Nutrient Availability from Douglas Fir Bark in Response to Substrate pH

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Abstract. Two studies were conducted to determine the influence of substrate pH on nutrient availability in Douglas fir bark. Douglas fir bark was amended with either calcium carbonate (CaCO3) or calcium hydroxide [Ca(OH)2] at 13 rates to generate substrates with low to high pH. A nonamended control was also maintained. The substrates received no other fertilizer amendments. Substrates were filled into nursery containers (2.8 L) and maintained in a nursery setting with 1.2 cm d–1 overhead irrigation. At 1 and 6 weeks after potting, four containers of each lime treatment were harvested to determine substrate pH and availability of 13 nutrients. Substrate solutions used for analysis were obtained with the saturated media extract method. Water-extractable phosphorus and DTPA-extractable boron, iron, copper, and aluminum decreased with increasing substrate pH. Other nutrients were either nonresponsive to substrate pH or the observed response was deemed more likely caused by calcium competition on cation exchange sites.

Ornamental container crops in the Pacific Northwest are grown primarily in Douglas fir bark (DFB). Similar to pine (Pinus taeda L.) bark in the southeast United States, DFB comprises the highest portion of most nursery substrates (60% to 80% of the substrate mix, pers. obser.). Chemical and physical properties of DFB, as they pertain to use in container substrates, have recently been documented by Buamscha et al. (2007b). They reported nonamended DFB to have low pH (3.7 to 4.4); little or no available nitrogen (N); relatively high water-extractable phosphorus (P; 10 to 28 mg L–1) and potassium (K; 78 to 162 mg L–1); low levels of calcium (Ca), magnesium (Mg), and sulfur (S); and moderate levels of some micronutrients. In a separate study, Buamscha et al. (2007a) documented that DFB alone provides sufficient micronutrients for annual vinca [Catharanthus roseus (L.) G. Don ‘Peppermint Cooler’] grown at low pH (4.5 to 5.5). Macronutrient and micronutrient availability may not be sufficient to support plant growth when substrate pH is higher. Altland (2006) reported reduced growth of Japanese maple (Acer palmatum var. atropurpureum Thunb.), hydrangea [Hydrangea macrophylla Thunb. (Ex J.A. Murr.) Ser. ‘Endless Summer’], and leucothoe [Leucothoe axillaris (Lam.) D. Don] caused by a pH-induced reduction of phosphorus (P), iron (Fe), manganese (Mn), boron (B), zinc (Zn), and copper (Cu) with increasing pH. Argo (1998) reviewed the effects of pH on nutrient availability in soilless substrates citing numerous sources and generally agreed with conclusions from Peterson (1980).

In view of the widespread use of DFB in the Pacific Northwest, and the corresponding lack of information available on its chemical properties, two experiments were initiated to document the influence of pH on nutrient availability. The objectives of these experiments were to determine the influence of two lime sources on DFB pH as well as nutrient availability with respect to changes in substrate pH.

Materials and Methods

Expt. 1. On 20 June 2006, pH of 13 batches of DFB (each 0.03 m3) was adjusted using 13 rates of either calcium carbonate (CaCO3; Imperial Limestone; J.A. Jack and Sons, Seattle, WA) or hydrated lime [calcium hydroxide, Ca(OH)2; Kemilime; Ash Grove Cement Co, Portland, OR] (Table 1). A nonamended control (no lime) was also included. Rates for each lime type were selected to provide substrates with a spectrum of low to high pH and were based on previous research by the authors (unpublished data). Calcium carbonate [97% CaCO3, 2% MgCO3, 97 calcium carbonate equivalency (CCE)] was processed such that 100% and 80% passed through 40 and 100 mesh, respectively. Hydrated lime [94% Ca(OH)2, 126 CCE] was processed such that 100% and 99% passed through 40 and 100 mesh, respectively. DFB was blended with a hammer-mill, passed through a 2.2-cm screen, and aged for ≥6 months (Marr Bros. Co., Monmouth, OR). Eight No. 1 containers (2.8 L) were filled with each bark batch and maintained in a retractive roof greenhouse (Cravo Equip. Ltd., Brantford, Ontario, Canada) in Aurora, OR. Containers were overhead-irrigated with ground water at 1.2 cm d–1 (Table 2). Four containers of each treatment were randomly selected and harvested 1 and 6 weeks after potting (WAP) by placing the entire contents of the container into a plastic bag for delivery to the laboratory. Bark samples were analyzed for pH, ammonium (NH4-N), nitrate (NO3-N), P, K, Ca, Mg, and sulfate (SO42–) using the saturated media extract (SME) method with deionized water as the extractant (Gavlak et al., 2003; Warncke, 1998). Boron, Fe, Mn, Cu, Zn, and aluminum (Al) were analyzed using a SME with diethylenetriaminepentaacetic acid (DTPA) as the extractant (Warncke, 1998). Following Gavlak et al. (2003), DFB was soaked in the extractant (either water or DTPA) for 24 h. Ammonium and NO3-N in extracted solutions were colorimetrically using a Lachat Quick Chem 8000 (Lachat Instruments, Milwaukee, WI). All other elements were analyzed with inductively coupled plasma-emission spectrometry (Thermo Jarrel Ash, Offenbach, Germany).
Table 1. Water and DTPA-extractable nutrients in Douglas fir bark after incorporation of two lime types with multiple rates.4

| Harvest time (weeks) | Lime type | Rate (kg m⁻³) | Water extraction | DTPA extraction |
|----------------------|-----------|---------------|------------------|------------------|
|                      |           | pH | P | K | Ca | Mg | SO₄ | Na | B | Fe | Mn | Cu | Zn | Al |
| 0                    | CaCO₃     | 0.6 | 5.4 | 7.1 | 24.9 | 5.8 | 1.7 | 5.4 | 6.7 | 0.20 | 54.8 | 10.6 | 0.40 | 2.4 | 22.9 |
|                      | Ca(OH)₂   | 4.4 | 7.2 | 3.0 | 17.4 | 18.8 | 2.0 | 6.2 | 8.2 | 0.09 | 7.3 | 12.6 | 0.22 | 1.9 | 1.0 |
| 6                    | CaCO₃     | 0.6 | 6.2 | 2.5 | 6.1 | 1.1 | 0.5 | 7.2 | 9.7 | 0.16 | 37.7 | 14.9 | 0.32 | 2.3 | 9.5 |
|                      | Ca(OH)₂   | 4.4 | 7.7 | 4.1 | 7.8 | 9.1 | 10.2 | 10.0 | 11.2 | 0.07 | 15.9 | 14.7 | 0.22 | 2.0 | 1.7 |

4Extractions performed 1 and 6 weeks after potting (WAP). Containers subjected to typical nursery irrigation (1.2 cm d⁻¹). Water and 0.005 M DTPA (diethylenetriaminepentaacetic acid) extractions were conducted over 24 h.

Results and Discussion

Results from the two repetitions of the experiment were similar; thus, data were pooled in Table 1 and presented together in Figures 1 through 3. As a result of lime amendment, substrate pH ranged from 4.8 to 9.4 across both experiments (Figs. 2 and 3). Substrate pH increased exponentially with increasing CaCO₃ rate (Figs. 1A and 1C). Williams et al. (1988) reported that pH of sphagnum peat increases quadratically with increasing lime rates up to 7 kg m⁻³. However, use of quadratic functions implies that pH would decline with increasing lime rate at some point beyond the observed range, which is unlikely. Exponential curves [pH = c + a (1 - bᵖ)] provide a more realistic fit to the data in that pH increases rapidly but then plateaus at some maximum value. Furthermore, parameter estimates of the exponential equation provide intuitive interpretation in that the solved estimate for c is pH of the substrate with 0 kg m⁻³ (or nonamended pH), the sum of c and a is equal to the maximum pH (or the point where the curve plateaus), and b (greater than 0) is a gauge of how rapidly pH increases from its minimum to maximum (steepness of the curve). Williams et al. (1988) suggest that as exchange sites become saturated with Ca²⁺ and Mg²⁺ ions, an increasing number of these ions were needed to further dissociate H⁺ into the substrate solution. This is a logical explanation considering the exponential relationship between lime rate and substrate pH. Substrate pH also increased exponentially with increasing Ca(OH)₂ rate (Figs. 1B and 1D).

Within a lime treatment, substrate pH increased from 1 to 6 WAP (Table 1). Across both lime types and experiments, adding more than 3 to 6 kg m⁻³ lime had little or no effect on substrate pH. Williams et al. (1988) reported slightly higher dolomitic lime rates were necessary to maximize pH in peat substrates.

Macronutrients. Extractable NH₄-N and NO₃-N levels were low throughout the study regardless of lime treatment and did not respond to substrate pH (data not presented).

Douglas fir bark contains very little N.ollen (1969) documented the C:N ratio of DFB as 49:1:1 with only 0.11% total N on a dry weight basis. Others have documented the influence of substrate pH on N form (Niemiera and Wright, 1986; Ogden et al., 1987)
in well-fertilized containers. However, considering low N levels inherent in DFB, it is not surprising that N in nonfertilized DFB substrate did not respond to pH.

Water-extractable P decreased with increasing pH at all collection dates (Fig. 2A). Lucas and Davis (1961) explained that P availability in an organic soil (greater than 50% organic matter) drops when pH is below 5.5 as a result of increased availability of Fe and Al, which form precipitates with soluble P. Our data show no such decrease in availability below pH 5.5. Bunt (1988) suggests differences in P uptake by plants results from changes in the form of water-soluble P from $\text{H}_2\text{PO}_4^-$ to $\text{HPO}_4^{2-}$, the former being 10 times more available for plant uptake than the latter. Argo and Biernbaum (1996) report the equilibrium constant between these two phosphate forms is 7.2, so that when substrate pH is greater than 7.2, the less available $\text{HPO}_4^{2-}$ predominates and plant-available P is greatly reduced. Argo and Biernbaum (1996) further demonstrate that when substrate pH is less than 7.2, plant P level is relatively unaffected regardless of the measurable decrease in water-extractable P with increasing pH. Our data show that total water-extractable P decreased (without increasing) over the substrate pH range of 4.8 to 9.4, although our analytical methods do not distinguish between the two species of water-soluble P, $\text{H}_2\text{PO}_4^-$, and $\text{HPO}_4^{2-}$. Peterson (1980) showed a similar trend to ours with his analysis of the effect of substrate pH on a peat-based mix.

Buamscha et al. (2007b) reported 10 to 28 mg L$^{-1}$ P in nonamended DFB analyzed immediately after collection from bark suppliers. However, by 1 WAP, water-extractable P in this experiment rarely exceeded 10 mg L$^{-1}$. Within a given lime treatment, water-extractable P decreased from 1 to 6 WAP ($P = 0.0001$). Warncke (1998) suggests that 3 to 5 mg L$^{-1}$ is sufficient for growth of most container crops using the SME procedure. Although extractable P is initially high in DFB, it is quickly leached from the substrate. Yeager and Wright (1982) reported similarly high levels of P in pine bark, but 67% of that P was leached after one simulated irrigation event.

Secondary nutrients. Levels of water-extractable Ca were more a function of Ca solubility of the lime products than of substrate pH. Within each harvest date, water-extractable Ca increased moderately with increasing CaCO$_3$ rates but increased more rapidly with increasing Ca(OH)$_2$ rates (Table 1). Higher Ca levels would be expected from Ca(OH)$_2$ amendments than CaCO$_3$ as a result of solubility and the percent Ca content of each product. Calcium hydroxide has a
solubility product of $K_{sp} = 4.68 \times 10^{-6}$, whereas that for calcium carbonate is $K_{sp} = 8.7 \times 10^{-9}$ (Lide, 2007), indicating over a thousand-fold difference in solubility. Furthermore, CaCO$_3$ is $\approx$37% Ca, whereas Ca(OH)$_2$ is $\approx$67% Ca. Argo (1998) argued that low pH does not reduce Ca availability, but instead low pH is the result of insufficient Ca sources (lime or high-alkalinity water) applied to the substrate. Our data tend to support this notion in that Ca availability is a function of lime type and rate and not a function of pH.

Similar to Ca, water-extractable Mg increased with increasing pH but was more likely a function of increasing lime rate (Figs. 2C and 2D). Although both lime sources were Ca-based, both had low levels of Mg contamination (less than 2%). It is also possible that Ca–Mg competition for cation exchange sites caused an increase in extractable Mg at higher rates of Ca(OH)$_2$. Peterson (1980) reported that Mg increased with increasing pH, in which pH was similarly adjusted with Ca(OH)$_2$ amendment.

Sulfate levels were affected by lime type and rate (Table 1); however, the differences in water-extractable sulfate levels across lime types and rates were minor (less than 5 mg L$^{-1}$) by 6 WAP. Sulfate anions are easily leached from container substrates (Yeager and Barrett, 1985). Nonetheless, sulfate levels did not decrease between 1 and 6 WAP ($P = 0.709$), and they were similar to levels reported by Buamscha (2007b) for nonamended and nonirrigated DFB (10 to 20 mg L$^{-1}$). Browder (2004) concluded that 7 to 15 mg L$^{-1}$ sulfate (as measured in a pour-through procedure) should be present for optimum growth of pin oak (Quercus palustris Münch) and japanese maple (Acer palmatum Thunb.). Handreck (1986) states that 6 mg L$^{-1}$ sulfate from a water extraction is sufficient for any crop. By this standard, sulfate levels are low to marginally sufficient. However, this is of little consequence because sulfate is provided in many fertilizer types such as ammonium sulfate [(NH$_4$)$_2$SO$_4$] used in controlled-release fertilizers, gypsum (CaSO$_4$), and sulfated micronutrients.

**Micronutrients.** Several studies have documented the micronutrient capacity of soilless substrates, each suggesting that the substrate alone may be a sufficient source of micronutrients to meet plant need without addition of supplemental micronutrient fertilizers (Buamscha et al., 2007a; Niemiera, 1992; Rose and Wang, 1999). Availability of micronutrients has been documented as pH-sensitive in organic soils and substrates (Lucas and Davis, 1961; Peterson, 1980); thus, the degree to which a substrate can provide sufficient micronutrients to support crop growth should always be qualified with a target pH range.

DTPA-extractable B decreased exponentially with increasing substrate pH (Fig. 3A). Extractable B decreased slightly from 1 to 6 WAP; however, the relationship between substrate pH and extractable B remained consistent across experiments and harvest dates. Lucas and Davis (1961) warn that there is a strong Ca–B relationship in organic soils, and some peat soils high in Ca are more prone to B deficiency as a result of elevated Ca. In DFB, the relationship between DTPA-extractable B and pH is more consistent and predictable than the relationship between DTPA-extractable B and water-extractable Ca (data not shown). Warncke (1998) suggests DTPA-extractable B should range from 0.7 to 2.5 mg L$^{-1}$; thus, extractable B would be considered low in nonamended DFB. Buamscha et al. (2007a) demonstrated that DFB, even amended with a micronutrient fertilizer package (Micromax; The Scotts Co., Marysville, OH), had lower than recommended extractable B levels 5 and 8 WAP, but higher than recommended foliar B in annual vinca (Catharanthus roseus (L.) G.
The relationship between B requirements in plant foliage and substrate-extractable B requires further study to improve recommended sufficiency ranges. DTPA-extractable Fe decreased exponentially with increasing substrate pH with Fe dropping below recommended levels at pH \( \approx 7 \) (Fig. 3B). Berghage et al. (1987) reported DTPA-extractable Fe decreased quadratically over the pH range of 3.5 to 7.5. Despite different mathematical models used to describe our data and that of Berghage et al. (1987), Fe response to pH in the two studies appears to be similar. Substrate Fe levels should range from 15 to 40 mg L\(^{-1}\) (Warncke, 1998). Douglas fir bark has sufficient extractable Fe so long as pH is below 7. Lucas and Davis (1961) commented that Fe deficiency is rarely a problem in organic soils as a result of an abundance of humic acids maintaining Fe levels.

Neither Mn nor Zn responded to substrate pH (data not shown). Warncke (1998) recommends extractable Mn levels in container substrates be from 15 to 40 mg L\(^{-1}\). Buamscha et al. (2007a) demonstrated that fresh and aged DFB amended only with nitrogen-phosphorus-potassium fertilizers provided sufficient Zn for annual vinca through 8 weeks of production despite low levels of DTPA-extractable Zn in the substrate. Substrate Fe levels should range from 15 to 40 mg L\(^{-1}\) (Warncke, 1998). After 6 weeks of irrigation, water-extractable Na ranged from 3 to 15 mg L\(^{-1}\). Increased Na levels over time were likely the result of accumulation from low levels of Na in irrigation water (Table 2). Increased Na levels over time were likely the result of accumulation from low levels of Na in irrigation water (Table 2).

Extractable Al in substrates is rarely considered. This is possibly the result of the general agreement that organic soils and soilless media contain low amounts of Al (Lucas and Davis, 1961; Yeager and Barrett, 1985). Significant amounts of Al (7.8 to 51.5 mg L\(^{-1}\)) were extracted from DFB in samples collected from bark suppliers (before amendment or irrigation in a nursery) (Buamscha et al., 2007b). DTPA-extractable Al decreased exponentially with increasing pH (Fig. 3D). Aluminum levels averaged 23.9 mg L\(^{-1}\) in nonamended bark 1 WAP (Table 1), although levels decreased over time. Wright (1989) reviewed Al interactions with soils and crops, and described Al speciation as complex, dependent on soil pH and other mineralogical factors and difficult to predict. Wright (1989) also explains that Al forms complex ligands with sulfate and soluble organic compounds, which alleviate Al toxicity. In contrast to the notion that Al is lacking or only present in low concentration in bark substrates, it is likely that it is present in relatively high levels (pH-dependent) but in nontoxic forms as a result of a consistent
supply of sulfate from bark (Table 1) and fertilizer amendments as well as the presence of soluble organic compounds in DFB. It is unclear what levels of DTPA-extractable Al should be considered toxic in nursery substrates.

Water-extractable P and DTPA-extractable B, Fe, Cu, and Al are responsive to pH in nonamended DFB. Other nutrients were either nonresponsive to substrate pH or the observed response was deemed more likely caused by Ca competition on cation exchange sites. Although Ca and its competitive effects on cation exchange sites may be an undesirable artifact in a study such as this, applications of lime (and thus Ca) is the primary mechanism by which nursery growers adjust substrate pH. Irrigation water alkalinity (dissolved CO$_3^{2-}$ and HCO$_3^-$) is another major factor affecting substrate pH, but across three sampling dates, Ca and alkalinity levels in Oregon nursery irrigation sources were highly correlated ($r = 0.80$, $n = 61$, unpublished data).

These results have several practical implications. Phosphorus levels across all lime treatments declined from 1 to 6 WAP, suggesting that DFB alone is not a sufficient source of P to sustain plant growth throughout a growing season. However, the common industry practice of incorporating a water-soluble source of P into the substrate as a starter fertilizer should be questioned. There is sufficient water-extractable P in the first few weeks of production contingent that substrate pH is low (less than 6). Water-extractable K declined steadily over time regardless of pH and thus should be supplemented in some sort of continuous manner throughout the production cycle of the crop. Like P, K is readily available from DFB soon after potting and thus its application in starter fertilizer packages is questionable. Calcium and Mg levels were dependent on lime rate. In typical nursery conditions, it would be difficult to appreciably raise substrate pH even low lime rates have a profound effect on nutrient availability in DFB and that lime should be used in moderation. However, it is uncertain if substrate pH would similarly affect nutrient availability in substrates receiving supplemental fertilizers typical of nursery production. Future research will address the impact of lime additions and substrate pH on nutrient availability in well-fertilized DFB substrates.

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