Pesticide Sorption to Soilless Media Components Used for Ornamental Plant Production and Aluminum Water Treatment Residuals

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ABSTRACT: Commercial producers of containerized ornamental plants almost exclusively use soilless media as the substrate for growing the plants. Soilless media are composed primarily of organic materials as opposed to mineral soils. Significant amounts of pesticides can leach from pots containing soilless media to which pesticides have been added as drenches or top-dressings. One of the goals of this project was to identify whether individual components comprising soilless media have differing affinities for the pesticides acephate, imidacloprid, metalaxyl, and plant growth regulator paclobutrazol. One-point 24 h equilibrium sorption assays were conducted to characterize sorption of the pesticides to sand, perlite, vermiculite, coir, peat, pine bark, and aluminum-water treatment residuals (Al-WTRs). Five-point isotherms were then constructed for the more sorptive peat and pine bark substrate components, and for the Al-WTRs. Results indicated significant differences in pesticide behavior with each substrate. Sorption of acephate to most of the substrate components was relatively low, comprising 21−31% of the initial amounts for soilless media components and 63% in Al-WTRs. Al-WTRs were highly sorptive for imidacloprid as evidenced by a partition coefficient of \( K_F = 3275.4 \) L kg\(^{-1}\). Pine bark was the most sorptive for metalaxyl-M with a measured \( K_F = 195.0 \) L kg\(^{-1}\). Peat had the highest affinity for paclobutrazol (\( K_F = 398.4 \) L kg\(^{-1}\)). These results indicate that none of component of soilless media has a universally high attraction for all of the pesticides studied.

INTRODUCTION

Soilless media are used throughout the ornamental plant production industry for growing containerized ornamental plants. Soilless media composition differs widely between growers and sources. This is partly due to the needs of specific ornamental crop species such as providing a good balance of root aeration and water retention, wettabiltiy, and low transport costs. Typical components of soilless media include a variety of organic materials, as well as inorganic and synthetic substrates. Common inorganic components include sand and processed materials such as perlite and vermiculite. Inorganic materials typically make up a small percentage of the overall volume of media used in the industry. The organic components, which make up the majority of the media, include peat, coir, pine bark, rice hulls, and many other plant-based materials depending on the region or climate. While field production of containerized ornamental plants relies almost entirely on soilless media, it should also be noted that the greenhouse production of vegetables, fruit, and ornamentals, as well as urban horticulture systems, also rely on soilless media because of its advantages of avoiding soil-borne pathogens, allowing production in areas where native soils are not suitable, and allowing better control of chemical, physical, and hydraulic characteristics relative to soil-based systems. Demand for high-quality food crops, cut flowers, potted plants, and bedding plants grown using soilless media will continue to increase as the global standard-of-living increases.

Plant production practices can contribute to the contamination of surface water with pesticides, but few studies have investigated factors contributing to losses of pesticides from ornamental plant production areas. Hinz and colleagues (2019) recently reported that significant losses of pesticides may occur from ornamental plants to which the pesticides were applied to the soilless media as liquid formulation drenches or as surface-applied granular formulations. Pesticide leaching from containerized plants is analogous to contaminant transport in the vadose zone, with the soilless media mimicking the porous system of soils.
of these materials. de Wilde and colleagues\textsuperscript{19,20} proposed using sorption of a limited number of pesticides to some of surface and ground water. However, only a few studies have investigated sorption of some components of soilless media in on-farm biopurification systems to remove pesticides from contaminated water. They evaluated sorption of lenacil, isoproturon, metalaxyl, isoxaben, and linuron on different components, and found that pea, coconut chips, and straw had higher sorption coefficients for the pesticides relative to sand, chopped willow, and dried cow manure. Other studies found that amending calcisols and regosols with composted pine bark, coir, and coffee grounds reduced the leaching potential of phenylurea herbicides.\textsuperscript{21} Pine bark and coir have also been reported to sorb-persistent organics such as organochlorine insecticides and triazine herbicides.\textsuperscript{24}

Table 1. Aqueous Extract pH and EC Characterization (Averages ± One Standard Deviation, \(n = 3\)) for Growing Media Samples and Aluminum Water Treatment Residuals (Al-WTRs)\textsuperscript{a}

| background   | sand       | perlite    | vermiculite | coir\textsuperscript{b} | peat\textsuperscript{b} | pine bark\textsuperscript{b} | Al-WTRs |
|-------------|------------|------------|-------------|--------------------------|--------------------------|-----------------------------|---------|
| pH          | 5.65 ± 0.12 | 7.50 ± 0.18 | 5.38 ± 0.23 | 5.85 ± 0.18               | 4.07 ± 0.16               | 4.61 ± 0.53                 | 5.20 ± 0.02 |
| 10 mM CaCl\(_2\) | 4.82 ± 0.03 | 6.42 ± 0.05 | 4.27 ± 0.11 | 4.25 ± 0.04               | 2.89 ± 0.04               | 3.48 ± 0.14                 | 5.01 ± 0.01 |
| 10 mM buffer | 6.31 ± 0.05 | 6.32 ± 0.08 | 6.11 ± 0.13 | 6.05 ± 0.07               | 4.77 ± 0.07               | 5.42 ± 0.15                 | 5.86 ± 0.01 |
| EC (dS m\(^{-1}\)) | 0.28 ± 0.05 | 0.24 ± 0.01 | 0.27 ± 0.04 | 0.24 ± 0.01               | 0.01 ± 0.00               | 0.18 ± 0.04                 | 0.10 ± 0.00 |

\(\textsuperscript{a}\)Measurements conducted at 22–23 °C. \(\textsuperscript{b}\)Organic GM matrices extracted with 10 mM potassium phosphate buffer (pH 6.5) and additionally limed with 2 mM Ca(OH)\(_2\).

Figure 1. Mean sorption ± one standard deviation (\(n = 3\)) of the initial spiked mass for acephate, imidacloprid, paclobutrazol, and metalaxyl-M in all matrices (background of 10 mM potassium phosphate buffer, pH 6.5). The GM and Al-WTRs matrices were spiked with initial concentrations from 4.8 to 5.3 mg L\(^{-1}\) (Table 2). Different letters indicate statistically significant differences between mean-pairs or materials (Holm–Sidak test).

Sorption or retention of pesticides to media components depends on both pesticide and material properties such as, chemical structure, organic carbon content, pH, electrical conductivity (EC), and ion-exchange capacity.\textsuperscript{17,18} Information on possible sorptive interactions between pesticides and individual components of the soilless media could lead to the development of formulations with greater potential for holding the pesticides in the pot and preventing contamination of surface and ground water. However, only a few studies have investigated sorption of a limited number of pesticides to some of these materials. de Wilde and colleagues\textsuperscript{19,20} proposed using some components of soilless media in on-farm biopurification systems to remove pesticides from contaminated water. They evaluated sorption of lenacil, isoproturon, metalaxyl, isoxaben, and linuron on different components, and found that pea, coconut chips, and straw had higher sorption coefficients for the pesticides relative to sand, chopped willow, and dried cow manure. Other studies found that amending calcisols and regosols with composted pine bark, coir, and coffee grounds reduced the leaching potential of phenylurea herbicides.\textsuperscript{21} Pine bark and coir have also been reported to sorb-persistent organics such as organochlorine insecticides and triazine herbicides.\textsuperscript{24}

Another potentially useful material for reducing leaching of pesticides from ornamental plant containers is water treatment residuals (WTRs). WTRs are byproducts of drinking water treatment plants.\textsuperscript{25,26} Efforts have focused on finding uses for these materials, which are otherwise disposed of in landfills or by other means. WTRs are mostly composed of fine soil particles, organic materials, and Fe and Al hydroxides depending on the salt used as the coagulant during the water purification process.\textsuperscript{27} These materials develop surface charges as a result of uncoordinated hydroxyl groups, which lead to surface reactivity.\textsuperscript{28} Al-WTRs have been proposed as sorbents for some inorganic constituents such as soluble forms of arsenic in soils\textsuperscript{29} and for field-reactive barriers for soluble phosphorous removal.\textsuperscript{30,31} Al-WTRs have also shown potential for immobilizing some emerging contaminants such as veterinary antibiotics (tetracyclines) in manure-amended soils.\textsuperscript{32} The sorption potential of Al-WTRs for pesticides and other organic contaminants has otherwise received little attention.

This study characterized the sorption/retention of a suite of selected pesticides on mineral (sand, perlite, vermiculite) and organic (coir, peat, and pine bark) components of typical soilless media formulations used by the containerized plant...
production industry. The potential for use of Al-WTRs as an amendment to sorb the pesticides was also evaluated. Study hypotheses were that organic soilless media components and Al-WTRs have a higher sorption capacity for the pesticides used in this study relative to the inorganic/mineral components.

## RESULTS AND DISCUSSION

### Solvent Selection.
A summary of the pH and EC values for each extractant–media–component combination (including Al-WTRs) is shown in Table 1. Relative to ornamental plant production guidelines, the 10 mM CaCl2 extractant did not produce a realistic matrix in terms of the proper conditions for ornamental plant root zone development because of the low pH (except perlite pH = 6.42 ± 0.05) and very high salinity values (EC ranging from 3.05 to 4.28 dS m⁻¹). Conversely, the potassium-phosphate buffer (pH 6.5) was an acceptable extractant for most components in terms of providing salinities within recommended values for ornamental plant production. In addition, the matrix produced by this buffered extractant also showed nearly enough capacity (without liming) to buffer against acidity associated with the peat, pine bark, and Al-WTRs relative to CaCl2 and water. The acidity of these materials is related to the buffering capacity (ionization of functional groups) in organic materials and the presence of uncoordinated hydroxy groups in Al-WTRs, which also have a large buffering capacity.

### One-Point Sorption Equilibria.
One-point sorption isotherm studies were conducted to provide an initial approximation of the interaction between all compounds of interest and each substrate component or the Al-WTRs. The data are summarized as means ± one standard deviation in

![Figure 1. Sorption of the pesticides was variable (Figure 1), but all exhibited some sorption that was greater than what would be expected by chance (ANOVA P values < 0.001). The largest amount of acephate (63.3%) sorbed to the Al-WTRs, while sorption to sand was the least (6.5%) (Figure 1). Sorption to perlite, vermiculite, coir, peat, and pine bark was intermediate, ranging from 21.0 to 31.0%. In comparison, sand and perlite had little affinity for imidacloprid, sorbing only 9.3 and 10.2%, respectively, while 43.0% of the initial amount adsorbed to the inorganic component vermiculite (Figure 1). Coir, peat, pine bark, and Al-WTRs had the highest affinities for imidacloprid, accounting for the sorption of 76.2, 91.2, 87.1, and 82.6% of the initial mass added to the solution, respectively. More than 35% of the initial mass of metalaxyl-M sorbed to all the materials evaluated (Figure 1). In this case, 60.3% of the initial mass sorbed to sand, which was the highest amount of sorption of any of the compounds to sand. The least amounts of metalaxyl-M sorbed to the perlite (35.0%) and Al-WTRs (41.0%), while sorption to pine bark was the greatest (79.2%). Sorption to vermiculite, coir, and peat ranged from 58.8 to 69.8%. No paclobutrazol sorption occurred on the sand or perlite (Figure 1). One-point isotherm spike, mg L⁻¹:

| Pesticide Type | Chemical Class | Molecular Weight (g mol⁻¹) | Water Solubility, mg L⁻¹ | Stability to Hydrolysis | Vapor Pressure, mm Hg | Half-life in Soil (and Water), Days |
|----------------|----------------|---------------------------|--------------------------|------------------------|-----------------------|-----------------------------------|
| acephate       | insecticide    | 183.2                     | 818,000                  | pH 5 & pH 7            | 1.7 × 10⁻⁷            | <3 (18, pH 9)                     |
| imidacloprid   | insecticide    | 255.6                     | 610                      | acidic & neutral pH    | 3 × 10⁻¹²             | 800 (164)                         |
| paclobutrazol  | plant growth regulator | 293.79                    | 26                       | pH 4, pH 7 & pH 9      | 1.28 × 10⁻⁹           | 700 (nd)                          |
| metalaxyl-M    | fungicide      | 631.3                     | 8400                     | stable                | 5.62 × 10⁻⁴           | 40 (16, pH 10)                    |

Table 2. Pesticide Active Ingredient Properties, Recommended Application Rates, and Spiking Levels for the Isotherm Experiments

| ActiveIngredient | Chemical Class | RecommendedApplication Rates | Spike Levels |
|------------------|----------------|-----------------------------|--------------|
| acephate         | organophosphate | 0.85 mg L⁻¹                  | 0.08 mg L⁻¹  |
| imidacloprid     | neonicotinoid     | 1.28 mg L⁻¹                  | 0.12 mg L⁻¹  |
| paclobutrazol    | triazole          | 3.20 mg L⁻¹                  | 0.32 mg L⁻¹  |
| metalaxyl-M      | pheny lamide      | 1.65 mg L⁻¹                  | 0.17 mg L⁻¹  |

Label Recommended Rates for Ornamentals

Spray-Mix Concentration, mg L⁻¹:

| Pesticide Type | Recommended Rate, mg L⁻¹ |
|----------------|--------------------------|
| acephate       | 875                      |
| imidacloprid   | 32                       |
| paclobutrazol  | 1093                     |
| metalaxyl-M    | 4.7                      |

Drench-Mix Concentration, mg L⁻¹:

| Pesticide Type | Recommended Rate, mg L⁻¹ |
|----------------|--------------------------|
| acephate       | 32                       |
| imidacloprid   | 15                       |
| paclobutrazol  | NA                       |
| metalaxyl-M    | NA                       |

Commercial Product:

| Pesticide Type | EPA Registration | Manufacturer | Sorption Isotherm Spike Levels |
|----------------|------------------|--------------|-------------------------------|
| acephate imidacloprid | 70506-8         | United Phosphorus, Pennsylvania | 4.75 mg L⁻¹                  |
| paclobutrazol      | 53883-232-73220  | Farmsaver.com, North Carolina   | 4.81 mg L⁻¹                  |
| metalaxyl-M        | 10938-8          | Syngenta, North Carolina        | 5.28 mg L⁻¹                  |

Label Recommended Rates for Ornamentals

Spray-Mix Concentration, mg L⁻¹:

| Pesticide Type | Recommended Rate, mg L⁻¹ |
|----------------|--------------------------|
| acephate imidacloprid | 875 mg L⁻¹              |
| paclobutrazol      | 32 mg L⁻¹                |
| metalaxyl-M        | 1093 mg L⁻¹              |

Drench-Mix Concentration, mg L⁻¹:

| Pesticide Type | Recommended Rate, mg L⁻¹ |
|----------------|--------------------------|
| acephate imidacloprid | 32 mg L⁻¹               |
| paclobutrazol      | 15 mg L⁻¹                |
| metalaxyl-M        | NA                       |

Commercial Product:

| Pesticide Type | EPA Registration | Manufacturer | Sorption Isotherm Spike Levels |
|----------------|------------------|--------------|-------------------------------|
| acephate imidacloprid | 70506-8         | United Phosphorus, Pennsylvania | 4.75 mg L⁻¹                  |
| paclobutrazol      | 53883-232-73220  | Farmsaver.com, North Carolina   | 4.81 mg L⁻¹                  |
| metalaxyl-M        | 10938-8          | Syngenta, North Carolina        | 5.28 mg L⁻¹                  |

One-point isotherm spike, mg L⁻¹:

| Pesticide Type | Recommended Rate, mg L⁻¹ |
|----------------|--------------------------|
| acephate       | 1.7, 22.8, 60.3, 160.0, 327.2 |
| imidacloprid   | 1.1, 8.5, 24.2, 29.5, 43.7  |
| paclobutrazol  | 1.2, 5.0, 10.9, 15.9, 21.8  |
| metalaxyl-M    | 0.8, 6.3, 14.5, 22.2, 41.5  |

Figure 1.

| Pesticide Type | Chemical Properties |
|----------------|---------------------|
| acephate       | insecticide, organophosphate |
| imidacloprid   | insecticide, neonicotinoid |
| paclobutrazol  | plant growth regulator, triazole |
| metalaxyl-M    | fungicide, phsy lamide |

Table 3.

**Source:** Toxicology Data Network, U.S. National Library of Medicine, Bethesda, MD (www.nlm.nih.gov/toxnet).

NA, not applicable.

Spike level(s) used for Al-WTRs, peat, and pine bark. nd, no data.
model parameters is shown in Table 3. The appropriateness of
the regression was assessed based upon the model
$R^2$. In general, better linear regressions and model goodness-of-fit are
related to higher $R^2$ values. Most sorption isotherms were
"L-type"37 and followed the Freundlich model which suggests
progressive saturation of the sorbate surfaces with subsequent
decreases in sorption as the concentration in solution
increases. However, there were several exceptions to this
general trend, including sorption of acephate to Al-WTRs,
imidacloprid to pine bark, and Al-WTRs, and paclobutrazol to
peat.

Sorption of acephate to Al-WTRs was best described by a
Langmuir isotherm indicating that the reactive surfaces of the
material would have a finite sorption maxima ($S_{\text{max}}$) of 1004.2
mg kg$^{-1}$ and an apparent sorption coefficient of 14.6 L kg$^{-1}$
(Figure 2). Pine bark had the highest affinity (i.e., largest
sorption coefficient) for acephate ($K_F = 89.0$ L kg$^{-1}$, $N = 0.83$),
followed by Al-WTRs ($K_F = 14.6$ L kg$^{-1}$), and peat ($K_F = 3.73$
kg$^{-1}$, $N = 1.31$).

While sorption of imidacloprid to peat was best described by
the Freundlich model, sorption to the pine bark and Al-WTRs

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Matrices} & \textbf{Acephate} & \textbf{Imidacloprid} & \textbf{Metalaxyl-M} & \textbf{Paclobutrazol} \\
\hline
\textbf{Acephate} & \textbf{K}_F (L kg$^{-1}$) & 3.73 [1.99] & 89.0 [27.8] & \\
& \textbf{N} & 1.31 [0.11] & 0.83 [0.08] & \\
& \textbf{$R^2$} & 0.98 & 0.96 & 0.91 & \\
\hline
\textbf{Imidacloprid} & \textbf{K}_F (L kg$^{-1}$) & 290.4 [18.3] & 157.4 [3.2] & 3275.4 [213.0] \\
& \textbf{N} & 0.77 [0.05] & 1$^d$ & 1$^d$ & \\
& \textbf{$R^2$} & 0.98 & 0.99 & 0.83 & \\
\hline
\textbf{Metalaxyl-M} & \textbf{K}_F (L kg$^{-1}$) & 54.9 [9.4] & 195.0 [14.3] & 3.36 [1.95] \\
& \textbf{N} & 1.20 [0.09] & 1.44 [0.1] & 2.08 [0.26] & \\
& \textbf{$R^2$} & 0.97 & 0.97 & 0.93 & \\
\hline
\textbf{Paclobutrazol} & \textbf{K}_F (L kg$^{-1}$) & 398.4 [13.8] & 88.4 [3.8] & 88.0 [3.8] \\
& \textbf{N} & 1$^d$ & 0.89 [0.05] & 0.78 [0.07] & \\
& \textbf{$R^2$} & 0.96 & 0.99 & 0.97 & \\
\hline
\end{tabular}
\caption{Sorption Isotherm Model Parameters (± One Standard Error) for Acephate, Imidacloprid, Metalaxyl-M, and Paclobutrazol in Peat, Pine Bark, and Al-WTRs Matrices$^{a, b}$}
\end{table}

The solutions were equilibrated in a background of 10 mM
potassium phosphate buffer (pH 6.5). $^d$ Freundlich model
nonlinear partition coefficient ($Se = K_F \times C_e^N$) where $Se$
is the sorbed concentration (mg kg$^{-1}$) and $Ce$ is the solution
concentration (mg L$^{-1}$). $N$ is the model exponent. $^c$The best fit
model was a Langmuir isotherm, where $Se = (S_{\text{max}} \times C_e)/(K_L + C_e)$.
$K_L$ is the affinity coefficient that corresponds with the apparent sorption
coefficient in the lower concentrations (14.6 ± 3.7 L kg$^{-1}$), and $S_{\text{max}}$
is the Al-WTRs maximum sorption capacity, in this case 1004.2 ± 88.0
mg kg$^{-1}$. $^d$The isotherm was linear (i.e., the exponent $N = 1$).
was best described by linear partitioning models, indicating no saturation of active sorption sites throughout the concentration ranges evaluated (Figure 3). Imidacloprid sorption coefficients for the Al-WTRs were an order of magnitude higher ($K_F = 3275.4 \text{ L kg}^{-1}, N = 1$) than for peat ($K_F = 290.4 \text{ L kg}^{-1}, N = 0.77$) and pine bark ($K_F = 157.4 \text{ L kg}^{-1}, N = 1$). In this case, over 99% of the applied mass sorbed to the Al-WTRs regardless of the initial concentration.

Sorption of metalaxyl-M to all three substrates was best described using Freundlich models (Figure 4). Metalaxyl-M had the highest affinity for pine bark ($K_F = 195.0 \text{ L kg}^{-1}, N = 1.44$), followed by peat ($54.9 \text{ L kg}^{-1}, N = 1.20$), and Al-WTRs ($3.4 \text{ L kg}^{-1}, N = 2.1$).

Sorption of paclobutrazol to pine bark and Al-WTRs was best described with Freundlich models, having sorption coefficients of $88.4 \text{ L kg}^{-1} (N = 0.89)$ and $88.0 \text{ L kg}^{-1} (N = 0.78)$, respectively (Figure 5). Sorption of paclobutrazol to peat was greater in this media and was described with a linear model, which produced a sorption coefficient of $398.4 \text{ L kg}^{-1} (N = 1)$.

Sorption of pesticides to soils, sediments, and other solid surfaces such as soilless media components is a complex, nonlinear phenomenon that depends on many factors related to the specific pesticide and reactive surfaces on/in sorbent. These properties include the solid-solution ratio, pH, EC, redox potential, presence of and types of functional groups, pH, EC, redox potential, presence of and types of functional groups, and organic matter content and composition. While determination of specific mechanisms for sorption was beyond the scope of this study, some speculation can be made which could direct future mechanist studies. Of all the chemical—sorbent combinations, the sorption coefficient of imidacloprid to Al-WTRs ($3275.4 \text{ L kg}^{-1}$) was $1–3$ orders of magnitude greater than any of the others. This high degree of sorption may be through interaction of the nitro-aromatic group with positively charged moieties within the Al-WTRs because nitro groups carry a net positive charge. The Al-WTRs should have regions with net positive charges at the pH values used to conduct these studies. Sorption was best described using a linear model. Because saturation did not occur within the range of concentrations evaluated, this linear model may fit within a Langmuir (assumes a 1:1 interaction between surface active moieties and sorbates) or Freundlich model (exponent $N = 1$; assumes more interactions than Langmuir). Experiments using higher concentrations of the pesticide are needed to determine which of these two models best describes sorptive interactions. The lower affinity of the other chemicals for WTRs was likely due to the lack of these strongly negatively charged functional groups. Sorption of acephate to WTRs was best described by a Langmuir model and displayed saturation kinetics (Figure 2) illustrating a finite number of sorptive sites. We speculate that sorption occurred between the positively charged sorbent active sites on the Al-WTRs and the polar carbonyl and phosphoryl functional groups. Sorption of metalaxyl-m and paclobutrazol to Al-WTRs was best described using Freundlich models, which allow for interactions between sorbent and solute through multiple mechanisms. Sorption in this case may have been due to a combination of hydrophobic nonpolar interactions as well as polar interactions with the −Cl and hydroxyl group in paclobutrazol and the carbonyl groups in metalaxyl-M. Both of these chemicals are more hydrophobic than acephate and imidacloprid (Table 2). Paclobutrazol sorption to Al-WTRs was the second greatest having a $K_F$ of $88.0 \text{ L kg}^{-1}$ as compared to $K_F$ values of 14.6 and 3.36 for acephate and metalaxyl, respectively. In this case, paclobutrazol’s $K_F$ is 6–26 times higher than the others.

The organic materials peat and pine bark are both derived from plant sources but differ in the degree of weathering with peat forming over thousands of years versus pine bark sources that are weathered for a few months to a few years. The specific chemical and physical properties of the pine bark substrates depend on the tree species, harvesting methods and season, and how and when the materials are processed. Pine bark is derived from phloem, which consists of lignin, cellulose, polysaccharides, and a variety of other components. Lignin is a biopolymer of oxidatively coupled alcohols including: hydroxycinnamyl alcohol, coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol. Likewise, cellulose is a complex biopolymer composed of β-1,4-glucopyranose units linked together through glycosidic bonds. Both of these complex molecules have abundant hydroxyl and methoxy functional groups that can participate in sorptive processes. Imidacloprid was the only chemical for which sorption to pine bark was best characterized using a linear model (Figure 3). As discussed earlier, this linear model may describe Freundlich or Langmuir sorptive interactions at higher concentrations than tested. As with the Al-WTRs, imidacloprid sorption to pine bark likely occurred through specific interactions; in this case, interactions between the polar hydroxyl and methoxy functional groups in the cellulose/lignins and the polar nitro group on imidacloprid. Interestingly, saturation of the active sites was not observed indicating an abundance of sorptive sites. Sorption of acephate, metalaxyl-m, and paclobutrazol was characterized by Freundlich models. Sorption of these compounds also did not reach saturation and was likely due to a combination of polar and hydrophobic interactions between the materials. As mentioned earlier, peat is derived from highly weathered plant materials, including lignin and cellulose. Important functional groups associated with weathered soil organic matter include carboxyl, phenolic-OH, carbonyl, sulfonic, sulhydryl, amine, imide, and nitrogen heterocycles. Peat is one of the most widely used soilless media substrate components in the ornamental plant production industry. Peat has been proposed as a sorbent for organic contaminants with potential use for biopurification systems. Paclobutrazol and imidacloprid had the highest affinities ($K_F$ values of 398 and 290 L kg$^{-1}$, respectively) for peat relative to acephate and metalaxyl ($K_F$ values of 3.7 and 54.9 L kg$^{-1}$, respectively). In this study, acephate, imidacloprid, and metalaxyl-m sorption was best characterized with Freundlich models, indicating nonspecific sorption processes. As with pine bark, sorption of these compounds was likely due to a variety of processes including polar interactions and hydrophobic interactions. Imidacloprid sorption may be facilitated through polar interactions of the chlorine as well as the nitro groups with sulhydryl, amine, imide, and heterocyclic N functional groups in the organic material. Sorption of metalaxyl-M to peat ($K_F = 54.9 \pm 9.4 \text{ L kg}^{-1}$) observed in this study is similar to that reported by de Wilde and collaborators ($K_F = 58.8 \text{ L kg}^{-1}$). In contrast, paclobutrazol sorption was best described using a linear model. In this case, saturation of sorption sites was not observed at the concentrations tested. As discussed earlier, this may be representative of the linear portion of Langmuir or Freundlich isotherms. Of the three materials, paclobutrazol sorption to peat was the greatest (Figure 5).
increased sorption relative to pine bark likely reflects the increased diversity and abundance of functional groups because of greater weathering. Paclobutrazol has an active hydroxyl group and an electron-withdrawing chlorine that may facilitate interactions of the molecule with polar or charged functional groups.

Interestingly, retention of the two most sorbed chemicals to peat (paclobutrazol and imidacloprid) was much less in pine bark, indicating significant differences in the physical and chemical properties of the materials. The physical and chemical properties of pine bark media components are known to change with aging, though they have not been thoroughly characterized. One important feature to consider is the particle size of the material. Pine bark used in these studies was homogenized with an average particle size of 9.5 mm (3/8 in.). Coarser pine bark particles such as found in actual production area.

One of the original motivations for this project was to identify whether soilless media recipes could be developed to optimize retention of pesticides in the container and minimize leaching. As seen in this study, sorption to soilless media components can be highly variable depending on the chemical and substrate component. As a result, at present, a targeted chemical-specific approach would be required to minimize leaching of pesticides from ornamental plant production containers. Further research is needed to determine whether other chemicals behave similarly, as well as testing the adequacy of Al-WTRs and other materials (e.g., different biochars) as amendments for soilless growing media formulations.

**MATERIALS AND METHODS**

**Chemicals and Reagents.** Four active ingredients were selected for the study, including the insecticides acephate and imidacloprid, the fungicide metalaxyl-M, and the plant growth regulator paclobutrazol. These pesticides were chosen based on their use in ornamental plant production and their contrasting chemical—physical properties. A summary of the chemical and physical characteristics of these pesticides is shown in Table 2. Analytical standards were obtained from Sigma-Aldrich PESTANAL (St. Louis, Missouri, USA) with >98.5% purity. Aqueous solutions of pesticides were prepared in reagent-grade water produced by a Nanopure Infinity UV System (Barnstead-Thermolyne; Dubuque, Iowa USA). Optima grade methanol, water, and formic acid for liquid chromatography—mass spectrometry analysis were purchased from Fisher Chemical (New Hampshire, USA). Ammonium formate (NH₄HCO₃), calcium chloride (CaCl₂), calcium hydroxide (Ca(OH)₂), potassium dihydrogen phosphate (KH₂PO₄), potassium hydrogen phosphate (K₂HPO₄), and KCl were obtained from Fisher Chemical (>95% purity for all). Sodium azide (NaN₃, 98% purity) was purchased from Sigma-Aldrich and used as a microbial biocide in aqueous solutions used for the sorption experiments.

**Media and Al-WTRs.** Samples of the most commonly used components of soilless media were donated by SUNGRO (Orlando, Florida, USA). Mineral media components included sand, perlite, and vermiculite; while organic components included peat, coir, and pine bark. All media components were thoroughly mixed before taking subsamples for characterization and cold storage. Al-WTRs were provided by a water treatment plant in Florida. Al-WTRs were stored in polyethylene containers at 4 °C until needed.

**Solvent Selection.** Containerized plant production methods use target pH and EC values in leachates as guidance for managing nutrients within the pots. Because these same properties can affect sorption of pesticides, evaluation of pesticide sorption must be conducted under similar conditions to maintain relevance. EC and pH were measured in extracts of individual media components using three common background extractants: ultrapure water, 10 mM CaCl₂, and 10 mM potassium phosphate buffer (8.34 mM KH₂PO₄ + 1.66 mM K₂HPO₄, pH 6.5). These three extractants were evaluated to determine their abilities to produce extracts with pH and EC values within the ranges suitable for ornamental plant production. The recommended pH and EC values for industrial production of potted ornamental plants are 5.5–6.5 (pH) and 0.8–1.6 dS m⁻¹ (EC). The media-to-solution ratio used to characterize pH and EC was 1:5 (v/v) based on recommended methods for analysis of loose growing media. Sodium azide (100 mg L⁻¹) was included in the phosphate buffer to minimize pesticide degradation due to microbial activity. Acidity was further neutralized in the buffered solutions with the organic components (coir, pine bark, and peat) by addition of calcium hydroxide (2 mM Ca(OH)₂). Individual media components and extract solutions (1:5 v/v) were added into 500 mL plastic bottles, which were then shaken for 1 h on an Eberbach horizontal shaker. After shaking, the bottles were placed on a lab bench for 15 min to allow settling of the larger particles. The clear supernatant solutions were filtered through Whatman #1 filter paper and immediately stored in amber glass bottles. The pH and EC measurements were made in 250 mL beakers at 22 °C. Extract pH was determined using a benchtop pH meter with a silver chloride electrode (Fisherbrand accumet AP100). EC was measured using a Digital-Aid portable EC meter (Clearwater, Florida, USA). Both pH and EC meters were calibrated according to manufacturer recommendations using standardized pH buffers (pH 4, 7, and 10, Fisher Chemical) and KCl solutions (1, 5, 10 mM), respectively. Following measurements, media extracts (water, 10 mM CaCl₂, and phosphate buffer) were stored at 4 °C for later use during the calibration and validation of the analytical methods.

**Sorption Isotherms.** To evaluate sorption, 2 g of each individual media component or the Al-WTRs and 20 mL of the most appropriate solvent (identified above) were added into 50 mL Teflon [poly(tetrafluoroethylene) PTFE] Oakridge...
Prior to analysis, sample solutions for most compounds were filtered through Target2 0.2 μm polyvinylidene fluoride (PVDF) syringe filters with a 30 mm housing (Thermo Scientific catalog #25000-6). The filtered solutions were transferred into 2 mL amber glass high-performance liquid chromatography (HPLC) vials. However, the filtration step reduced the recoveries of paclobutrazol from most substrates by 31–50%, except in the peat and Al-WTRs matrices which had recoveries of 134 and 95%, respectively. As a result, the PVDF filtration step was omitted for analysis of paclobutrazol samples. Instead, these samples were centrifuged in the same 50 mL Oakridge Teflon tubes (15 min, 5000 rpm) where the batch equilibrium study was conducted. Afterward, 2 mL aliquots were taken from the clear supernatant and were directly injected into the analytical system for analysis.

Pesticide concentrations in the aqueous supernatants from the sorption isotherm studies were analyzed at the Organic Contaminants Analytical Research Laboratory housed in the Soil and Water Sciences Department (University of Florida, Gainesville), using the liquid chromatography conditions described by CDFA (2013). Briefly, acephate, imidacloprid, metalaxyl-M and paclobutrazol were analyzed by direct injection (10 μL) into a Waters 2695 HPLC (Waters Corp., Milford MA, USA) equipped with a Phenomenex Synergi Hydro-RP column (80 Å, 50 × 2 mm, 4 μm) and coupled to a Micromass Quattro Ultima MS/MS system (Waters Corp., Milford MA, USA) operated in the single-ion monitoring mode with one quantifier and one qualifier m/z. The m/z transitions used included m/z 184 > 125 (quantifier) and 184 > 143 (qualifier) for acephate, m/z 256 > 175 (quantifier) and 256 > 209 (qualifier) for imidacloprid, m/z 280 > 192 (quantifier) and 280 > 220 (qualifier) for metalaxyl-M, and m/z 294 > 70 (quantifier) and 294 > 125 (qualifier) for paclobutrazol. Conditions used to perform m/z transitions are summarized in Table 4. Run time per sample was 15 min, with retention times of 1.16 min (acephate), 2.50 min (imidacloprid), 8.84 min (paclobutrazol), and 9.22 min (metalaxyl-M).

The potential for co-extraction of interfering constituents was evaluated by comparing instrument responses for each pesticide spiked into extractant alone and spiked into the media extracts. When substantial deviations in responses occurred between the two, matrix-matched calibration curves were warranted. As a result of these studies, calibration curves were built in reagent-grade water, as well as in pesticide-free extracted matrices described earlier. Most calibration standard
curves included concentrations of 10, 50, 100, 200, 400, 600, and 800 ng mL⁻¹. The minimum acceptable R² for calibration curves was 0.99. To evaluate the influence of the filtering step on accuracy and recoveries, pesticides were spiked into extraction solutions in tubes without substrates, which were then shaken as previously described followed by analysis by direct injection before and after filtration. The limits of detection (LODs) were calculated using pesticide-free matrices extracted from each substrate component using the isotherm incubation method described earlier. Each pesticide was spiked into the pesticide-free supernatant to achieve concentrations of 10, 50, 100, 200, 400, 600, 800 ng mL⁻¹ before analysis (Table 5). The spiking levels differed between pesticides and individual media components because of matrix effects on analyte signals. The LOD was calculated using LOD = sd × t, where sd is the standard deviation of the spikes (n = 8), and t is the one-tailed t statistic for 99% confidence with n − 1 degrees of freedom (Smith, 1999).³⁹ LODs ranged from 0.02 to 0.10 mg L⁻¹ for acephate, 0.02–0.19 mg L⁻¹ for imidacloprid, 0.02–0.08 mg L⁻¹ for paclobutrazol, and 0.02–0.10 mg L⁻¹ for metalaxyl-M (Table 5).

Statistical Analysis. Statistical analysis was performed using SigmaPlot 14 (Systat Software Inc., San Jose, California, USA). Pesticide sorption coefficients (and corresponding variance estimates) were optimized using linear and nonlinear regression procedures based on the Marquardt–Levenberg algorithm. Media component effects on sorption of the initial mass applied was evaluated with one-way analysis of variance (ANOVA) with the significance level set at 0.05. The Holm–Sidak method was used for multiple comparisons after detecting significant differences between sorption means in the one-way ANOVA procedure. The goodness-of-fit of the linear regression models selected for the sorption isotherms was evaluated using the coefficient of determination (R²).⁴⁰,⁴¹

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Notes
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ABBREVIATIONS
Al-WTRs, aluminum-water treatment residuals; Ce, solution concentration; EC, electrical conductivity; HPLC—MS/MS, high-performance liquid chromatography tandem mass-spectrometry; Kᵣ, Freundlich sorption coefficient; Se, sorbed concentration; LOD, limit of detection; Nᵣ, Freundlich isotherm exponent; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride; Sₘ₉₉, Langmuir isotherm sorption maximum

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