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Relating initial paraquat injury to final efficacy in selected weed species influenced by environmental conditions

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Research Article

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Nomenclature:
Paraquat; giant ragweed, *Ambrosia trifida* L.; horseweed, *Conyza canadensis* (L.) Cronq; Palmer amaranth, *Amaranthus palmeri* S. Watson; purple deadnettle, *Lamium purpureum* L.; waterhemp, *Amaranthus tuberculatus* (Moq.) J.D. Sauer

Keywords:
Adjuvant; application time of day; bipyridilium; light intensity; methyl-viologen; temperature; Weibull

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Abstract

Weed control of paraquat can be erratic and may be attributable to differing species sensitivity and/or environmental factors for which minor guidance is available on commercial labels. Therefore, the objectives of this research were to quantify selectivity of paraquat across select weed species and the influence of environmental factors. Experiments were performed under controlled conditions in the greenhouse and growth chamber. Compared with purple deadnettle (dose necessary to reduce shoot biomass by 50% = 39 g ai ha^{-1}), waterhemp, Palmer amaranth, giant ragweed, and horseweed were 4.9, 3.3, 1.9, and 1.3 times more sensitive to paraquat, respectively. The injury progression rate over 3 d after treatment (DAT) was a more accurate predictor of final efficacy at 14 DAT than the lag phase until symptoms first appeared. For example, at the 17.5 g ha^{-1} dose, the injury rate of waterhemp and Palmer amaranth was, on average, 3.6 times greater than that of horseweed and purple deadnettle. The influence of various environmental factors on paraquat efficacy was weed specific. Applications made at sunrise improved control of purple deadnettle over applications at solar noon or sunset. Lower light intensities (200 or 600 μmol m^{-2} s^{-1}) surrounding the time of application improved control of waterhemp and horseweed more than 1,000 μmol m^{-2} s^{-1}. Day/night temperatures of 27/16 C improved horseweed and purple deadnettle control compared with day/night temperatures of 18/13 C. Though control was positively associated with injury rates in the application time of day and temperature experiments, a negative relationship was observed for waterhemp in the light-intensity experiment. Thus, although there are conditions that enhance paraquat efficacy, the specific target species must also be considered. These results advocate paraquat dose recommendations, currently based on weed height, be expanded to address sensitivity differences among weeds. Moreover, these findings contrast with paraquat labels stating temperatures of 13 C or lower do not reduce paraquat efficacy.

Introduction

Paraquat was commercialized in 1961 as the first nonselective, soil-inactivated herbicide (Hawkes 2014). Only glyphosate and glufosinate have since been commercialized with these same elusive properties desirable for no-tillage crop production. Historically, glyphosate has been preferred over paraquat as a preplant herbicide, because of the superior efficacy of glyphosate on grass and perennial weed species (Duke 2018). As the persistent spread of glyphosate-resistant weeds continues, the utility of glyphosate has narrowed while paraquat has gained renewed interest for control of these weed biotypes. For example, from 2017 to 2018, use of paraquat as a preplant herbicide in soybean [*Glycine max* (L.) Merr.] in the United States increased by 58% [USDA 2019].

Paraquat is an inhibitor of photosynthesis as an electron diverter of photosystem I (PSI). In the presence of light, the divalent paraquat cation accepts an electron from plastocyanin at PSI. The reduced paraquat radical quickly reacts with dioxygen, forming superoxide. In turn, this reaction oxidizes the paraquat radical back to the stable divalent state where it may once again be photoreduced. This cyclical action generates a buildup of superoxide and, via subsequent reactions, other reactive oxygen species (ROS) (Hawkes 2014). As the accumulation of ROS exceeds the detoxifying capacity of the antioxidant system, lipid peroxidation ensues, resulting in a loss of cell-membrane integrity and causing foliage to wilt. In full sunlight, visual injury symptoms are apparent only a few hours after treatment (HAT), with complete foliar necrosis by 3 d after treatment (DAT) (Shaner 2014).

Foliar absorption of paraquat is rapid; more than half of applied paraquat was absorbed within 1 HAT on several species (Brian 1967). Paraquat is extremely hydrophilic (log of the octanol/water partition coefficient = −4.5); consequently, apoplastic transport predominates (Shaner 2014). However, active transport into the symplast via cell membrane–bound polyamine carriers does occur (Hart et al. 1993). Although transport of foliar-applied paraquat to belowground structures has been reported in quackgrass [*Elymus repens* (L.) Gould] (Putnam and Ries 1968) and potato (*Solanum tuberosum* L.) (Calderbank and Slade 1966), in most species, the redox properties of paraquat at PSI prompt such rapid desiccation that mobility is self-limited (Hawkes 2014). For example, in mile-a-minute (*Mikania micrantha* Kunth), only 3% of absorbed paraquat translocated from the treated leaf by 72 HAT (Ipor and Price 1994).

Delaying the photoreduction of paraquat by keeping treated plants in darkness increases translocation and, upon exposure to light, improved control compared with plants kept in continuous light (Slade and Bell 1966). Thus, it is plausible that any factor that limits irradiance around the time of application may benefit final efficacy. Evaluating paraquat on failed corn (*Zea mays* L.) stands, Norsworthy et al. (2011) reported an 85% increase in efficacy from applications made at sunset versus sunrise. Similarly, the percentage of surviving horseweed plants after paraquat applications at sunrise, midday, and sunset were 34%, 75%, and 4%, respectively (Montgomery et al. 2017). Paraquat applications to mile-a-minute under 75% shade improved control 37% to 43% compared with plants in no shade (Ipor and Price 1994). Using chlorophyll fluorescence as a surrogate measure of horseweed control, Lehoczki et al. (1992) reported greater paraquat activity from applications made under a light intensity of 80 μmol m^{-2} s^{-1} compared with 1,500 μmol m^{-2} s^{-1}. Although quantifying the rate at which paraquat injury symptoms developed was not an objective of these works, based on early control ratings (e.g., 3 or 7 DAT), slower injury progression tended to be associated with greater overall paraquat efficacy. Because injury from paraquat can develop within a few hours, ratings at earlier time points would provide more clarity on this relationship.

Air temperature also influences paraquat efficacy. For example, injury to kidney bean (*Phaseolus vulgaris* L.) increased concomitantly with temperature (Barnes and Lynd 1967; Merkle et al. 1965). On horseweed, Eubank et al. (2012) observed poor control (30% to 50%) from applications at 8 C compared with 16 C (72% to 88% control). These observations may be explained by differences in translocation because nearly 30% more absorbed paraquat moved from the treated leaf of foxtail barley [*Hordeum murinum* L. ssp. *leporinum* (Link) Arcang.] at 30 C versus 15 C (Purba et al. 1995). The rate of injury progression from paraquat cannot be discerned from these studies; however, anecdotal observations indicate early paraquat activity is greater at warmer temperatures.

Commercial recommendations for paraquat applications include the addition of nonionic surfactant (NIS) or crop oil concentrate (COC) (e.g., Anonymous 2018, 2019). Previous research has predominantly focused on NIS and tends to agree this adjuvant improves paraquat efficacy over no adjuvant (Ekins et al. 1970; Evans and Eckert 1965; Putnam and Ries 1968). The degree to which NIS enhances paraquat efficacy, however, appears to be species specific (Smith and Foy 1967). Work by Putnam and Ries (1968) indicates greater control from the addition of NIS arises from increased foliar absorption rates, causing injury to occur sooner than with paraquat alone.

Regarding use as a preplant herbicide for corn and soybean, suggested doses of commercial paraquat products depend on weed height, with little acknowledgment of sensitivity differences between weed species (Anonymous 2018, 2019). Moreover, references to environmental conditions that affect efficacy are minimal, stating temperatures below 13 C or overcast skies may slow activity, but not alter performance. As previously discussed, these statements do not entirely align with the scientific literature and may explain observations of inconsistent control from paraquat across species and/or environments (Askew et al. 2019; Blackburn and Weldon 1965; Eubank et al. 2008; Wilson et al. 1985).

Surveys conducted throughout the midwestern United States indicate growers rank Palmer amaranth, waterhemp, and giant ragweed among the most problematic summer annual weeds in agronomic crops, and horseweed and purple deadnettle as problematic winter annual weeds (Gibson et al. 2005; Kruger et al. 2009; Van Wychen 2015, 2019). Although weeds with a later emergence window, such as Palmer amaranth and waterhemp, may not be prevalent at the time of a preplant paraquat application for corn and full-season soybean, they are among the predominant weeds in wheat stubble fields prior to planting double-crop soybean (Hager 2020). Scant literature exists on how environmental or application factors influence paraquat efficacy among these weed species, except horseweed. Furthermore, although the speed of paraquat symptomology has been implicated as a potential predictor of overall control, research directly oriented to address this theory across multiple species and environmental factors is deficient in the literature. Therefore, the objectives of this research were to (1) compare the relative sensitivity of five problematic weed species to paraquat, (2) identify environmental or application factors that influence paraquat efficacy on these weed species, and (3) determine if initial paraquat injury is a useful predictor of final efficacy.

Materials and Methods

Plant Propagation

Palmer amaranth, waterhemp, giant ragweed, horseweed, and purple deadnettle seeds were planted in separate, 25- by 50-cm flats containing commercial potting mix (Metro-Mix®; SunGro Horticulture, Agwam, MA). Prior to planting, purple deadnettle seeds were imbibed and incubated with a 0.2% KNO_3 solution for 24 h at 25 C to promote germination. Flats were placed in a greenhouse with day and night temperatures of 30 and 25 C (±5 C), respectively, with high-pressure sodium bulbs supplementing natural lighting and programmed for a 16-h photoperiod. When the first true leaves had formed, individual plants were transplanted into 10- by 10-cm pots filled with commercial potting mix. Pots were watered daily and fertilized weekly with a macro- and micronutrient fertilizer [Jack's Classic Professional (20-20-20); JR Peters, Allentown, PA] to promote optimal plant growth. Unless stated otherwise, all herbicide applications were made 1 h after supplemental lights turned on in the morning and on days with a forecast of full sun. Plant heights at the time of all applications were 8 to 10 cm for Palmer amaranth and waterhemp, 10 to 12 cm for giant ragweed, and 6 to 8 cm for purple deadnettle; horseweed (rosette stage) diam was 8 to 10 cm.

Dose Response

Paraquat (Gramoxone® 2.0 SL; Syngenta Crop Protection, Greensboro, NC) doses of 0, 1.1, 2.2, 4.4, 8.8, 17.5, 35, 70, and 140 g ai ha^{-1} were applied with NIS (Activator 90; Loveland Products, Loveland, CO) at 0.25% vol/vol using a single-nozzle (XR8002EVS; TeeJet® Technologies, Urbandale, IA) spray booth calibrated to deliver 140 L ha^{-1} at 276 kPa. Visual estimations of injury were recorded at 2, 4, 6, 8, 12, 24, 48, and 72 HAT using a scale of 0 (no wilted or necrotic tissue) to 100 (completely necrotic tissue). At 14 DAT, apical meristems were rated using a

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binary scale of 1 (green tissue present) or 0 (green tissue absent). After this rating, shoot tissue was cut at the soil level, dried at 43 C until constant weight, and weighed.

Environmental and Application Factors

On the basis of preliminary research to obtain a moderate level of paraquat efficacy, Palmer amaranth and waterhemp were treated with 17.5 g ha^{-1} paraquat, while giant ragweed, horseweed, and purple deadnettle were treated with 35 g ha^{-1}. Nontreated plants were included as control groups. Unless stated otherwise, NIS was included at 0.25% vol/vol in the spray solution and applications were made as previously described. Visual estimations of injury were recorded at 6, 12, 24, 48, and 72 HAT with the exception of the application time of day, described in the next paragraph. Shoot biomass was measured at 14 DAT as previously described.

Application time of day

Three days before paraquat treatment, timers for supplemental lighting were adjusted to turn on 1 h after sunrise and turn off 1 h before sunset. The daylength at this time was approximately 12 h. On the day of application, plants were sprayed 1 h after sunrise (hereafter, sunrise), at solar noon, or 1 h before sunset (hereafter, sunset). At 48 HAT, greenhouse lighting was adjusted to the 16-h photoperiod as previously described. Injury ratings were recorded at 24 and 48 HAT for each respective application time of day and again at 72 and 168 HAT, relative to the sunrise application.

Light intensity

Plants were moved from the greenhouse to a growth chamber (Conviron® Controlled Environments, North Branch, MN) 3 d before paraquat treatment. Growth chamber settings were 27 C, 70% relative humidity, and a 16-h photoperiod with light intensities of 1,000, 600, or 200 µmol m^{-2} s^{-1} photon flux density. These values were selected to simulate full sun, partly cloudy, or cloudy days in West Lafayette, IN, as confirmed using a quantum sensor (Apogee Instruments, Logan, UT). Plants were returned to the greenhouse at 48 HAT.

Temperature

Plants were moved from the greenhouse to a growth chamber 3 d before paraquat treatment. Growth chamber settings were 70% relative humidity, 1,000 µmol m^{-2} s^{-1} light intensity on a 16-h photoperiod, and day/night temperatures of 27/16 or 18/13 C. Temperatures were selected to simulate a preplant application for double-crop soybean following wheat harvest (late June) or in the spring (mid-April to mid-May) and were based on 30-yr averages in West Lafayette, IN [NOAA 2017]. Plants were returned to the greenhouse at 48 HAT.

Adjuvant

Paraquat was applied with 1% vol/vol COC (Prime Oil; Winfield Solutions, St. Paul, MN), 0.25% vol/vol NIS, or no adjuvant.

Experimental Design and Analysis

Experiments were arranged as randomized complete block designs with four replications, except for the temperature experiment, which consisted of five replications. All experiments were performed twice. PROC UNIVARIATE (SAS, version 9.4; SAS Institute, Cary, NC) and Levene's test were used to test ANOVA assumptions, and appropriate transformations were applied when necessary. PROC MIXED was used to perform ANOVA, treating replication (block) and experimental run as random effects. Means were separated using Fisher's protected LSD ($\alpha = 0.05$).

For the following models, initial selection was guided by our knowledge of the subject matter and data to select models with meaningful biological parameters in addition to corrected Akaike information criterion values (Anderson 2008). Additional measures of goodness of fit (root mean square error and model efficiency coefficient) for each experiment are provided in Supplementary Table 1. Shoot biomass and apical meristem data from the dose-response experiment were fit using PROC NLIN to a four-parameter log-logistic model (Equation 1):

$$f(x) = C + \frac{D - C}{1 + \exp(b[\log x - \log e])} \qquad [1]$$

where C is the lower limit, D is the upper limit, b is the slope of the curve around e, x is the paraquat dose, and e is the dose necessary to reduce shoot biomass by 50% (GR_{50}) or terminate 50% of apical meristems (ED_{50}) (Seefeldt et al. 1995). Although a three-parameter log-logistic model provided the best fit, based on corrected Akaike information criterion values, the four-parameter model was selected to remain consistent with the majority of dose-response analyses in the weed science literature; furthermore, interpretation of the results did not differ between the two models. Injury data of 0 to 72 HAT from paraquat doses near the GR_{50} values were fit to a four-parameter Weibull model modified from Brown (1987) (Equation 2):

$$f(t) = M(1 - \exp[-(k[t - l])^c]) \qquad [2]$$

where M is the maximum percent injury, k is the injury progression rate, t is time, l is the lag phase until first injury symptoms, and c is the shape parameter. To determine if differences in the injury progression rate or lag phase between species were indicative of differences in shoot biomass reduction at 14 DAT, k and l were used as predictor variables in multiple regression (PROC REG). M was excluded from regression analysis to reduce multicollinearity.

Because of the delayed rating schedule for the time of day, light intensity, temperature, and adjuvant experiments compared with the dose-response experiment, injury data could not be fit to the Weibull model. Rather, these data were fit to a two-parameter exponential rise to maximum model (Equation 3):

$$f(t) = M(1 - \exp[-kt]) \qquad [3]$$

where M is the maximum percent injury, k is the injury progression rate, and t is time (Archontoulis and Miguez 2015). Regression analysis was used to evaluate the relationship of k as a predictor variable for shoot biomass reduction at 14 DAT.

Results and Discussion

Dose Response

Waterhemp and Palmer amaranth were most sensitive to paraquat with GR_{50} (biomass reduction) values of 8 and 12 g ha^{-1}, respectively, whereas horseweed and purple deadnettle were least sensitive with GR_{50} values of 30 and 39 g ha^{-1}, respectively (Table 1). Paraquat sensitivity of giant ragweed was intermediate, with a

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Table 1. Parameter estimates of paraquat dose resulting in GR_{50} of shoot dry weight and ED_{50} to apical meristems on five weed species determined at 14 d after treatment and derived from a four-parameter log-logistic model (Equation 1).

Species	Life cycle[a]	PS	Parameter				Sensitivity ratio[c]	Parameter				Sensitivity ratio
			C	*D*	*b*	GR_{50} (95% CI)[b]		*C*	*D*	*b*	ED_{50} (95% CI)	
						g ai ha^{-1}					g ai ha^{-1}	
Waterhemp	SA	C4	−2	100	−0.8	8 (4 to 12)	4.9	0	100	−6.4	18 (8 to 28)	3.1
Palmer amaranth	SA	C4	4	97	−1.2	12 (8 to 16)	3.3	0	98	−7.6	18 (15 to 21)	3.1
Giant ragweed	SA	C3	9	103	−1.1	21 (5 to 37)	1.9	0	103	−1.2	40 (28 to 52)	1.4
Horseweed	WA	C3	−11	105	−1.4	30 (18 to 42)	1.3	0	101	−2.4	52 (44 to 60)	1.1
Purple deadnettle	WA	C3	−8	99	−1.0	39 (19 to 59)	1.0	0	101	−1.9	56 (38 to 74)	1.0

[a]Abbreviations: *b*, slope of the curve around GR_{50} or ED_{50}; *C*, lower limit; *D*, upper limit; ED_{50}, 50% lethality to apical meristems; GR_{50}, 50% reduction of shoot dry weight; PS, photosynthetic pathway; SA, summer annual; WA, winter annual.
[b]$n = 8$. Species with confidence intervals that do not overlap were concluded to differ in sensitivity to paraquat.
[c]Comparison of GR_{50} or ED_{50} relative to the least sensitive species, purple deadnettle.

Table 2. Parameter estimates of paraquat injury on five weed species from 0 to 72 h after treatment derived from a four-parameter Weibull function (Equation 2).

Dose	Species	*M*[a]	*K* (SE)	*l*	*c* (SE)
g ai ha^{-1}		% (SE)		h (SE)	
8.8	Palmer amaranth	57 (2)	0.24 (0.06)	1.2 (1.1)	1.6 (0.6)
	Waterhemp	60 (2)	0.30 (0.12)	2.6 (1.9)	1.3 (0.9)
	Giant ragweed	47 (6)	0.11 (0.06)	4.0 (2.5)	0.8 (0.4)
	Purple deadnettle	12 (2)	0.11 (0.05)	5.9 (1.3)	1.0 (0.7)
	Horseweed[b]	3 (1)	—	60 (4.5)	—
17.5	Palmer amaranth	75 (2)	0.29 (0.05)	1.7 (0.4)	1.1 (0.3)
	Waterhemp	75 (2)	0.26 (0.06)	1.1 (0.4)	3.4 (1.5)
	Giant ragweed	70 (3)	0.11 (0.07)	1.6 (0.7)	1.0 (0.2)
	Purple deadnettle	30 (2)	0.12 (0.02)	3.6 (1.4)	3.0 (0.7)
	Horseweed	15 (3)	0.03 (0.01)	13.6 (4.1)	1.3 (0.8)
35	Palmer amaranth	89 (1)	0.24 (0.02)	1.7 (0.3)	1.4 (0.2)
	Waterhemp	83 (2)	0.30 (0.10)	1.1 (0.8)	2.1 (0.9)
	Giant ragweed	80 (4)	0.18 (0.04)	1.9 (0.2)	0.7 (0.1)
	Purple deadnettle	64 (3)	0.24 (0.10)	4.0 (1.5)	1.1 (1.0)
	Horseweed	70 (8)	0.05 (0.01)	7.6 (0.9)	0.8 (0.3)

[a]Abbreviations: —, unable to be determined; *c*, shape; *k*, injury progression rate; *l*, lag phase until first injury symptoms; *M*, maximum injury.
[b]Data did not fit model. Values are averages based on visual injury ratings.

GR_{50} value (21 g ha^{-1}) similar to the other weed species. Evaluations based on the presence of green tissue supported the biomass data, with waterhemp and Palmer amaranth exhibiting greater sensitivity to paraquat than giant ragweed, horseweed, and purple deadnettle (Table 1). Sensitivity differences to paraquat among these weed species may be attributable to life cycle and photosynthetic pathway because, generally, summer annual species were more sensitive than winter annual species and species with a C4 photosynthetic pathway were more sensitive than C3 species. Winter annuals are inherently cold tolerant through adaptations such as a thickened leaf cuticle and enhanced ROS-detoxifying system (Preston and Sandve 2013) and thus may hinder paraquat absorption and subsequent ROS accumulation. Moreover, the greater photosynthetic rate of C4 versus C3 species suggests more rapid electron shuttling through PSI for redox of paraquat (Pearcy and Ehleringer 1984).

The injury progression rate was greatest for Palmer amaranth and waterhemp at the 8.8 and 17.5 g ha^{-1} paraquat dose, and by 72 HAT, these species had incurred 45% greater injury compared with horseweed and purple deadnettle (Table 2; Figure 1). At these doses, the rate of injury was similar between giant ragweed and purple deadnettle. However, symptomology progressed over a longer time on giant ragweed, resulting in injury levels nearer to that of Palmer amaranth and waterhemp by 72 HAT. Although increasing the paraquat dose to 35 g ha^{-1} resulted in greater injury at 72 HAT across all species, the effect on injury rate and lag phase was negligible for Palmer amaranth and waterhemp. For giant ragweed and purple deadnettle, increasing the dose from 8.8 to 17.5 g ha^{-1} reduced the lag phase, whereas increasing the dose from 17.5 to 35 g ha^{-1} increased the rate of injury. There were substantial differences for both the injury rate and lag phase for horseweed compared with other species. In addition to an injury rate more than three times slower, the lag phase was 3.6 to 12.5 h longer than the other species, depending on paraquat dose. Across all three doses, results of multiple regression indicated the injury progression rate over 72 HAT was a more accurate predictor of shoot biomass reduction at 14 DAT than the lag phase until first symptomology (Figure 1, inset). Comparisons in the literature are difficult because studies in which paraquat efficacy was evaluated on several weeds, the progression of injury was not reported (Blackburn and Weldon 1965; Wehtje et al. 1992a, 1992b).

Environmental and Application Factors

The visual injury rating schedule for these experiments did not conform to the Weibull model, therefore, a different model (Equation 3) was required to describe the rate of injury progression. Thus, a constraint of this research is that rate parameters from the following experiments are not directly comparable to those from the dose-response experiment.

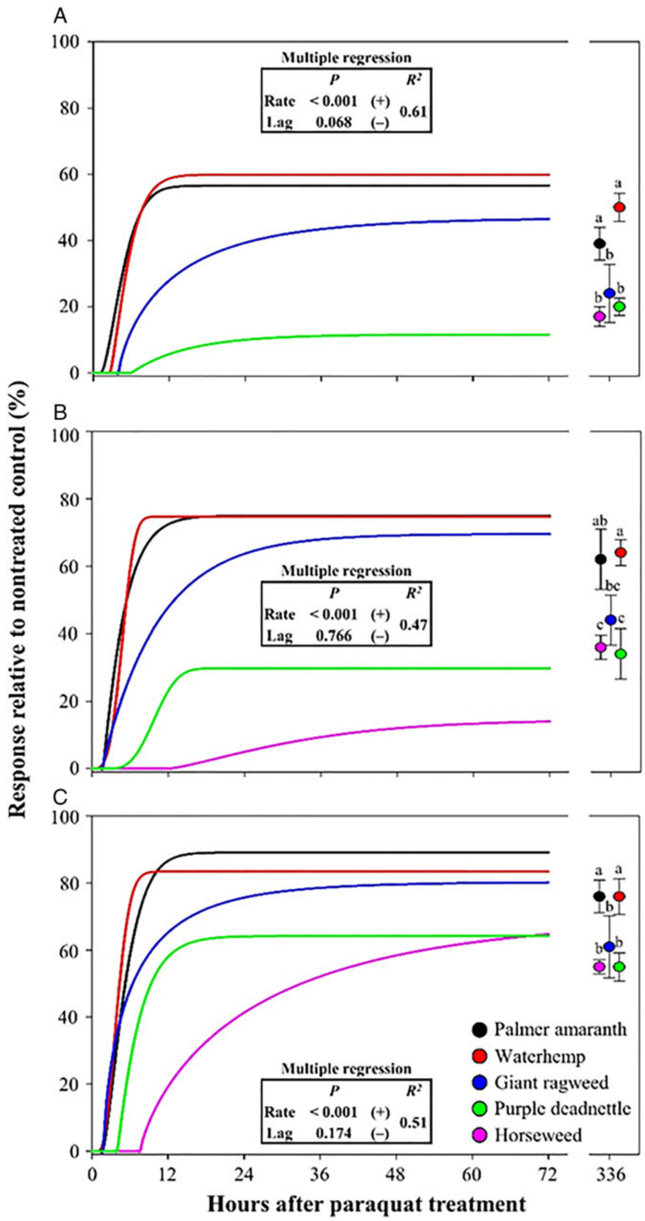

Figure 1. Injury progression (0–72 h) and shoot biomass reduction (336 h/14 d) from paraquat doses of: (A) 8.8 g ai ha^{-1}, (B) 17.5 g ha^{-1}, and (C) 35 g ha^{-1} on five weed species. Injury progression (% visual estimate) is represented by solid lines fit to a four-parameter Weibull function (Equation 2); parameter estimates are provided in Table 2. Horseweed data for the 8.8 g ha^{-1} dose did not fit the model. The circular symbols with SE bars ($n = 8$) represent the mean shoot biomass reduction (% dry weight from nontreated) with mean separation per Fisher's protected LSD ($\alpha = 0.05$), and letters indicate statistical significance. The injury progression rate and lag phase until first injury symptoms at each paraquat dose were used as predictor variables for shoot biomass reduction through multiple regression. Regression statistics are shown as an inset table with ± indicating the relationship direction (i.e., species with a greater rate of injury over 72 h had greater biomass reduction at 14 d).

Application time of day

By 14 DAT, paraquat application time of day only affected shoot biomass reduction in purple deadnettle with 23% and 34% greater control from sunrise applications compared with solar noon and sunset applications, respectively (Figure 2). Applications made at sunrise or solar noon resulted in a greater rate of injury compared with sunset applications on all species except giant ragweed. However, a greater injury rate was only associated with greater shoot biomass reduction in purple deadnettle (Figure 2E, inset). These results are in contrast to previous paraquat application-time-of-day studies whereby sunset applications on horseweed (Montgomery et al. 2017) and corn (Norsworthy et al. 2011) provided greater control than applications made earlier in the day. The authors surmised improved control from sunset applications was due to increased absorption and translocation of paraquat at night. Indeed, the slower rate of injury from sunset applications does indicate less self-limiting mobility potential of paraquat. However, because this delay in symptomology did not translate into greater overall control, deviations from past research may be explained by perturbations of other environmental factors. The studies by Montgomery et al. (2017) and Norsworthy et al. (2011) were performed in the field; thus, the plants were more susceptible to temperature and relative humidity interactions than under greenhouse conditions. Both these factors affect translocation of other herbicides with self-limiting mobility (Coetzer et al. 2001; Ritter and Coble 1981).

Light intensity

Paraquat injury on Palmer amaranth, waterhemp, and purple deadnettle progressed faster from increasing light-intensity treatments, whereas, the injury rate for giant ragweed and horseweed tended to decline with increasing light intensity (Figure 3). Light intensity had no effect on shoot biomass reduction at 14 DAT on Palmer amaranth, giant ragweed, and purple deadnettle. At a light intensity of 200 μmol m^{-2} s^{-1}, waterhemp shoot biomass was reduced 26% to 28% more than at 600 and 1,000 μmol m^{-2} s^{-1} (Figure 3B). Horseweed control was 17% to 18% greater at 200 and 600 μmol m^{-2} s^{-1} than at 1,000 μmol m^{-2} s^{-1} (Figure 3D). The improved control at lower light intensities was associated with a slower rate of injury on waterhemp, whereas there was no significant relationship between these variables on horseweed. Results for waterhemp are consistent with previous reports on other weeds supporting findings that delayed paraquat activity from lower light intensities may yield greater overall control (Ipor and Price 1994; Lehoczki et al. 1992).

Temperature

The rate of paraquat injury was greater across all species under 27/16 C day/night temperatures versus 18/13 C (Figure 4). On the summer annual weeds, Palmer amaranth, waterhemp, and giant ragweed, earlier symptomology at warmer temperatures did not translate to greater shoot biomass reduction at 14 DAT. However, on winter annual weeds, injury rate was positively associated with overall control; shoot biomass reduction of horseweed and purple deadnettle was 34% and 28% greater, respectively, under the warmer temperature regime. Greater absorption of paraquat by kidney bean (a summer annual) was ascribed to an increase in cell-membrane permeability at elevated temperatures (Barnes and Lynd 1967; Merkle et al. 1965). In the winter annual hare barley [*Hordeum leporinum* (Link) Arcang.], acropetal translocation of paraquat nearly doubled at 30 C versus 15 C (Purba et al. 1995). Although increased absorption of paraquat at warmer temperatures may explain the faster rate of injury observed on all species, greater control at 14 DAT of winter annual weeds, compared with summer annual weeds, may be attributable to prolonged translocation. Biokinetics of winter annuals tend to be inherently slower than that of summer annuals and, thus, more sensitive to elevated temperatures (Preston and Sandve 2013).

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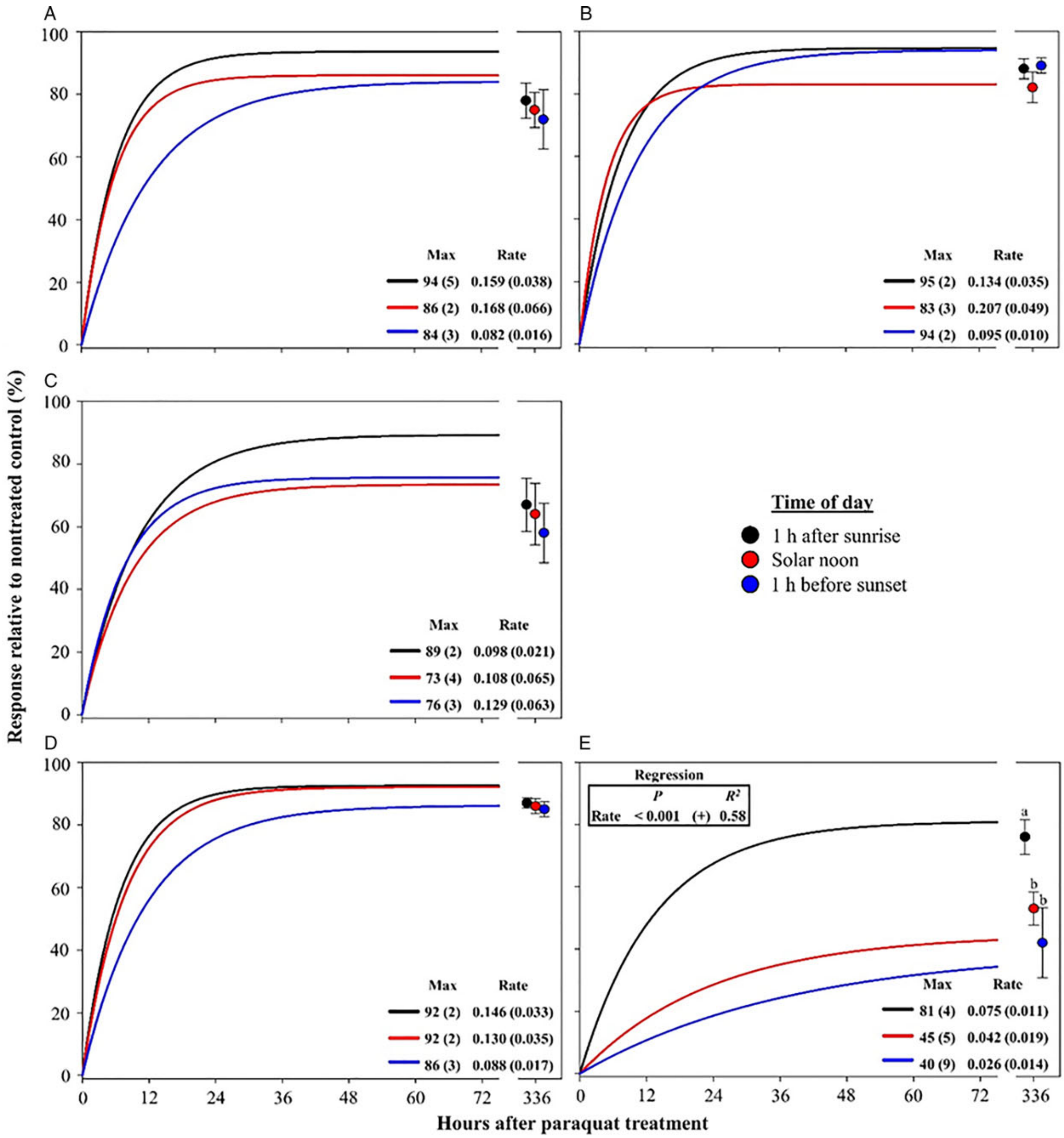

Figure 2. Injury progression (0–72 h) and shoot biomass reduction (336 h/14 d) from paraquat as influenced by application time of day on (A) Palmer amaranth, (B) waterhemp, (C) giant ragweed, (D) horseweed, and (E) purple deadnettle. Paraquat doses were (A, B) 17.5 g ai ha^{-1} and (C–E) 35 g ha^{-1}. Injury progression (% visual estimate) is represented by solid lines fit to an exponential model (Equation 3) with parameter estimates (SE) shown within each graph. The circular symbols with SE bars ($n = 8$) represent the mean shoot biomass reduction (% dry weight from nontreated) with mean separation per Fisher's protected LSD ($\alpha = 0.05$), and letters indicate statistical significance when ANOVA specified a significant treatment effect. The injury progression rate for each species was used as a predictor variable for shoot biomass reduction through regression analysis. When the relationship was significant ($P \leq 0.05$), regression statistics are shown as an inset table, with ± indicating the relationship direction (i.e., application timings causing a greater rate of injury over 72 h on purple deadnettle resulted in greater biomass reduction at 14 d). Abbreviation: Max, maximum.

Application With Adjuvant

Compared with no adjuvant, shoot biomass reduction at 14 DAT was not influenced by the addition of COC or NIS to paraquat on any species (Supplementary Figure 1). Moreover, inclusion of an adjuvant had a negligible effect on the progression of injury symptoms; SEs of rate parameters largely overlapped and the difference in maximum injury ratings between treatments was not greater than 13%. These results are in contrast to previous findings indicating the addition of NIS improved paraquat efficacy (Ekins et al. 1970; Evans and Eckert 1965; Putnam and Ries 1968). However, the species evaluated in this work are possibly less responsive to adjuvant-enhanced paraquat solutions. Smith and Foy (1967) reported the benefit of NIS on paraquat efficacy was much greater on corn than kidney bean. This differential response is further supported by work documenting greater paraquat uptake with the addition of NIS on orchardgrass (*Dactylis glomerata* L.), but not on tomato (*Solanum lycopersicum* L.) (Bland and Brian 1975). Research by Bland and Brian (1975) also revealed adjuvants with COC-like properties (i.e., formulated to permeate membranes) reduce paraquat translocation, likely as a result of excessive

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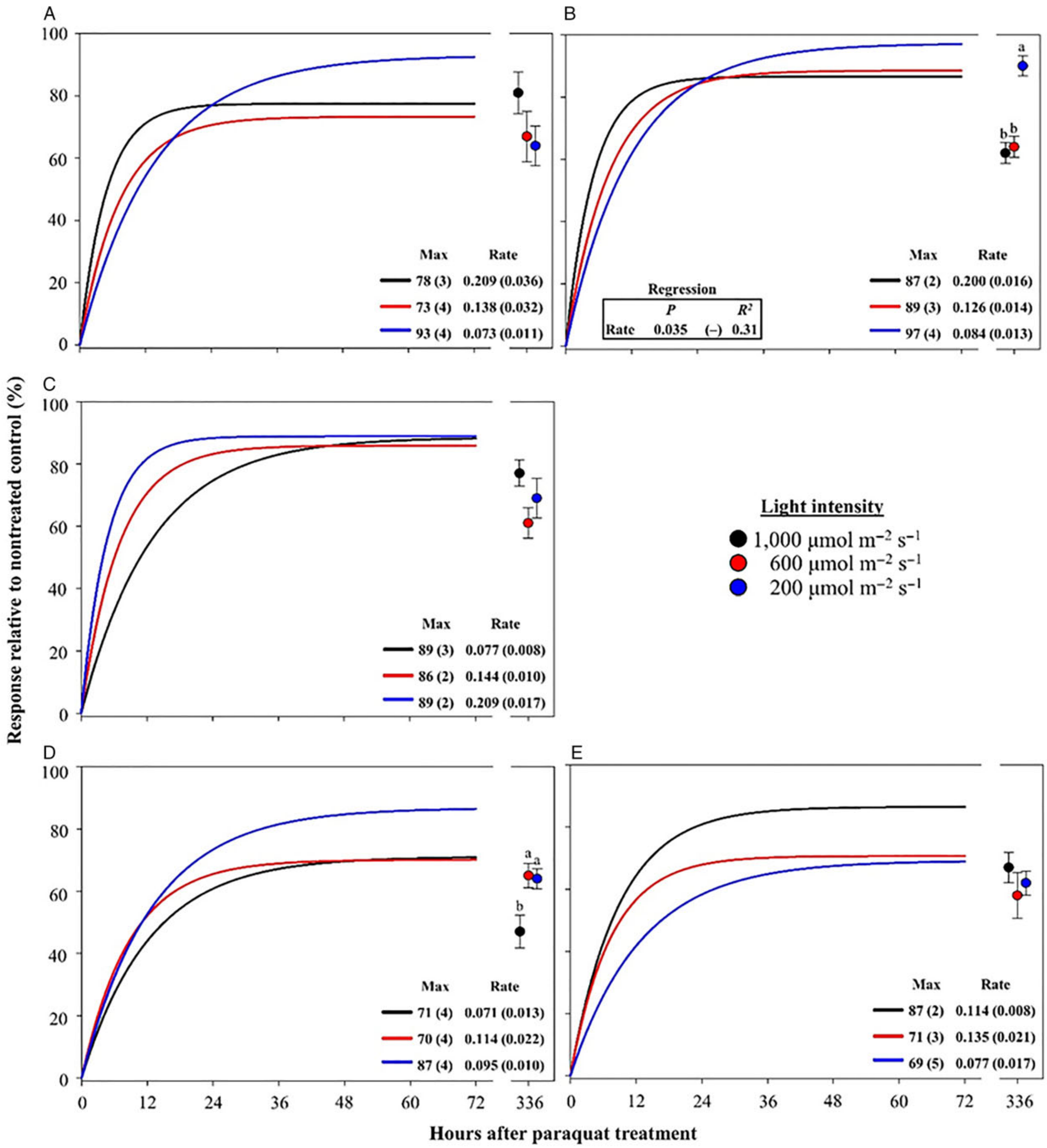

Figure 3. Injury progression (0 to 72 h) and shoot biomass reduction (336 h/14 d) from paraquat as influenced by light intensity on: (A) Palmer amaranth, (B) waterhemp, (C) giant ragweed, (D) horseweed, and (E) purple deadnettle. Paraquat doses were (A, B) 17.5 g ai ha^{-1} and (C–E) 35 g ha^{-1}. Injury progression (% visual estimate) is represented by solid lines fit to an exponential model (Equation 3) with parameter estimates (SE) shown within each graph. The circular symbols with SE bars ($n = 8$) represent the mean shoot biomass reduction (% dry weight from nontreated) with mean separation per Fisher's protected LSD ($\alpha = 0.05$), and statistical significance is indicated by letters when ANOVA specified a significant treatment effect. The injury progression rate for each species was used as a predictor variable for shoot biomass reduction through regression analysis. When relationship was significant ($P \leq 0.05$), regression statistics are shown as an inset table, with ± indicating the relationship direction (i.e., light intensities causing a lower rate of injury over 72 h on waterhemp resulted in greater biomass reduction at 14 d). Abbreviation: Max, maximum.

retention of the hydrophilic paraquat in the leaf cuticle and epicuticular wax. This suggests a hydrophilic route of entry (Hess and Foy 2000) for paraquat is least restrictive and may often benefit from improved leaf wetting provided by NIS. We also acknowledge the lack of adjuvant treatment differences could be attributable to the experiment being performed in the greenhouse. Under field conditions, extreme environmental conditions may result in thicker leaf cuticles, whereby the dose transfer of paraquat could be improved by NIS or COC.

In this study, we document considerable differences in sensitivity to paraquat among five common weeds of agronomic crops. On average, C4 species were three times more sensitive than C3 species and, likewise, summer annuals were 2.5 times more sensitive than winter annuals. Provided these sensitivity differences and the problematic nature of the weed species evaluated, it is advisable to expand paraquat rate recommendations beyond weed height (Anonymous 2018, 2019) and consider the specific target species. Prior research regarding the effect of environmental factors on

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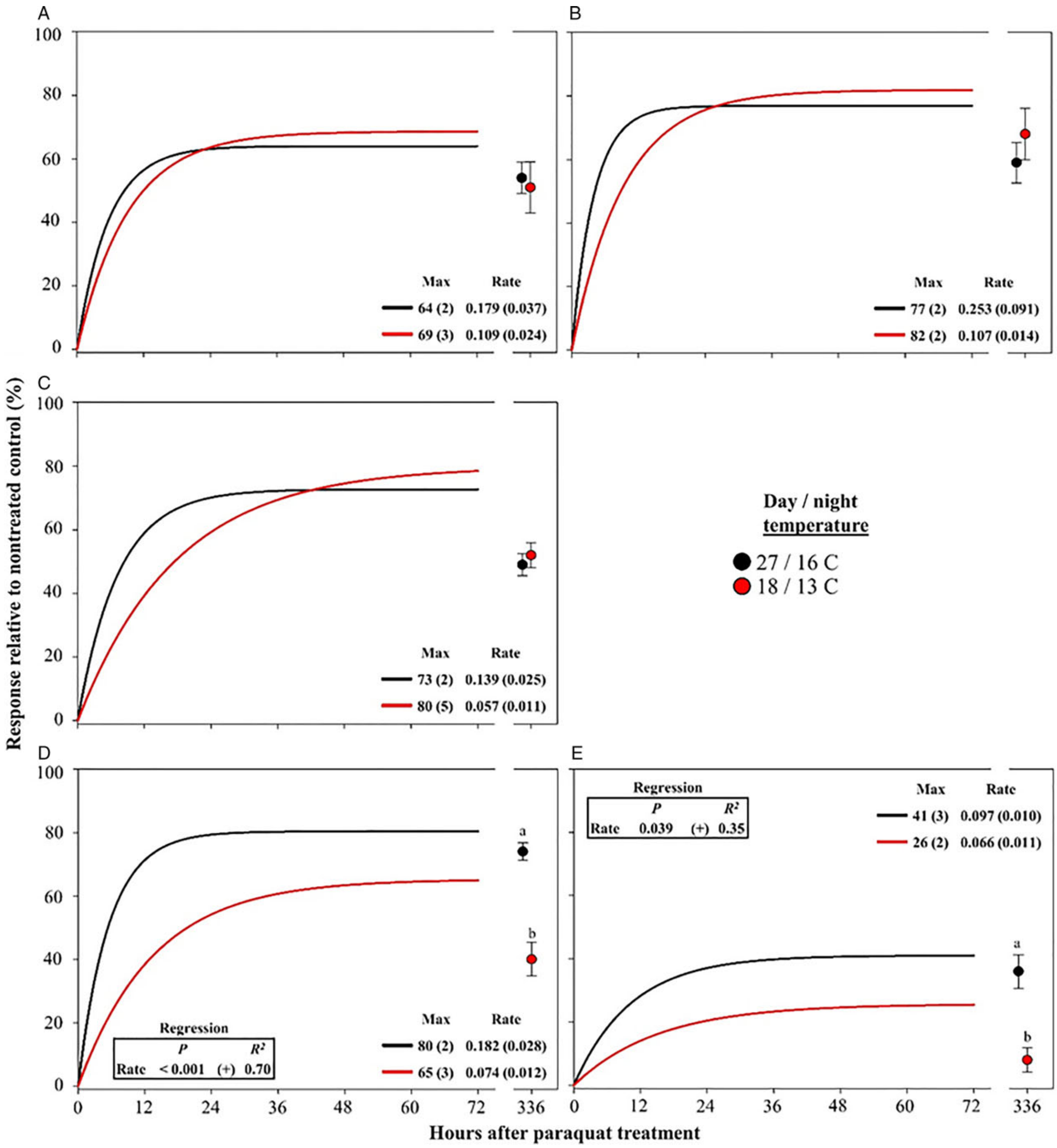

Figure 4. Injury progression (0–72 h) and shoot biomass reduction (336 h/14 d) from paraquat as influenced by air temperature on (A) Palmer amaranth, (B) waterhemp, (C) giant ragweed, (D) horseweed, and (E) purple deadnettle. Paraquat doses were (A, B) 17.5 g ai ha^{-1} and (C–E) 35 g ha^{-1}. Injury progression (% visual estimate) is represented by solid lines fit to an exponential model (Equation 3) with parameter estimates (SE) shown within each graph. The circular symbols with SE bars ($n = 8$) represent the mean shoot biomass reduction (% dry weight from nontreated) with mean separation per Fisher's protected LSD ($\alpha = 0.05$), and statistical significance is indicated by letters when ANOVA specified a significant treatment effect. The injury progression rate for each species was used as a predictor variable for shoot biomass reduction through regression analysis. When the relationship was significant ($P \leq 0.05$), regression statistics are shown as an inset table, with ± indicating the relationship direction (i.e., temperatures causing a greater rate of injury over 72 h on horseweed and purple deadnettle resulted in greater biomass reduction at 14 d). Abbreviation: Max, maximum.

paraquat efficacy has predominately consisted of single-species experiments. By expanding the scope of species investigated, our results indicate the influence of application time of day and light intensity are largely species specific, with no apparent commonalities between weeds with the same photosynthetic pathway or life cycle. In contrast, cooler temperatures (18/13 C day/night) surrounding the time of application reduced paraquat efficacy on the winter annual, but not summer annual, weeds. These results do not align with commercial paraquat labels stating temperatures of 13 C will slow activity but not alter performance (e.g. Anonymous 2018, 2019). Our research was not designed to determine the specific temperature threshold at which paraquat efficacy is no longer reduced. However, based on these findings, paraquat applications would be recommended when day/night temperatures are above 18/13 C when winter annual weeds such as horseweed and purple deadnettle are present. Although results did not show a benefit to paraquat efficacy by the addition of NIS or COC, it is prudent that applicators abide by all label requirements,

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because utility of these adjuvants may be more apparent under field conditions and on other weed species not evaluated in this work. Furthermore, the use of NIS may optimize paraquat efficacy by allowing for foliar uptake through a hydrophilic route.

By assessing paraquat symptomology at earlier time points compared with previous studies, injury rate parameters were derived over 72 HAT and effectively predicted differences in control at 14 DAT, such that greater control was achieved on species with faster injury progression. Because research on the differential sensitivity to paraquat among weeds is limited, this relationship may prove useful in the field as a means of gauging, at an early stage, which species are more likely to escape control. A common perception for herbicides eliciting rapid progression of leaf necrosis (e.g., paraquat, glufosinate) is that this damage limits herbicide translocation and potential efficacy (Hawkes 2014; Steckel et al. 1997). Slow initial paraquat activity, particularly from applications at sunset or low light intensities, has been proposed to enhance overall efficacy (Dinis-Oliveira et al. 2008; Norsworthy et al. 2011). However, differing injury rates within a species, caused by various environmental factors, rarely corresponded to differences in control, with a few exceptions. Improved control of purple deadnettle was associated with a greater injury rate from sunrise applications, improved control of waterhemp was associated with a lower injury rate from low light intensity, and improved control of horseweed and purple deadnettle was associated with a greater injury rate at elevated temperatures. Thus, whereas certain environmental conditions can optimize paraquat efficacy, the specific target weed species must also be considered. Indeed, classical herbicide physiology experiments addressing the environment and species interaction to paraquat would provide clarity by identifying potential absorption or translocation differences between weeds. Plants grown under controlled environments generally are exposed to fewer abiotic and biotic stressors that can alter plant anatomy and herbicide efficacy. Thus, a limitation of greenhouse and growth chamber experiments is that treatment effects may differ compared with those observed in a field setting, and field experiments with precise environmental monitoring would be useful to further validate the findings of this research. As paraquat becomes more widely used as an alternative preplant herbicide to glyphosate, results of this work may be used to deliver more impactful recommendations than what currently exist on commercial paraquat labels.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1017/wet.2020.109

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