Barricade (prodiamine) Persistance in Pinebark:Sand Substrate[1]

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Abstract

Barricade (prodiamine) herbicide is used for preemergence weed control in container-grown plants and has been shown to injure certain landscape plants. This research investigated Barricade's (prodiamne's) persistence and movement in a pine bark:sand substrate with greenhouse grown azaleas treated with Barricade (prodiamine). A bentgrass bioassay study indicated similar Barricade (prodiamine) distribution throughout the containers through 60 days after application (DAA). Barricade (prodiamine) residues extracted from the substrate were similar within specific horizons at 30 and 60 DAA indicating a downward herbicide migration within the container. Barricade (prodiamine) may be adsorbed to fine substrate particles and move in the container with the displacement of fine particles during irrigation and substrate settling.

Index words: prodiamine; herbicide; herbicide movement in soil-less substrate; herbicide injury; herbicide persistence.

Species used in this study: Hino crimson azalea (*Rhododendron obtusum* (Lindl.) Planch. 'Hino Crimson'); bentgrass (*Agrostis palustris* Huds. 'Penncross'); large crabgrass (*Digitaria sanguinalis* (L.) Scop.).

Herbicides used in this study: Barricade (prodiamine) [2,4-dinitro-N^3, N^3-dipropyl-6-(trifluoromethyl)-1,3-benzenediamine].

Significance to the Nursery Industry

Barricade (prodiamine) is a commonly used preemergence herbicide in the production of container grown landscape plants. Injury to sensitive species maybe related to the movement and persistence of Barricade in a pine bark:sand substrate as little dissipation was noted 60 days after application.

Introduction

Barricade (prodiamine) is commonly used in container plant production for preemergent control of grass and broadleaf weed species. Effective and long-term control of many weed species, including hairy bittercress (*Cardamine hirsuta* L.), large crabgrass (*Digitaria sanguinalis* (L.) Scop.), redroot pigweed (*Amaranthus retroflexus* L.), common lambsquarters (*Chenopodium album* L.), Florida betony (*Stachys floridana* L.), spotted spurge (*Euphorbia maculata* L.), yellow woodsorrel (*Oxalis stricta* L.), and Virginia pepperweed (*Lepidium virginicum* L.) were reported (1, 4, 7, 8, 17). However, application rates required to achieve efficacious weed control often exceed labeled rates.

Barricade is a member of the dinitroaniline family of herbicides that includes Surflan (oryzalin), Treflan (trifluralin), Balan (benefin) and Pendulum (pendimethalin). Dinitroaniline herbicides bind to plant tubulin preventing formation of plant microtubules (22). Cells become ovoid, mitosis is disrupted and root and shoot tips swell in the elongation zone. Barricade has a water solubility of 0.013 mg·liter^{-1} at 25C, very low vapor pressure (2.4×10^{-8} mm Hg at 25C), strong adsorption to organic matter (K_{oc} = 13,000 ml·g^{-1}), and field half-life is estimated at 120 days (14). It has the lowest water solubility and highest K_{oc} value of the dinitroaniline herbicides.

Injury to container-grown plants from applications of Barricade has been reported. Shoot and root weights of bedding plants were reduced following an application of Barricade at 1.1 kg·ha^{-1} (1.0 lb ai·A^{-1}) as compared to untreated (13). Restricted root development of azaleas [*Rhododendron indicum* (L.) Sweet. 'Formosa'; *Rhododendron obtusum* (Lindl.) Planch. 'Coral Bells'] were noted at Barricade rates of 9 kg ai·ha^{-1} (8.2 lb ai·A^{-1}) (6× the labeled rate) and higher (19). Shoot height and root growth were reduced in container grown pampas grass [*Cortaderia selloana* (Schult. and Schult f.) Asch. and Graebn.] treated with Barricade at 1.7 kg ai·ha^{-1} (1.5 lb ai·A^{-1}) (10). Root growth of Abelia (*Abelia × grandiflora X A. Schumannii* Rehd.) and shoot and root growth of azalea (*Rhododendron obtusum* Planch. 'Tradition') were inhibited after repeat applications of Barricade at 4.5 kg ai·ha^{-1} (4.1 lb ai·A^{-1}) (4).

Barricade formulation may affect injury. Herbicide injury was not observed on a variety of woody landscape plants following a granular application of Barricade at high rates (7). However, shoot weights of crape myrtle (*Lagerstroemia indica* L. 'Potomac') and waxleaf ligustrum (*Ligustrum japonicum* Thunb.) were reduced 16 wk after application of a granular formulation though injury was not noted from a sprayable formulation (5). No injury to container-grown herbaceous perennials was noted from applications of sprayable prodiamine (WG) at 2× maximum rates (3). Hosta (*Hosta spp.* Tratt. 'Hyacinthina') and daylily (*Hemerocallis spp.* L. 'Sammy Russell') were also not injured following application of a sprayable formulation of Barricade (25).

Due to its very low water solubility and high organic partition coefficient, Barricade may persist in a soilless container substrate, moving downward in the container through displacement of smaller substrate particles by applied irrigation, resulting in injury to the root system of sensitive plant taxa. A chemical's mobility in a substrate is determined by the

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relative affinity of the chemical for the organic and water compartments of the substrate, the water solubility of the herbicide, the amount of water passing through the substrate, and the organic composition of the substrate. Mobility of several herbicides in soilless substrates was investigated. Depth to which Ronstar (oxadiazon) leached in columns was greater in a potting substrate containing redwood bark as compared to a substrate containing peat, and the depth to which Goal (oxyfluorfen) moved downward was dependent upon dose and irrigation volume (15). Barricade (WG) applied to newly potted pampas grass inhibited root growth to a greater degree than other dinitroaniline herbicides in the lower 10 cm of a pine bark:sand (6:1 v/v) substrate at 60 and 75 days after application (DAA) (12). Goal (oxyfluorfen) was detected in middle and bottom thirds of a pine bark:sand (9:1 v/v) substrate though Surflan (oryzalin) was only detected in the top layer (9). Surflan (oryzalin) remained in the top 4 cm of a pine bark:sand substrate after five extractions with only small amounts of Surflan (oryzalin) leaching below 2 cm (24). Eptam (EPTC) leached to lower depths than either Lasso (alachlor) or Pennant (metolachlor) in peat:sand (4:1 v/v) columns (16). Pennant (metolachlor) was found to be immobile in a soil column study (11). Gallery (isoxaben) remained in the top 5 cm of a peat substrate through 191 DAA (18). These studies reinforce that the mobility of a herbicide is a function of the chemical properties of the compound, and the composition of the soil or substrate to which it is applied.

A series of studies investigated the persistence and movement of Barricade in a pine bark:sand container substrate. Specific research objectives were to quantify the persistence and vertical movement of Barricade in pine bark:sand container substrate.

Materials And Methods

Greenhouse studies were conducted to investigate persistence and movement of prodiamine in container substrate. Uniform liners of Hino crimson azalea were planted off center in 3.8 liter (4 qt) containers containing a pine bark:sand (4:1 v/v) substrate with a pH of 5.3. Containers had been cut in half vertically, reassembled with duct tape and wrapped in aluminum foil. One day after planting containers were treated with either Barricade 65 DG[4] at 1.6 kg ai·ha^{-1} or left untreated. Application was over the top by CO_2 backpack sprayer operated at 234 kPa (40 psi), and application volume was 281 liters·ha^{-1} (30 gpa). Irrigation (510 ml; 2.5 cm) was manually applied to containers after herbicide application and daily throughout the study. There were four replications of all treatments and the study was repeated.

Azalea plants were harvested on 1, 7, 14, 30, and 60 DAA, and containers were divided in half vertically by pushing a glass pane between the container halves. The half of the container, which did not house the azalea, was placed on its side, covered with aluminum foil, and stored in the dark at 4C for 1 to 3 mo until bioassay analysis was performed. Roots were removed from the azalea plants, washed to detach substrate, and dried at 40C for 7 d. Dried roots were then ashed for 8 hr at 500C to determine inorganic (sand) weight of roots. Reported root weights were determined by subtracting the ashed weight from the dry weight.

As a bioassay procedure to detect herbicide presence, container halves were situated on side, divided into four parallel horizons (surface, two middle and bottom) 4 cm deep, and ≈ 100 seeds of creeping Bentgrass (*Agrostis palustris* Huds. 'Penncross') were sown down a median line from container top to bottom. Container halves were placed in a greenhouse under optimal growing conditions and continuous mist (16 sec every 8 min). After 7 d, shoot heights of 10 randomly selected bentgrass seedlings throughout each of the four quadrants were measured. No differences were observed in the emergence of Bentgrass between the horizons.

In order to further quantify prodiamine persistence and downward movement in containers, the substrate from all treatments collected on 30 and 60 DAA was subjected to an extraction and analysis procedure. Fifty g of container substrate was removed from each of the four horizontal quadrants of the pot profile and dried at 100C for a minimum of 24 h. Ten g of dried substrate was ground in a Wiley mill for 10 sec and placed in an amber 100 ml glass container with 25 ml methanol. The mixture was placed in a warm water bath (55–60C) and shaken at a rate of 15 revolutions per min for one h. The solution was returned to ambient temperature prior to vacuum filtration through #5 Whatman (Whatman, Inc. 9 Bridewell Place, Clifton, NJ) filters in a Buchner funnel. The solvent was further filtered through 0.2 μ membrane filters into graduated test tubes. Volume was reduced to 10 ml under a slow stream of N. Two ml of the methanol extract were removed and evaporated to dryness. The dried extract was dissolved in 2 ml of 65:35 acetonitrile:water with 2% acetonitrile, vortexed for 10–20 sec, and filtered through 0.2 μ membrane filters into high pressure liquid chromatography (HPLC) autosampler vials. Samples were analyzed using an HPLC fitted with a C_{18} reverse phase column [Rexchrom (Regis Technologies, 8210 Austin Avenue, Morton Grove, IL) S3-100-ODS, 3μm, 100A]. Solvent conditions were 65:35 acetonitrile:water with 2% acetonitrile for 20 min, 100% acetonitrile 20 to 25 min and reequilibration with starting mobile phase 25 to 30 min. The flow rate was 0.5 ml·min^{-1} and injection volume was 50 μl. The diode array detector was set at 220 nm. Retention time for Barricade was 11.9 min, percent recovery for the extraction and analysis procedure was calculated to be 63%, and Barricade quantification and qualification were determined by comparison to external Barricade standards.

An additional experiment was conducted to investigate sorption of Barricade to the components of a pine bark:sand (85:15) substrate. Pine bark was separated into three equal volume fractions by size (coarse, medium and fine). The three pine bark fractions and a 100% sand treatment were placed in cell packs (24 to a tray), seeded with *Digitaria sanguinalis* (large crabgrass) (10 seeds per cell), and placed in a greenhouse under mist. Each four-cell pack serves as a replication. On the day after planting, Barricade 65WG was applied at the rate of 1.6 kg ai·ha^{-1} (1.5 lb ai·A^{-1}) using a hand held spray bottle. Four replications of each substrate were treated with Barricade and four replications served as untreated controls. Percent emergence was recorded weekly, and at 6 WAT, crabgrass shoots were harvested and fresh weights were recorded. Three days after harvest, crabgrass was replanted in the containers, and observations and data collection were conducted as after the first planting.

Statistical methods. Data were subjected to ANOVA and means were separated by LSD (0.05). No interactions were noted in results from the two Barricade movement in substrate studies and data from the studies were combined.

Table 1. **Results of bentgrass bioassay in horizons of container substrate treated with Barricade 1 to 60 days after application (DAA). Means are the percent reduction in shoot height compared to the control.**

	Bentgrass shoot height reduction					
	Container horizon[z]					Average across horizons
DAA	0 to 4 cm	4 to 8 cm	8 to 12 cm	12 to 16 cm	LSD (0.05)	
Barricade	%					
1	33	18	17	13	13	20
7	28	16	14	4	18	15
14	31	16	2	6	16	11
30	32	19	7	2	8	15
60	26	21	14	5	10	21
LSD (0.05)	NS	NS	12	13	—	NS

[z]Container substrate was divided into four horizons with top horizon designated as 0 to 4 cm.

Results And Discussion

The bentgrass bioassay detected Barricade in all four container horizons through 60 DAA (days after application) (Table 1). On 1 and 30 DAA, levels in the 0 to 4 cm (top) horizon of the container substrate were greater than levels detected in the other three horizons based on bentgrass shoot height reduction. At 7 DAA, levels in the 0 to 4 cm horizon were higher than those in 12 to 16 cm (bottom) horizon. At 14 and 60 DAA the 0–4 level reduced bentgrass height compared to the two lowest horizons. Levels did not vary within the top two horizons from 1 through 60 DAA, and levels in the bottom two horizons were similar on all sampling days except at 14 DAA. In both bottom horizons, levels decreased at 14 DAA, and increased by 60 DAA. Average effects of Barricade throughout the container horizons were not different between sampling days (Table 1). Barricade appears to be very stable and persistent when applied to a pine bark substrate with initial downward movement resulting from the first irrigation application, and only minimal subsequent downward movement. The amount of organic matter (pine bark) present in the container substrate used in our study appears to have quickly adsorbed Barricade. Results are as expected as the high K_{oc} and low water solubility of Barricade indicate that the chemical would quickly and strongly bind to organic matter.

Results concur with those of other researchers (9, 16, 18, 20, 24). Barricade (WG) applied to newly potted pampas grass inhibited root growth to a greater degree than other dinitroaniline herbicides in the lower 10 cm of container substrate at 60 and 75 DAA (10, 12). Downward movement of Barricade in a fine sandy loam soil was reported with depth of movement dependent upon rainfall totals (6).

Barricade was detected in the container substrate at levels ranging from 10 to 21 $mg \cdot kg^{-1}$ (Table 2). Assuming equal distribution in the top cm of the container, Barricade concentration after application would be 34 $mg \cdot kg^{-1}$ based on an application rate of 1.6 kg $ai \cdot ha^{-1}$ (1.5 lb $ai \cdot A^{-1}$) and a bulk density of the container substrate of 0.5 $g \cdot cm^{-3}$. Approximately one-half of that level was detected at 30 and 60 DAA. Barricade levels within specific horizons were similar at 30 and 60 DAA reflecting the persistence of the herbicide in a pine bark:sand substrate. Between horizons, however, higher levels were found in the 8 to 12 cm horizon than in the top two horizons 30 DAA, but horizon levels were similar 60 DAA. Extraction and quantification of residue confirms persistence through 60 DAA and implies a downward migration of prodiamine within the container. Results appear to contradict bioassay results. However, soil and substrate bioassays measure only the bioavailable fraction of the herbicide, and compounds that have high K_{oc} values may remain adsorbed to the substrate. A bioassay would not detect this and results may, therefore, not be representative of actual amount of herbicide in a substrate (2). Extraction with organic solvents may more accurately indicate mobility and persistence of prodiamine in a container substrate.

Differences in root weights were found among treatments 60 DAA. Barricade-treated azalea plants had lower root weights than untreated plants (data not shown). Other

Table 2. **Barricade amounts (mg/kg) detected in substrate of container horizons (0 to 4 cm top; 4 to 8 cm, 8 to 12 cm, and 12 to 16 cm bottom) 30 and 60 days after application (DAA).**

	Barricade amounts				
	Container horizon[z]				
DAA	0 to 4 cm	4 to 8 cm	8 to 12 cm	12 to 16 cm	LSD *(0.05)*
	$mg \cdot kg^{-1}$				
30	10.1	7.7	20.9	15.9	7.6
60	9.5	11.2	12.5	13.2	NS
LSD (0.05)	NS	NS	NS	NS	

[z]Container substrate was divided into four horizons with top horizon designated as 0 to 4 cm.

reports of container plant root weight reduction from Barricade and Surflan applied at higher rates are found in the literature (4, 19, 21).

Research on the mobility of Ronstar (oxadiazon) in a rice hulls:peat:pine bark (1:1:1 v/v) indicated that Ronstar adsorbed to fine substrate particles (9, 23, 24), which are maybe mechanically displaced downward in a container. This hypothesis was tested in a separate experiment. The pine bark:sand substrate was divided into four fractions (coarse, medium, and fine pine bark, and sand) based on particle size, and assayed with crabgrass to investigate adsorptive capacity of the fractions. Through repeated seedings of crabgrass, reduction in seedling dry weights was consistently greater in the coarse and medium pine bark fractions than in the 'fines' fraction, indicating higher available Barricade levels (data not shown). Decreased herbicidal activity in the 'fines' fraction may result from a greater number of binding sites and increased adsorption of Barricade. While not conclusive, this appears to support the premise that mobility of Barricade in a soilless substrate is a function of the downward displacement of substrate 'fine' particles.

Barricade may caused long-term injury to a variety of plant taxa. Injury is usually manifested as stunting, chlorosis, and reduced root and shoot growth. Persistence and mobility studies indicated that Barricade persists in a pine bark:sand container substrate with little dissipation noted at 60 DAA. Barricade mobility in the container substrate appears to be through displacement of fine substrate particles. Roots of sensitive plant species are, therefore, exposed temporally and spatially to Barricade at levels sufficient to cause injury.

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