet the media, bringing the columns to “container capacity.” All leachate from this initial flush of water was discarded. 200 ml of deionized water was added to each column weekly, the leachate
was collected, and its electrical conductivity was measured. This study was conducted in a controlled-temperature lab (23ºC +/- 1.4 ºC).

**Tracking Nutrients, Electrical Conductivity, and pH of a Nutrient Solution before and after Percolating through Ceramic Media and Peat/Vermiculite**

The same column set-up as was used in the above experiment was also used here, but no PCF was added. A nutrient solution with known nutrient concentrations was added to the columns daily (Table B – 1) in order to determine the fate of the nutrients when allowed to interact with the media. Columns of medium sand (Ottawa) were included as a control.

Each day, 200 ml of nutrient solution were added to the columns and allowed to percolate through for approximately ½ hour (this amount of time allowed for 97.5 to 100.0% recovery of the solution volume). The electrical conductivity and pH of the leachate solutions were measured each day, while nutrient concentrations were measured every three days for the first 43 days of the experiment and every seven days thereafter. The same parameters were measured on the stock nutrient solution.

The solutions were acidified with 0.7 ml 16 N nitric acid (HNO₃) per 13 ml solution and analyzed by ICP-OES speciation analysis (Thermo IRIS Intrepid II, Thermo Scientific Inc., Waltham, MA). Nitrate and ammonium concentrations in the solutions were measured using colorimetric nutrient tests (LaMotte Smart Colorimeter, Chestertown, MD).

**Results and Discussion**

When PCF was added to columns of peat/vermiculite and ceramic media, leachate electrical conductivities were greater from ceramic and peat/vermiculite media than the
electrical conductivities of leachate from PCF incorporated into inert sand and the electrical conductivity of PCF placed in pure water (Figure C – 1). This study was done in response to these baffling results, as the PCF nutrient release was not expected to be higher in media than in pure water or inert sand.

Figure C – 1: Leachate solution electrical conductivities of four substrates containing 6.5 g of Osmocote, Nutricote, and Polyon. The electrical conductivity of the ceramic and peat/vermiculite leachates is inflated relative to those of sand and water due to chemical exchange and reaction dynamics in soilless media.
A nutrient solution with known nutrient concentrations, electrical conductivity, and pH was poured through columns of ceramic media and peat/vermiculite on a daily basis, and the leachate was collected and analyzed for the same parameters. It was hoped that tracking these parameters over time would show potential dynamic chemical interactions that may take place between plant-growth media and plant nutrients.

Just as in the media columns with PCF shown in Figure C – 1, the electrical conductivities of the media leachate solutions in this study were initially lower than those of the stock solution and Ottawa sand leachate, but, over time, increased to exceed their electrical conductivities (Figure C – 2).

Figure C – 2: The electrical conductivity of a stock nutrient solution, which was poured through three solid substrates. Also included are the electrical conductivities of the leachate solutions from the three substrates after the stock nutrient solution percolated through them. The same trend seen in Figure C – 1 of inflated media leachate electrical conductivities relative to the stock solution was seen in this study.
Our hypothesis to explain the electrical conductivity trends was that, perhaps, nutrient exchange reactions were taking place in which ions with lower contributions to electrical conductivity were displacing media-sorbed ions into solution with greater contributions to electrical conductivity. Figure C – 3 displays the concentrations of leachate nutrients before and after percolating through the media columns. Confirming our hypothesis, each nutrient had a unique interaction with each media that was dynamic with time. All of the micronutrients were in concentrations so low as to have negligible effects on electrical conductivity. However, among the macronutrients, calcium, magnesium, and nitrate were in higher concentrations in the leachate solutions than they were in the stock solution; while phosphorus and ammonium were in lower concentrations in the leachate than the stock solution. Sulfur and potassium went through the columns with minimal or no interaction.
Figure C – 3: Nutrient concentrations of a nutrient solution before and after percolating through columns of solid substrates or media. Dynamic interactions and reactions of the nutrients with the media occur over time. The cumulative effect of the varied nutrient-media interactions contributed to the inflation of media leachate electrical conductivities relative to the stock solution seen in Figure C – 2.
In order to determine whether the combined effects of all the nutrient-media interactions were, at least in part, responsible for the trends in media leachate electrical conductivity presented in Figure C – 2 and discussed above, the nutrient concentrations from Figure C – 3 were used to calculate a theoretical electrical conductivity (procedure from Standard Methods for the Examination of Water and Wastewater, pp. 2-46). This parameter was calculated in order to factor in the relative contributions of each ion to electrical conductivity, as each ion has a unique contribution. The absolute differences in the calculated electrical conductivities of the leachate and stock nutrient solutions were calculated and are presented in Figure C – 4. This figure shows that, in both ceramic and peat/vermiculite media, after a flush of readily soluble nutrients, nutrient concentrations were lower in the leachate solutions than the stock solution, and that the concentrations climbed over time relative to the stock solution. This nutrient trend mirrors the trend seen in the electrical conductivity graphs over the same timeframe, and, we conclude, is partially responsible.
<table>
<thead>
<tr>
<th>Time (d)</th>
<th>Absolute Difference (S m(^{-1}) out - S m(^{-1}) in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peat/Vermiculite</th>
<th>Absolute Difference</th>
<th>Leachate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic</td>
<td>0.00</td>
<td>Leachate</td>
</tr>
<tr>
<td>Ottawa Sand</td>
<td>-0.05</td>
<td>Leachate</td>
</tr>
</tbody>
</table>

Figure C – 4: Using the measured nutrient concentrations of the stock and leachate solutions, the electrical conductivities of the solutions were calculated. This was done to account for the varied contributions of each nutrient ion to electrical conductivity.

In addition to dynamic trends of media-nutrients interactions affecting the electrical conductivity trends observed in this study, it was hypothesized that changes in media pH may be contributing. The electrical conductivity coefficient for the hydrogen ion is high (an average of 7x higher) relative to the other ion coefficients listed in the Standard Methods for the Examination of Water and Wastewater book, meaning that acidity in solution may have a significant contribution to electrical conductivity. In addition to the direct effect of acidity on pH, acidity also makes most ions more soluble and reduces ion pairing in solution. Figure C – 5 shows the response of electrical conductivity to changing pH in the stock nutrient solution used in this study; the grid
outlines the range of pH values observed in this study and its potential effect on electrical conductivity. According to this analysis, the pH decreases observed could be accounting for as much as a 10% increase in electrical conductivity.

Figure C – 5: The effect of altering pH on the electrical conductivity of the nutrient solution described in Table B – 1. The grid shown on the graph outlines the pH range observed in the media in this study and its potential effect on the electrical conductivity (~10% increase over the entire range).

Over time the pH of the all leachate solutions and the stock nutrient solution was observed to fall (Figure C – 6). It was hypothesized that the decrease in pH was due to the reactions of nitrification. To test this hypothesis, the pH of the stock solution was manually raised to its original value and observed for future pH changes. Nitrification is inhibited at low pH values because H⁺ ions are a nitrification product; so an increase in solution pH was expected to increase the rate of nitrification, creating a rapid, subsequent
drop in pH. As can be seen in Figure C–6, the manually raised pH of the solution immediately fell back to a lower pH value, indicating nitrification. Thus, our conclusion is that decreases in leachate pH due to nitrification took part in inflating the electrical conductivity values observed in these studies (Figures C–1 and C–2).
Electrical Conductivity and pH of a Nutrient Solution, Before and After Percolating through Media

![Graph showing electrical conductivity and pH over time with media types and pH events labeled.]

Figure C – 6: The electrical conductivity and pH of stock and media leachate nutrient solutions over time. The decrease seen in pH around day 35 is evidence of nitrification. The rapid decrease in pH in the stock solution after manually raising the pH at day 55 suggests that nitrification was responsible for the observed decline in pH in all solutions. These decreases in pH were potentially responsible for the small inflations of electrical conductivities observed beginning at about day 35.