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Metolachlor Herbicides: What Are the Facts?

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Background

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> Metolachlor herbicides are a part of the chloroacetamide chemical family in the Weed Science Society of America (WSSA) Group 15 herbicide class. Group 15 herbicides inhibit seedling shoot growth (mode-of-action) by inhibiting the formation of very long chain fatty acids (site-of-action). Metolachlor is typically used as a preemergence (PRE), residual herbicide in corn (*Zea mays* L.), cotton (*Gossypium hirsutum* L.), soybean [*Glycine max* (L.) Merr] and a variety of other crops for the control of grasses and small-seeded broadleaves such as pigweeds (*Amaranthus* spp.).

There are a variety of commercial herbicide products available containing metolachlor that differ due to formulations and chemical principles. A few examples of these products include Dual Magnum[®], Dual II Magnum[®], Me-Too-Lachlor[™], Charger Max[®], Stalwart[®] and Parallel[®], among others. Some of these products can be differentiated due to the addition of a safener (benoxacor) to the formulation. A safener is typically added to the metolachlor formulation for use in corn to reduce injury; however, the safener only reduces injury to corn. Injury to other crops can occur depending on rate and environmental concerns (Figure 1). Additionally, crop death can occur if metolachlor is applied to nonlabeled crops such as rice (Oryza sativa L.), shown in Figure 1D. The addition of a safener to a metolachlor formulation is typically noted with "II" in the trade name of the herbicide. For example, Dual Magnum[®] = no safener and Dual II Magnum[®] = safener added. Metolachlor herbicides also differ based on the chemical composition of the product, specifically the concentration of metolachlor isomers.

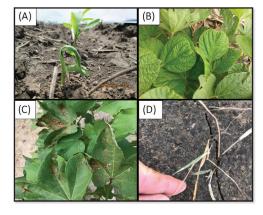


Figure 1. Crop injury symptoms of chloroacetamide (metolachlor) herbicides: buggy-whipping of corn (A), a drawstring effect on the center soybean trifoliate (B), speckling of cotton (C), and seedling death of rice (D).

Metolachlor Isomers

An isomer is defined as each of two or more compounds that contain the same number of atoms of the same elements (i.e., the same molecule), but differ in structural arrangement and properties. Metolachlor is one such herbicide that contains different isomers. Within a metolachlor herbicide, there are four different isomers of the active ingredient. These four isomers can be grouped into two categories, S- and R-metolachlor isomers. Think of a sports car versus a minivan. Both vehicles are made up of the same materials, and relatively speaking, contain equal amounts of those materials. However, those underlying materials are constructed in unique ways to produce two distinctly different vehicles. They may travel at different speeds, have different fuel mileage efficiency, and because of their shapes, may or may not fit into certain garages or parking spaces.

The S-metolachlor isomers are much more active in terms of herbicidal

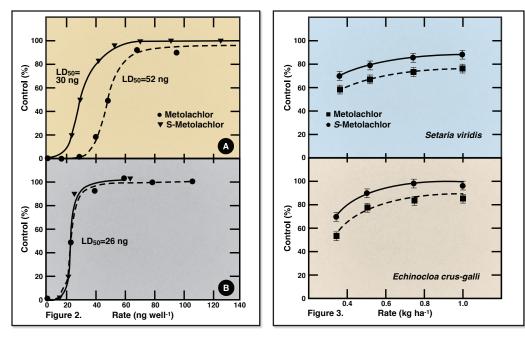


Figure 2 (left). Illustration of the increased efficacy of the *S*-metolachlor isomer on creeping bentgrass (*Agrostis stolonifera*) using dose response curves. The LD_{50} was a rate of metolachlor estimated to cause 50 percent injury. (A) Comparison of metolachlor and *S*-metolachlor activity on a gram-for-gram basis. (B) Comparison of metolachlor and *S*-metolachlor activity corrected for *S*-metolachlor content of each herbicide (metolachlor, 50 percent *S*-metolachlor; *S*-metolachlor, 88 percent *S*-metolachlor). Figure from Shaner et al. (2006).

Figure 3 (right). Herbicidal activity of metolachlor and *S*-metolachlor on green foxtail (*Setaria viridis*) and barnyardgrass (*Echinochloa crus-galli*). Figure from Shaner et al. (2006).

activity when compared to the *R*-metolachlor isomers (O'Connell et al. 1998; Shaner et al. 2006). This can be observed in Figures 2 and 3. In Figure 2 panel A, the dose response curves highlight the lower LD_{50} (metolachlor rate required to achieve 50 percent control) required for *S*-metolachlor compared to general metolachlor (equal ratio of *S*- and *R*-isomers) on creeping bentgrass. Additionally, Figure 3 illustrates that at equivalent use rates, products containing primarily the *S*-metolachlor isomers provided greater levels of weed control on both green foxtail (*Setaria viridis*) and barnyardgrass (*Echinochloa crus-galli*) compared to products with equal ratios of *S*- and *R*-isomers.

As a result of this increased efficacy from the S-metolachlor isomer, some manufacturers put metolachlor herbicides through a resolving process to limit the amount of R-metolachlor isomers present within the mixture. Dual Magnum[®] and other resolved formulations contain approximately 88 percent of the more active S-isomers and approximately 12 percent of the less active R-isomers (Hartzler, 2004). Unresolved formulations contain approximately equal ratios (50:50) of the S- and R-isomers. The product manufacturer labels list the resolved isomer as S-metolachlor, and generally the unresolved R-isomer as metolachlor.

Once again, let's consider the vehicle analogy. If we are renting a vehicle for travel, and our goal is to get to the destination as quickly as possible and with the best fuel mileage, the sports car (*S*-metolachlor) would be a better option than the minivan (*R*-metolachlor). Although the minivan (*R*-metolachlor) will also travel to the destination, users would benefit and achieve their overall goal of traveling faster while having better fuel mileage (increased weed control with lower product use rates) by using the sports car option (*S*-metolachlor).

Palmer Amaranth Resistance

Metolachlor herbicides have excellent residual activity and efficacy on Palmer amaranth prior to its emergence (Meyer et al. 2015). Metolachlor provides an alternative mode-of-action for use on preemerged weeds, creates flexibility for the postemergence (POST)

application and reduces selection pressure for resistance to POST-applied herbicides. As a result, it has often been a recommended component in managing Palmer amaranth and herbicide resistance. A mixture of metolachlor and a protoporphyrinogen oxidase-(PPO) inhibiting herbicide has been one of the most common combinations to accomplish this task following widespread occurrence of glyphosate-resistant Palmer amaranth, especially in soybean production systems. Examples of products containing this modeof-action mixture would be Prefix[®], Authority Elite 7 EC[®] and BroadAxe XC[®], among others.

In recent years, Palmer amaranth resistance to PPO inhibitors has steadily increased in the state of Arkansas (Varanasi et al. 2018). Incidentally, this led to increased selection for the evolution of herbicide resistance to metolachlor. When applied to PPO inhibitor-resistant Palmer amaranth, the combination of metolachlor plus a PPO inhibitor resulted in metolachlor being the only effective herbicide in this PRE program or the only effective residual applied POST.

Since 2016, less than acceptable Palmer amaranth control with metolachlor has been observed in field research sites located near Crawfordsville and Marion in Crittenden County, Arkansas. The Palmer amaranth at these sites was previously determined to be PPO inhibitor-resistant (Schwartz-Lazaro et al. 2017; Varanasi et al. 2018). Recently, Palmer amaranth populations from these sites were officially confirmed resistant to metolachlor (Heap 2019). Figure 4 illustrates with dose response curves the eight- and ten-fold levels of resistance to *S*-metolachlor from the Crawfordsville and Marion populations, respectively. Additionally, 90 percent control on the silt loam soils at these sites was not achieved in either population with a 1x rate (1 pint/ acre) of *S*-metolachlor (Dual Magnum[®]). Figure 5 shows the reduced activity on Palmer amaranth from the Marion site compared to two *S*-metolachlor susceptible Arkansas populations.

The mechanism of metolachlor resistance within these populations was identified as metabolic (mediated by glutathione S-transferase). This mechanism conferred field-level resistance to S-metolachlor and is extremely problematic because Palmer amaranth with this trait may be more prone to exhibit resistance or increased tolerance to other sites-of-action. Fortunately, no cross resistance to other Group 15 herbicides (dimethenamid-P, Outlook[®]; acetochlor, Warrant[®] and pyroxasulfone, Zidua[®]) has been identified at this time, albeit a slight reduction in sensitivity has been documented. For this reason, relying on dimethenamid-P, acetochlor or pyroxasulfone alone for residual control is not recommended and could result in rapid resistance to these herbicides.

Additional screenings for S-metolachlor resistance in Palmer amaranth have resulted in a range of responses from accessions collected across Arkansas (Figure 6). Twelve out of 150 Palmer amaranth populations tested resulted in less than 90 percent control. Further experiments are currently being conducted to confirm S-metolachlor resistance within these accessions. Plants from six of these 12 Palmer amaranth accessions that survived a 1 pint/acre rate of Dual Magnum[®] were analyzed for overexpression of genes associated with resistance to chloroacetamide herbicides. Five of the six accessions analyzed showed plants contained an overexpressed gene

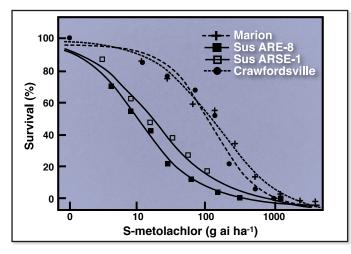


Figure 4. Dose response curves of four Arkansas Palmer amaranth populations demonstrating an eight- and ten-fold resistance to *S*-metolachlor in the populations from Crawfordsville and Marion, respectively. A rate of 1000 g ai ha⁻¹ *S*-metolachlor is approximately 1 pint/acre of Dual Magnum[®].



Figure 5. *S*-metolachlor dose response on Palmer amaranth highlighting the susceptible populations (bottom two rows) and resistant Marion population (top row). The red line indicates the LD_{50} (estimated dose to achieve 50% control), and the 1x rate of *S*-metolachlor is 1 pint/acre of Dual Magnum[®].

that had been previously implicated in resistance to chloroacetamide herbicides like S-metolachlor.

Moving forward, the use of diversified strategies will be critical for the successful management of Palmer amaranth. Successful management will require the use of weed control tactics such as tank-mixing multiple effective modes-of-action, cultural management strategies (e.g., crop rotation, cereal cover crops, enhancing crop competitiveness, weed seedbank management, etc.) and mechanical control methods (e.g., tillage) among others. Herbicides alone will not address this resistance issue long term. Metolachlor is still a viable option in herbicide programs for grass control and other smallseeded broadleaves. Moreover, metolachlor still provides acceptable Palmer amaranth control across much of Arkansas, especially when tank-mixed with other effective modes-of-action.

Recommendations

To successfully use metolachlor herbicides and reduce the likelihood of further development of herbicide resistance, we recommend the following:

- 1. Use metolachlor products that contain greater amounts of the S-isomer. This isomer has greater herbicidal activity and requires lower use rates compared to products containing the R-isomer.
- 2. If unresolved metolachlor products are used, be aware that they require greater use rates than products containing higher concentrations of S-metolachlor, but equivalent levels of control can be achieved. In panel B of Figure 2, it can be observed that if product use rates of the metolachlor herbicides were corrected to provide the equivalent of 100 percent S-metolachlor isomers, the LD₅₀ (dose required to achieve 50 percent control) was equal between the resolved and unresolved metolachlor products. Approximately 1.5 pints per acre metolachlor will be needed for every pint of S-metolachlor applied to achieve comparable levels of control.
- 3. Use full-labeled rates calculated based on soil type for the correct amount of active ingredient per acre.

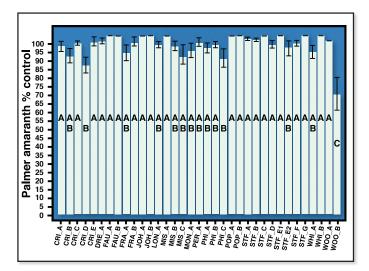


Figure 6. Response of Arkansas Palmer amaranth accessions to *S*-metolachlor (1 pint/acre of Dual Magnum[®]) in 2018.

- 4. Use diversified weed management strategies to mitigate the evolution of herbicide resistance (Norsworthy et al. 2012).
- 5. Consider rotation to other Group 15 herbicides such as dimethenamid-P (Outlook®), acetochlor (Warrant®) and pyroxasulfone (Zidua®) as these products are also efficacious on Palmer amaranth, and crossresistance has not been identified at this time. However, a slight reduction in sensitivity has been documented; therefore, relying on dimethenamid-P, acetochlor or pyroxasulfone alone for residual control is not recommended and could result in rapid resistance to these herbicides.
- 6. S-metolachlor is still a viable option in most environments for Palmer amaranth control, and no grasses have documented Group 15 resistance in Arkansas. Care should be taken to use S-metolachlor and other Group 15 herbicides in conjunction with herbicides utilizing an alternative mode-of-action (i.e., metribuzin) to prolong the life of this effective herbicide.

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