Increased Soil Sorption of Pendimethalin due to Deposition of Guayule-Derived Detritus

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Guayule is a perennial shrub native to the Chihuahuan Desert of the southwestern United States and northern Mexico and is a member of the Compositae family that produces high-molecular-weight latex. Commercial production of natural latex is dominated by Hevea [Hevea brasiliensis (Willd. ex A. Juss.) Müll. Arg.] from Southeast Asia; however, more recently guayule has been shown to be a commercially viable source of natural latex. According to Nakayama (2005), there have been at least three previous periods when guayule has been investigated as an alternative source of natural rubber and latex, but each time competition from Hevea prevented economically viable commercialization. Currently, allergies to Hevea latex have become a serious problem in the United States and Europe among health care workers and patients who undergo multiple surgeries (Owby et al., 1994). Guayule latex has the advantage of being a potential source of circumallergenic natural latex for the manufacture of medical and other latex products (Siler and Cornish, 1994, 1995; Siler et al., 1996). This added value of guayule latex, as an alternative to Hevea for those with allergies, has led to the construction of a commercial-scale latex extraction plant and the planting of more than 2000 ha of guayule in the southwestern United States.

Previously, considerable effort has been directed toward the selection and breeding of guayule to increase the rubber, and indirectly latex, content and yield (Ray et al., 2005). Comparisons made in Australia found that rubber content in lines isolated in the 1940s had a rubber content roughly equal to new improved selections (7.9%) but that the total rubber yield for the new lines were as high as 620 kg ha−1, compared with 381 kg ha−1 for the older lines (Coffelt et al., 2009a,b; Dissanayake et al., 2004). Estilai (1991) also reported that new selections produced 40 to 127% more rubber than old cultivars. In addition to rubber, guayule has very high resin content, up to 9% based on total dry matter (Dissanayake et al., 2004; Estilai, 1991; Banigan et al., 1982). Guayule resin has also been found to have economic potential as a termaticide (Nakayama, 2005; Nakayama et al., 2001; Bultman et al., 1998), wood preservative (Nakayama et al., 2001; Bultman et al., 1991; Chow et al., 2008), and an additive to epoxies and coatings (Thames and Kaleem, 1991; Thames and Wagner, 1991; Belmares et al., 1980). Banigan et al. (1982) found that 15% of guayule biomass was resin, rubber, and wax. Future improvements to guayule strains will include increases in both rubber and resin (Nakayama, 2005, Ray et al., 2005; Veatch et al., 2005).

The rubber and resin content of guayule has also been shown to be positively correlated to total biomass (Ray et al., 2005) and season (Schloman et al., 1986). As a perennial shrub, guayule’s latex yield will also increase with age (Coffelt et al., 2009b;
Foster and Coffelt, 2005) due to increased biomass. Typically, guayule is harvested after 2 yr and then allowed to regrow from the stump and harvested again after 2 yr of regrowth. This results in a buildup of leaves and plant detritus underneath the shrub for 4 or more yr before tillage and replanting.

Based on climate needs and location, typical crops that would be planted following guayule could include guayule re-planted or cotton. Weed control in both cotton and guayule includes application of the pre-emergent herbicide pendimethalin. Pendimethalin is one of the few herbicides registered for weed control in guayule (Arizona Department of Agriculture, 2003) and is commonly used in cotton production throughout the U.S. Southwest (McCloskey et al., 2000).

Pendimethalin is a selective herbicide used to control annual grasses and broadleaf weeds. In Arizona, it is typically used as a pre-emergent or early post-emergent herbicide in cotton. Pendimethalin has also been registered as a special local needs herbicide for use in guayule in Arizona (Arizona Department of Agriculture, 2003). Pendimethalin (Fig. 1) is a yellow crystalline solid with a water solubility of 0.275 mg L$^{-1}$, a degradation half-life ($t_{1/2}$) of 44 d (Ahrens, 1994), and an octanol–water partition coefficient of 152,000 (log $K_{ow} = 5.18$) (Montgomery, 1993, p. 318–319). Currently no data exist regarding the effect of organic residues from continuous guayule cultivation for 4 yr can affect the sorption of pendimethalin.

**MATERIALS AND METHODS**

The soil used in this experiment was a Casa Grande clay loam (a fine-loamy, mixed, superactive, hyperthermic Typic Natrargid) located on the University of Arizona Maricopa Agricultural Research Center that had been under guayule cultivation. Samples were taken from adjacent fields in November 2006 where guayule had been grown for various lengths of time. Guayule had been grown continuously for 12, 26, 32, and 38 mo and these treatments are referred to as G-12, G-26, G-32, and G-38, respectively. In addition, samples were taken from a field where guayule had never been grown (control) and a field where guayule had been grown for 36 mo harvested, the soil was ripped to 50 cm, cultivated, laser leveled, and then planted with a green manure crop of barley (Hordeum vulgare L.) that was disked in, and the field was left fallow for 5 mo before sampling (G-F). Guayule was grown on 1-m-wide beds and furrow irrigated every 2 to 4 wk depending on soil water depletion. Soil samples were taken throughout the field, 0 to 10 cm deep, from the bed directly beneath growing guayule plants and the samples were composited, dried, and sieved through a 2-mm sieve. Each sample was mixed for homogeneity and subsamples taken for chemical and physical analysis (Table 1).

Table 1. Some selected properties of Casa Grande clay loam (a Typic Natrargid) used to determine pendimethalin sorption characteristics.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Time†</th>
<th>Growing seasons‡</th>
<th>Clay</th>
<th>Organic C (%)</th>
<th>Cation exchange capacity cmol\textsubscript{k} kg\textsuperscript{-1}</th>
<th>pH</th>
<th>Electrical conductivity dS m\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>22.5</td>
<td>0.29</td>
<td>16.8</td>
<td>7.7</td>
<td>2.5</td>
</tr>
<tr>
<td>G-12</td>
<td>12</td>
<td>1</td>
<td>22.5</td>
<td>0.33</td>
<td>13.4</td>
<td>8.2</td>
<td>5.6</td>
</tr>
<tr>
<td>G-26</td>
<td>26</td>
<td>2</td>
<td>31.6</td>
<td>0.51</td>
<td>17.9</td>
<td>8.1</td>
<td>3.8</td>
</tr>
<tr>
<td>G-32</td>
<td>32</td>
<td>3</td>
<td>28.2</td>
<td>0.62</td>
<td>18.1</td>
<td>7.8</td>
<td>3.8</td>
</tr>
<tr>
<td>G-38</td>
<td>38</td>
<td>4</td>
<td>29.8</td>
<td>0.76</td>
<td>15.1</td>
<td>7.9</td>
<td>5.3</td>
</tr>
<tr>
<td>G-F</td>
<td>36</td>
<td>4 + fallow§</td>
<td>28.8</td>
<td>0.52</td>
<td>17.4</td>
<td>8.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

† Number of months guayule was continuously grown on the soil.

‡ Number of guayule summer growing seasons before sampling.

§ Four growing seasons with guayule followed by green manure (barley) and one summer fallow.

![Fig. 1. Chemical structure of the herbicide pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine).](Image 367x659 to 511x760)

For the current study, an emulsifiable concentrate of pendimethalin with a concentration of 455 g L$^{-1}$ was obtained from BASF (Florham Park, NJ). Pendimethalin solutions of 0.25, 0.50, 0.75, 1.00, and 1.25 mg L$^{-1}$ were prepared using the emulsifiable concentrate and a water solution made by adding NaCl and CaCl$_2$ to 18 MΩ water to create an electrical conductivity (EC) of 1 dS m$^{-1}$ and a sodium adsorption ratio (SAR) of 2. An additional treatment of the EC 1 SAR 2 water without the herbicide was also prepared. Unless otherwise stated, this water was used in all studies reported here. Sorption was determined by placing 20 mL of each pendimethalin solution in 50-mL Teflon centrifuge tubes containing 5 g of soil. Centrifuge tubes were shaken for 18 h at 17°C and centrifuged for 15 min at 2000 × g and 15 mL of the supernatant was removed for concentration by solid-phase extraction followed by analysis. Preliminary studies showed that the amount of pendimethalin adsorption after 15 h was within 2% of that adsorbed after 18, 24, 48, and 72 h. It was determined that 18 h would be used for equilibration to minimize potential loss due to degradation. Each treatment was replicated three times.

The concentration of pendimethalin in solution after equilibrium was determined using gas chromatography–mass spectrometry (GC-MS). Solid-phase extraction was used to concentrate and transfer the pendimethalin remaining in the aqueous phase to the solvent for GC-MS analysis. Solid-phase extraction cartridges packed with C-18 were preconditioned in succession with 9 mL of acetone and 9 mL of water followed by air drying for 5 min. Cartridges were loaded with 15 mL of post-sorption supernatant followed by two 5-mL water rinses and 5 min drying. Pendimethalin was eluted using 3 mL of acetone followed by 3 mL of methanol. Samples were then evaporated to dryness and brought to 0.5 mL with acetone, resulting in a 30 times concentration.

Pendimethalin adsorbed to the soil was also quantified using GC-MS. After removing the supernatant for aqueous-phase analysis, the soil...
and remaining solution were centrifuged for 15 min at 2000 × g. The supernatant was removed and the tube was weighed to account for water remaining in the pore space. Sufficient acetone was added to bring the total liquid volume to 20 mL. Centrifuge tubes were shaken for 18 h at 17°C and centrifuged for 15 min at 2000 × g, and 5 mL of the supernatant was removed, evaporated to dryness, and then brought to 0.5-mL volume with acetone.

Pendimethalin was analyzed using a gas chromatograph equipped with a mass selective detector quantifying the ion at 252 +. Operating conditions included the use of a 30-m 0.25-mm glass capillary column coated with 0.25 μm of 5% phenyl methyl siloxane, an injector temperature of 250°C, an initial oven temperature of 60°C for 0.5 min with a ramp of 10°C min−1 up to 250°C, then a ramp of 20°C min−1 up to 280°C and isothermal holding for 4 min, and a He carrier gas flow rate of 1.0 mL min−1. The mass detector source was held at 230°C and the temperature of 280°C, an initial oven temperature of 60°C for 0.5 min

Data analysis was performed using the linear form of the Freundlich equation:

\[ C_s = K_D C_L^{1/n} + b \]  

where \( C_s \) is the amount of pendimethalin sorbed per mass of soil, \( C_L \) is the solution-phase concentration of pendimethalin, \( K_D \) is the adsorption coefficient, \( b \) is the intercept term, and \( N \) accounts for the degree of nonlinearity in the sorption isotherm. The linear form reduces \( N \) to 1 and the resulting slope of the equation is the adsorption coefficient and is referred to as the distribution coefficient, \( K_D \).

RESULTS AND DISCUSSION

All soils had pendimethalin concentrations below the detection limit (<0.1 μg kg−1) before treatment. Pendimethalin had been used for the establishment of guayule in the fields investigated; however, it was only used as a preplant treatment. Samples were taken a minimum of 12 mo following the last application and \( t_{1/2} \) for pendimethalin is <45 d (Kulshrestha and Singh, 1992) in aerated soil with complete degradation after 4 d under flooded conditions (Kulshrestha and Singh, 1992). The fields where soil samples had been taken were flood irrigated. The outcome of time and irrigation resulted in an expected loss of >99.9% of the applied compound before sampling. The mass of pendimethalin in the sorbed and aqueous phases was used to determine a mass balance. In all cases, >97% of the applied pendimethalin was recovered in the aqueous and sorbed phases.

Isotherms for pendimethalin sorption to soil were linear and are shown in Fig. 2, with \( K_D \) values ranging from 49 to 1800 L kg−1. All treatments had a higher \( K_D \) than the control and the \( K_D \) increase corresponds to the length of time guayule was grown on the soil except for the G-F treatment. Pendimethalin \( K_D \) values in the literature range from 30 to 854 L kg−1 (USDA-ARS, 2006) for soils with organic C contents ranging from 0.46 to 2.90%, with \( K_D \) increasing as soil C increases. Our results also show the same general trend.

It is generally accepted that sorption of neutral organics to soil is dominated by soil organic matter. Carringer et al. (1975) found that dinitroaniline herbicides (including pendimethalin) were strongly adsorbed by organic matter. They also found that the dinitroaniline herbicides trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine] and profluralin [N-(cyclopropylmethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)benzenamine] were not sorbed and slightly sorbed, respectively, by soil minerals, with the remainder being associated with the organic fraction. Blumhorst et al. (1990) found that soil clay content from various sources had no effect on pendimethalin availability but that organic matter from various sources did affect (\( P = 0.05 \)) pendimethalin availability. It has also been shown that increased sorption decreases herbicide availability and efficacy (Harrison et al., 1976). This would indicate that the differences in sorption observed were related to changes in organic matter content or composition and that the increase in sorption could decrease efficacy.

Continuous guayule cultivation resulted in a modest increase in soil organic C (Fig. 3) from 0.29 to 0.76% after 38 mo. The organic matter increase during the 38-mo period was expected due to the perennial nature of guayule and the lack of tillage, which allowed any detritus to build up on the soil surface. Based on the increase in organic C measured, the accumulation rate was approximately 12 mg C kg−1 soil mo−1. The only exception was the G-F treatment, where guayule was harvested and tilled, followed by a barley crop, which was incorporated into the soil, and a fallow period, resulting in sampling a total of 1 yr following harvest. The reduction from 0.76 to 0.52% is expected due to dilution caused by tillage and reduced organic C content resulting from natural oxidation. In addition, the type of organic matter found in the G-F treatment would be expected to be different than the other treatments due to the addition of the barley as a green manure. The organic matter present in the soil under actively growing guayule is the combination of new plant detritus and the preexisting organic matter. Weathering as a result of high temperatures and a long growing season would result in a significant portion of the detritus being oxidized, leaving behind only recalcitrant organics to build up in the soil.

Banigar et al. (1982) found that guayule was up to 10% resin, wax, and rubber. The concentrations of resin are highest in leaves and younger stems (Schloman et al., 1986) while rubber is concentrated within the stems >1 yr old (Coffelt et al., 2009a,b). Leaves and younger stems are also more likely to be deposited and accumulate under actively growing guayule, resulting in an increase in the ratio of rubber and resin compared with detritus-derived organics deposited by other plants.

Guayule resins have also been found to be highly resistant to weathering in soil environments (Bultman et al., 1991; Gupta et al., 2004). Wood impregnated with guayule resin as a preservative was deployed undisturbed in different soil environments and the preservative maintained efficacy for >45 mo (Bultman et al., 1991). This would indicate that a portion of the resins deposited from the guayule detritus would be very resistant to weathering and accumulate in the soil beneath actively growing guayule.

The sorptive capacity of guayule-derived organic matter for pendimethalin is greater than non-guayule-derived organic matter. The relationship between the measured \( K_D \) and soil organic C is plotted in Fig. 4. The solid line is the linear interpolation of the control, G-12, and G-F treatments. Organic matter in the control, G-12, and G-F treatments was not expected to be domi-
Fig. 2. Adsorption isotherm for pendimethalin to Casa Grande clay loam with guayule-derived organic matter: (a) control that had not had guayule grown, guayule grown for (b) 12, (c) 26, (d) 32, and (e) 38 mo, and (f) guayule grown for 36 mo followed by a green manure (barley) and 5 mo of fallow; $C_{S}$ is the amount of pendimethalin sorbed per mass of soil and $C_{L}$ is the solution-phase concentration of pendimethalin. Note that the $x$ axis scale is not consistent from plot to plot. Error bars represent ±1 SEM.
Fig. 3. The accumulation of organic C (OC) with time in a Casa Grande clay loam soil where guayule was grown. The relationship is linear, with an organic C increase of 0.016% per month.

Fig. 4. The relationship between the distribution coefficient, \( K_D \), and organic C content (OC) for non-guayule-derived organic matter (solid line) and guayule-derived organic matter (broken line).

Table 2. Linear sorption distribution coefficient (\( K_D \)) and organic C distribution coefficient (\( K_{OC} \)) of pendimethalin to soil under guayule cultivation.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>( K_D ) (L kg(^{-1}))</th>
<th>( R^2 )</th>
<th>( K_{OC} ) (L kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>49</td>
<td>0.96</td>
<td>16,900</td>
</tr>
<tr>
<td>G-12</td>
<td>68</td>
<td>0.97</td>
<td>20,600</td>
</tr>
<tr>
<td>G-26</td>
<td>510</td>
<td>0.98</td>
<td>100,000</td>
</tr>
<tr>
<td>G-32</td>
<td>954</td>
<td>0.92</td>
<td>153,900</td>
</tr>
<tr>
<td>G-38</td>
<td>1830</td>
<td>0.99</td>
<td>389,400</td>
</tr>
<tr>
<td>G-F</td>
<td>112</td>
<td>0.98</td>
<td>21,500</td>
</tr>
</tbody>
</table>

As an approximation, the G-12 treatment had 0.04% more organic C than the control (Table 1). If it is assumed that the increased organic matter was from guayule and all of the original organic matter was still present, then at least 12% of the organic matter was derived from guayule; if, however, some of the original organic matter had been oxidized during the preceding year, then the amount of guayule-derived organic matter would be greater. Therefore, it is reasonable to assume that the G-12 treatment would represent the beginning point of the transition from non-guayule-derived soil organic matter to guayule-derived organic matter.

In addition to \( K_D \), the organic C normalized sorption coefficient, \( K_{OC} \), obtained by dividing \( K_D \) by the fraction of organic C, is reported in Table 2. The \( K_{OC} \) for the control treatment is approximately 18% lower than that of the G-12 treatment and 20% lower than that of the G-F treatment. These differences could be related to the amount of guayule-derived organic matter; in particular, the G-12 treatment had an approximately 12% increase in guayule-derived organic matter and a corresponding 18% increase in \( K_{OC} \).

The broken line in Fig. 4 is a plot of the relationship between \( K_D \) and organic C for the soils where the organic matter was transitioning to dominance by guayule-derived organic matter. The linear relationship for the non-guayule-derived organic matter has a correlation coefficient of 0.98 while the relationship between \( K_D \) and guayule-derived organic C is a second-order polynomial with a correlation coefficient of 0.99. The difference between the sorption potential of the guayule- and non-guayule-derived organic matter can also be seen in the \( K_{OC} \) values reported in Table 2. If the sorption potential for both types of organic matter were similar, then the \( K_{OC} \) values should also remain relatively constant. But, as can be seen, the \( K_{OC} \) of the G-38 treatment is 23 times greater than the control and it is also the treatment with the most guayule-derived organic matter.

The results presented here indicate that soil organic matter from below actively growing guayule has a higher sorption capacity for pendimethalin than soils where guayule has not been grown, indicating that application rates may need to be adjusted to compensate for the increased \( K_{OC} \) for soils where guayule has been grown for >12 mo. It would appear, however, that after guayule was grown for 36 mo followed by a green manure crop, a combination of time and tillage resulted in a \( K_{OC} \) of slightly more than 1.2 times the control, compared with a maximum \( K_{OC} \) 2.5 times greater than the control for the soil where guayule had been grown for 38 mo. This means that in a cotton rotation, the use of pendimethalin would not appear to be affected when guayule was grown before cotton as long as a sufficient time had passed before planting cotton. Our initial findings indicate that 8 mo was sufficient to return the sorption capacity to pre-guayule levels; however, further research is needed to determine the minimum time needed. One potential obstacle to using pendimethalin for weed control in guayule was made apparent from these

Table 2. Linear sorption distribution coefficient (\( K_D \)) and organic C distribution coefficient (\( K_{OC} \)) of pendimethalin to soil under guayule cultivation.
The use of pendimethalin during regrowth following the first harvest of guayule may require higher application rates to control weeds. This is an important consideration since weed competition with the guayule regrowing from the stump remaining after the first harvest has the potential to reduce yield during the next 2 yr.

REFERENCES


