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ORIGINAL ARTICLE

Contact herbicidal activity optimization of methyl capped polyethylene glycol ester of pelargonic acid

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Abstract
The loss of important contact herbicides like paraquat opens opportunities for more potentially sustainable solutions demanded by consumers and organizations. Frequently, for adequate weed control, the alternatives to classical synthetic products need well-defined and executed labels and even more detailed use descriptions. One novel candidate with rare contact activity is a pelargonic acid ester of methyl polyethylene glycol (PA-MPEG) with advantages over free pelargonic acid (PA), such as reduced volatility and ease of formulation. Here, we report on the role of the application parameters such as spray volume, rate, sprayer set-up, and climate conditions for weed control with PA-MPEG. At a dose rate of 12.8 kg ae ha^{-1} in a spray volume of 500 L ha^{-1}, control of *Digitaria sanguinalis* (L.) Scop. and *Solanum nigrum* L. was excellent. These values for product rate and spray volume are lower than applications with commercial PA herbicides, at equal or better efficacy. Coverage was too low at spray volumes of 100 to 200 L ha^{-1}, for adequate contact activity of both PA-MPEG and PA. Weed control was significantly increased when PA-MPEG application was made at lower boom height with reduced distance to weed canopy, or under warm and dry climate conditions. The results indicate the potential of PA-MPEG under optimal use conditions as a new contact herbicide in integrated weed management.

Keywords Pelargonic acid · Weed canopy · Coverage · Climate conditions · Application parameters

Introduction

Free linear nonanoic acid, which is also commonly known as pelargonic acid (PA), its salts, or related octanoic and decanoic (C_8–C_{10}) fatty acids have been used to control weeds for over 30 years as nonselective contact herbicides that damage only the plant part in spray contact with the product (Ciriminna et at. 2019; Coleman and Penner 2006; Dayan and Duke 2010; EPA 2020). Therefore, good spray coverage given by high spray volume and growing young plants is essential for good weed control (Webber and Shrefler 2006). PA is fast-acting and causes desiccation symptoms on the treated organ within only a few hours. This differs greatly from systemic herbicides, where visible symptoms may develop only after several days to weeks after application (Fukuda et al. 2004; Jeschke et al. 2019; Lederer et al. 2004). The root system is not directly affected because PA herbicidal activity is limited to the above-ground contact area with no translocation, thus weeds may show regrowth from their roots or rhizomes. Therefore, repeated applications might be required for long-lasting control by exhausting energy reserves in underground plant organs and also eroding leaf surface waxes (Krauss et al. 2020; Webber et al. 2014). The mechanism of action of PA is related to effective foliar uptake via the cuticle and erosion of surface waxes, and a moderate increase in cuticular transpiration can sometimes be observed (Ciriminna et al. 2019). The main mode of action (MoA) is related to the release of lipids after membranes disintegration (Fukuda et al. 2004; Lederer et al. 2004), and it was recently suggested that tissue desiccation and ultimately leaf death are related to an interruption of water cohesion in the cell walls (Campos et al. 2022) and thus the soil–plant–atmosphere continuum.

The withdrawal or restriction of contact herbicides like paraquat or diquat (Dinham 2004; EUR-Lex 2020) and the

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ongoing concerns about glyphosate use (Carvalho 2017; Van Bruggen et al. 2018) justify further investigation of the potential improvement of PA (Coleman and Penner 2008; Travlos et al. 2020). This burndown herbicide is considered one alternative to glyphosate in certain applications (Fogliatto et al. 2020), and it is suggested to be incorporated in weed management programmes in agricultural (broadacre and plantations) (Kanatas et al. 2020, 2021) and non-agricultural (industrial, railways garden, etc.) uses (Barker and Prostak 2014). However, PA remains largely unutilized by farmers even in those instances in which its use could be indicated. For example, in 2019, only 0.7% of the potato fields in Belgium were treated with PA, and similarly, Spanish farmers used PA just in 0.3% of the vineyard area (Kleffmann group 2021). Also, PA is sometimes mistakenly compared to glyphosate; for example, applying it to well-established weeds (50 cm tall), which leads to a false expectation of efficacy and ill-use of the product (Baur and Campos 2019; personal communication). Besides the high use rate and prices of PA (Ciriminna et al. 2019), this lack of knowledge by farmers to properly integrate this herbicide into weed management programmes, and the undefined instructions on the label like on the role of weather conditions, continue to make PA a niche product for the plant protection market (Fogliatto et al. 2020; Marrone 2019).

The use of alternatives to conventional herbicides needs to be optimized. While PA products have been registered since 1992, optimum application parameters such as nozzles, pressure, boom height, or climate conditions are still barely known.

Recently, new compounds based on short-chain (C_6–C_{12}) fatty acids (FA) were suggested as promising contact herbicides (Baur et al. 2019). Particularly pelargonic acid ester of a methyl polyethylene glycol (PA-MPEG) showed excellent performance in weed control, being the lead compound for further studies (Campos et al. 2021). PA-MPEG gave an effective biological performance like PA herbicides, and as a liquid, it is non-volatile and has no unpleasant smell, unlike PA (Campos et al. 2021). This PA ester derivative with own herbicidal activity is identified with the Chemical Abstract Service (CAS) number 109909–40-2. PA-MPEG is not just a pre-drug of PA that is de-esterified to the active form of PA in contrast to many ester herbicides like cyhalofop-butyl (Ruiz-Santaella et al. 2006) or 2,4-D ester (Peterson et al. 2016). Yet, it acts as the ester. PA-MPEG can be directly diluted in water and ready to use without formulation efforts because of its physicochemical properties such as liquid state, high water solubility, and wetting power due to both, low static and dynamic surface tension. Therefore, PA-MPEG may become a potential tool for weed control under optimum and well-defined use conditions.

In this study, we first define the optimum rate and spray volume of PA-MPEG for adequate weed control, then evaluate application factors such as sprayer parameters and environmental conditions on PA-MPEG efficacy.

Materials and methods

Chemicals

Pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) was provided by Clariant (Gendorf, Germany). For its synthesis, please refer to Campos et al. (2021). PA-MPEG was diluted directly in tap water without formulation ingredients for the application. For comparison purposes with PA herbicides, PA-MPEG content is 340 g of PA acid equivalent (ae) per liter. Beloukha® (BLK) from Belchim Crop Protection NV (Londerzeel, Belgium) and VOROX® Unkrautfrei Express (VRX) from Compo GmbH (Münster, Germany) were selected as commercial PA herbicides (Table 1).

Plant material

Seeds of *Digitaria sanguinalis* (L.) Scop. and *Solanum nigrum* L. acquired from Herbiseed (Reading, UK) were sown separately in 9 × 9 cm plastic pots containing an artificial substrate (Typ B Hawita Fruhstorfer. Hawita Gruppe

Table 1 Basic data and application rates for the experimental herbicide and commercial PA products used in the trials

Product	Active ingredient (ai) content (g L^{-1})	Acid equivalent (ae) content (g L^{-1})	Rate (L ha^{-1})	Other rates (kg ai or ae ha^{-1})	Spray volume (L ha^{-1})
PA-MPEG[a]	1001.0	340.0	5–50*	1.7–17*	100–1000*
Beloukha® (BLK)[b]	680.0	680.0	16	10.9	200–400
VOROX® Unkrautfrei Express (VRX)[c]	273.6	273.6	130	30.9	1000

*Rates and spray volumes tested in this study

[a]Clariant, Gendorf, Germany

[b]Belchim Crop Protection NV, Londerzeel, Belgium

[c]Compo GmbH, Münster, Germany

GmbH, Vechta, Germany). One week after emergence, weeds were thinned, and only one plant per pot was left. The weeds were grown in a phytotron under natural sunlight and augmented with supplemental sodium vapour lights with a photosynthetic photon flux density of 200 mE m^{-2} s^{-1}. The photoperiod was 16/8 light/dark. The temperature was regulated to 22 °C daytime and 17 °C night-time. Relative humidity (RH) was fixed at $55 \pm 5\%$. Weeds were bottom watered twice a week to maintain adequate moisture. Herbicide applications were performed to *Digitaria sanguinalis* at the start of the tillering, corresponding to growth stage 21–22 according to the *Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie* (BBCH) scale and *S. nigrum* at the growth stage of six true leaves (BBCH 16).

Spray application

Treatments were applied with a custom-built spray chamber (Ing-Büro CheckTec, Braunschweig, Germany) with flat-flan nozzles from Lechler GmbH (Metzingen, Germany) mounted 50 cm above the weed canopy. The spray pressure was 300 kPa. Spray applications from 100 to 400 L ha^{-1} were obtained by applying spray through a nozzle with an orifice size of 02 by adapting the speed of the sprayer in the spray chamber from 6.3 to 1.9 km h^{-1}. Likewise, spray applications of 500 and 1000 L ha^{-1} were gained using a tip nozzle with an orifice size of 06 at 2.4 and 1.5 km h^{-1}, respectively.

Experimental design and data collection of phytotron trials

Trials were conducted as randomized complete block design. Treatments were replicated four times for each weed species. A non-treated control was always included for comparison. Based on previous studies, evaluations were performed 2 and 7 days after treatment (DAT). Visible injuries (desiccated and necrotic tissues) were assessed for weed control on a 0 to 100% scale, where the value "0%" meant no weed control (no dead plants) and "100%" was complete weed control (all plants dead). Table 2 depicts the rating scale of weed control (Campos et al. 2021).

Impact of carrier volume and PA-MPEG concentration on weed control efficacy

Two phytotron trials were performed. In the first experiment, PA-MPEG at 17 kg ae ha^{-1} (dose selected based on Campos et al. (2021)) was sprayed at four spray volumes (100, 200, 500, and 1000 L ha^{-1}). Commercial PA herbicides were used as positive controls according to label recommendations (Table 1). The second trial evaluated the efficacy of four PA-MPEG concentrations (2.5, 5, 7.5, and 10% v/v) applied by using 200 and 500 L ha^{-1} spray volumes. These concentrations represent PA-MPEG rates of 1.7, 3.4, 5.1, and 6.8 kg of PA acid equivalent (ae) ha^{-1} for a spray volume of 200 L ha^{-1}, and 4.3, 8.5, 12.8, and 17 kg ae ha^{-1} for 500 L ha^{-1}. No commercial reference was sprayed in this second test.

Effect of nozzle type, spray pressure, and spray boom height on weed control efficacy of PA-MPEG.

In this experiment, changes in the variables pressure, nozzle, and boom height were studied one at a time to examine their influence on PA-MPEG efficacy. The pressures were 100, 200, and 300 kPa, and the nozzles were a flat fan (LU-120–02) and an air induction (ID-120–02), both from Lechler GmbH. The boom height used was 10, 25 and 50 cm from the target. The standard application was made using a flat nozzle (LU-120-02) at a spray pressure of 300 kPa, and fifty centimetres from the top of the weed species. PA-MPEG was applied with a suboptimal rate and spray volume (5.1 kg ae ha^{-1} in 200 L ha^{-1}) for better differentiation of sprayer parameters on efficacy.

Influence of temperature and relative humidity on weed control efficacy of PA-MPEG

Once the weed species had reached the right BBCH stage for treatment, they were placed under the test climatic conditions three days before spraying to avoid abiotic stress at the time of application. They were maintained under these conditions until 7 DAT (end of the experiment). Different

Table 2 Rating score used to interpret the weed control efficacy

Weed control efficacy (%)	Description
0–19	No control. Plants are entirely tolerant (weeds alive)
20–39	Poor control. Plants are moderately tolerant with transient desiccated/ wilted symptoms
40–59	Moderate control. Plants are moderately susceptible. Desiccated tissues
60–79	Good control. Plants are susceptible. Necrotic tissues
80–100	Excellent control. Plants are highly susceptible (weeds killed)

sections of the Clariant phytotron were set to the test climatic conditions to carry out the study. A total of 5 scenarios were studied. Weeds were placed at temperatures (day/night) of either 10/5 °C, 22/17 °C, or 33/25 °C at a constant 55% RH to examine the impact of temperature. To study the influence of RH, weeds were maintained at an RH of either 30, 55, or 97% and 22/17 °C, day/night, respectively. Untreated weeds were always placed in each test climatic condition for comparison. PA-MPEG was applied with a suboptimal rate and spray volume (5.1 kg ae ha^{-1} in 200 L ha^{-1}) for better efficacy differentiation.

Study of PA-MPEG spray coverage

Individual leaves of *D. sanguinalis* and *S. nigrum* were used for determining PA-MPEG spray coverage. They were placed on a plate and sprayed with PA-MPEG containing the fluorescent tracer Blankophor CBB from Tanatex Chemicals (Ede, Netherlands) at 1 g L^{-1}. The application was made using different pressures (100, 200, and 300 kPa) or tip nozzles (LU-120–02 and ID-120–02) in the sprayer. After spray evaporation, the leaves were placed on a black background, and the fluorescent blue signal was photographed under ultraviolet light (UPV® Black-Ray® B-100 High-Intensity UV Lamp) provided by Labortechnik (Wasserburg, Germany). A colour phase analysis was performed using the software LAS X from Leica Mycrosystems (Wetzlar, Germany) to quantify the percentage of the leaf covered by the spray. Obtained values represented the leaf surface covered by the PA-MPEG spray solution from the total area of the leaf.

Influence of nozzle and pressure on spray droplet size of PA-MPEG

Characterization of droplet size was conducted with the laser diffractometer MAL1082034 and the Spraytec 3.20 software from Malvern Instruments (Heidelberg, Germany), which were installed in a custom-built spray cabin from CheckTek (Braunschweig, Germany). Evaluations for the flat nozzle (LU-120–02) were conducted at 200 and 300 kPa. The air induction nozzle (ID-120–02) was only tested at 300 kPa. Before application, the required nozzles and pressures were set up on the sprayer. PA-MPEG spray solution was sprayed for twenty seconds. The obtained data were a volumetric population of droplets calculated from an average of 5000 droplets taken for five seconds and means of 6 repetitions.

Cuticular penetration

Cuticular penetration of PA-MPEG and VRX was studied after applying 10 μL droplets of the spray solution to the outer surface of enzymatically isolated cuticular membranes (CM) placed on a steel chamber with a lid and measuring the acceptor in contact with the inner side of CM. Details are described elsewhere (Baur 1999; Baur and Schönherr 1997). Penetration was started after water evaporation of the droplet. The aliquots of the acceptor solution were drawn and analysed by a 1290 Infinity HPLC from Agilent (Santa Clara, USA). The geometric mean of the penetration values per treatment was obtained from 10 repetitions and two measurements (6 and 24 h) after application. The kinetics indicated the mean of active ingredient (ai) penetration across the cuticle at different times.

Controlled conditions: HLPC was in an airtight chamber where the temperature was set up to the tested temperatures (5 and 25 ± 0.5 °C). Humidity around CM was controlled by using saturated salt solutions that give constant humidities in the nearby air of the CM (Baur 1999; Baur and Schönherr 1997). The humidity points were tried with $CaCl_2$ (30% RH), Ca(NO3)2 (56% RH), and KNO3 (93% RH).

Statistical analysis

The data were subjected to analysis of variance (ANOVA) using ARM software (Gylling Data Management Inc., Brookings, US). Individual treatment means were separated using Tukey's honestly significant difference (HSD) test at an alpha level of 0.05. Before the analysis, the normality and homoscedasticity of the assessment values were verified using the functionalities of the software. Data were automatically transformed by the software when needed.

Results

Impact of carrier volume and PA-MPEG concentration on weed control efficacy

PA-MPEG and BLK became more effective as the spray volume increased, not affected by the decreasing concentration (Fig. 1). At water volumes above 500 L ha^{-1}, PA-MPEG weed control was higher than 90% and equal to that provided by the commercial PA herbicide (VRX) with a spray volume of 1000 L ha^{-1}. PA-MPEG in 100 or 200 L ha^{-1} gave a weed control efficacy of around 40% for both weed species as BLK did at label recommendation.

At a given water volume, PA-MPEG efficacy was highly dose-dependent (Fig. 2). While the maximum weed control was achieved at a dose of 6.8 kg ae ha^{-1} at spray volume of 200 L ha^{-1}, and 17 kg ae ha^{-1} at 500 L ha^{-1}, weed control was not significantly higher than the one given by 5.1 or 12.8 kg ae ha^{-1}. Accordingly, the threshold doses of PA-MPEG could be established at 5.1 kg ae ha^{-1} for a 200 L ha^{-1}spray volume and 12.8 kg ae ha^{-1} for a spray volume

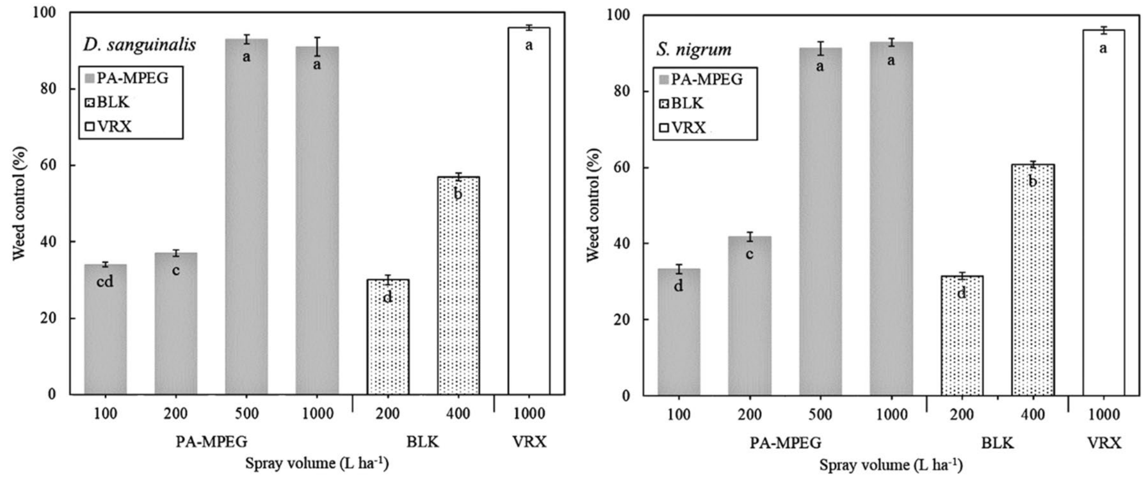

Fig. 1 Control of *Digitaria sanguinalis* and *Solanum nigrum* treated with pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 17 kg ae ha^{-1} as influenced by spray volume. Beloukha (BLK) applied at 10.9 kg ae ha^{-1} in 200 and 400 L ha^{-1}spray volume, and VOROX® Unkrautfrei Express (VRX) at 30.9 kg ae ha^{-1} in 1000 L ha^{-1} were used as standard references. Means labelled with common letters are not significantly different by the Tukey HSD test at the 5% level of significance. Bars represent standard errors

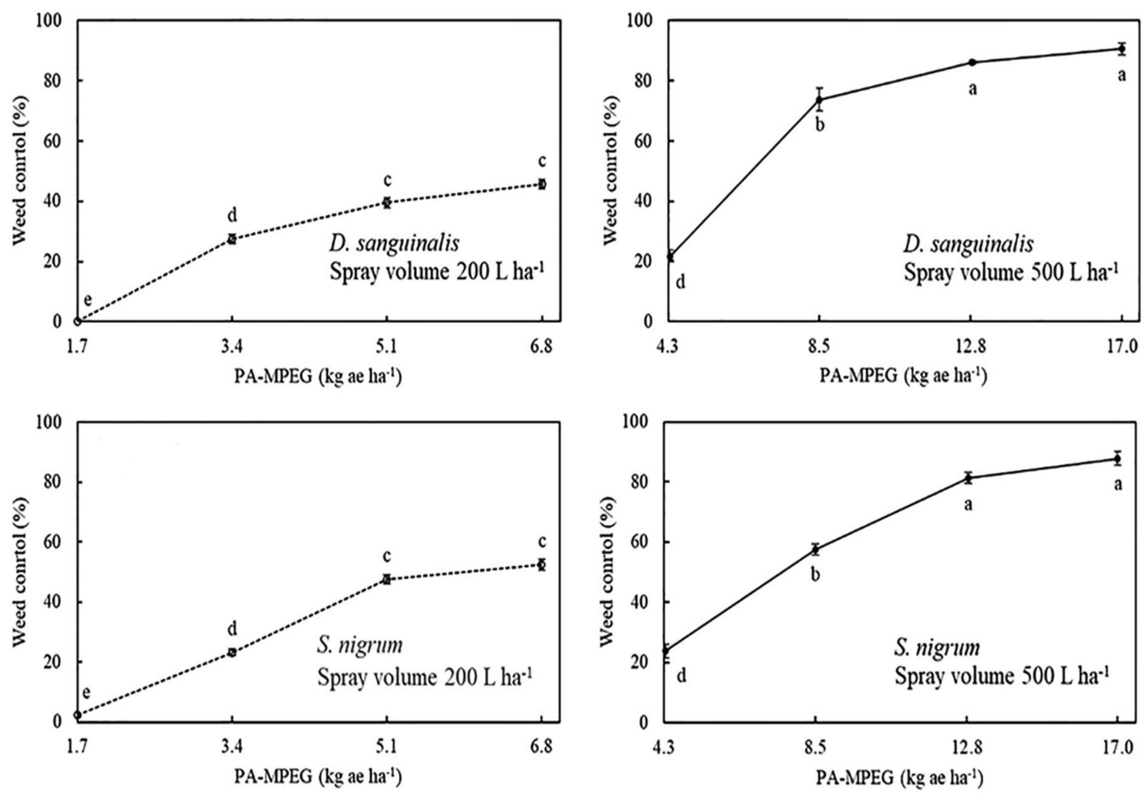

Fig. 2 Control of *Digitaria sanguinalis* and *Solanum nigrum* as affected by PA-MPEG rate at 200 and 500 L ha^{-1} spray volumes. Means labelled with the same letter are not significantly different by the Tukey HSD test at the 5% level of significance. Bars represent standard errors

of 500 L ha^{-1} (Fig. 2). *Digitaria sanguinalis* and *S. nigrum* control decreased drastically for PA-MPEG rates below 5.1 kg ae ha^{-1} in the tested spray volumes.

Effect of nozzle type, spray pressure, and spray boom height on weed control efficacy of PA-MPEG

PA-MPEG efficacy was not significantly affected by using

Table 3 Control of *Digitaria sanguinalis* and *Solanum nigrum* with pelargonic acid ester methyl polyethylene glycol (PA-MPEG) applied at 5.1 kg ae ha^{-1} in a spray volume of 200 L ha^{-1} through different tip nozzles, spray pressures, and boom height

Nozzle type	Spray pressure (kPa)	Spray boom height (cm)	Weed control (%)	
			D. sanguinalis	*S. nigrum*
ID-120-02[a]	300	50	34.8 ± 1.7 c*	45.0 ± 0.8 c*
LU-120-02[b]	100	50	33.8 ± 1.5 c	47.3 ± 1.0 bc
LU-120-02	200	50	32.0 ± 1.7 c	47.3 ± 1.0 bc
LU-120-02	300	50	32.0 ± 1.2 c	46.0 ± 0.6 bc
LU-120-02	300	25	54.8 ± 1.7 b	51.0 ± 2.1 b
LU-120-02	300	10	64.3 ± 2.7 a	59.3 ± 1.4 a

[a]Air induction nozzle (Lechler GmbH, Metzingen, Germany)

[b]Flat nozzle (Lechler GmbH, Metzingen, Germany)

*Means followed by common letters in a column are not significantly different by the Tukey HSD test at the 5% level of significance

different nozzles or pressures in the application (Table 3). In contrast, boom height was a significant factor for PA-MPEG efficacy on both weeds, with the shorter boom height of 10 cm achieving greater weed control than the 25 and 50 cm boom height.

Influence of temperature and relative humidity on weed control efficacy of PA-MPEG

Maximum weed control of PA-MPEG was found when plants were located at elevated day/night temperatures (33/25 °C), as shown in Fig. 3. A decrease in the RH from 97 to 30% also caused an increase in PA-MPEG efficacy, particularly on *S. nigrum.* At low temperature (10/5 °C) or the ambient temperature of 22/17 °C combined with high relative humidity (97%), weeds were quite tolerant and did not show clear PA-MPEG injuries.

Spray coverage of PA-MPEG with different nozzle types and spray pressure

There was no striking difference in spray coverage percentage in PA-MPEG when varying nozzle or pressure for both weed species. PA-MPEG application gave a uniform and complete coverage of the surface leaf (above 80%) in all tested variations. For a plant with a non-wettable surface like *D. sanguinalis,* coverage was generally at least 10% higher as shown in Fig. 4 (blue-coloured areas).

Droplet size distribution of PA-MPEG at different spray applications

The droplet diameter decreased as the pressure increased. The $D_{v0.5}$ value fell by 25% when increasing the pressure from 200 to 300 kPa (Table 4). The air induction nozzle also caused an increase in droplet diameter in comparison to LU-120–02, decreasing the driftable fines droplet (% V < 105) by more than 50%.

Cuticular Penetration

PA-MPEG and PA penetration were quite dependent on temperature for a liquid adjuvant. Increasing temperature from 5 to 25 °C caused a two and threefold increase in initial penetration of PA-MPEG and PA (formulated as VRX). PA-MPEG penetrated particularly faster at lower temperature, while PA-MPEG and PA were similar at 25 °C (Fig. 5). In contrast, while penetration of PA-MPEG was faster at different relative humidities, the dependence of weed control on relative humidity was low.

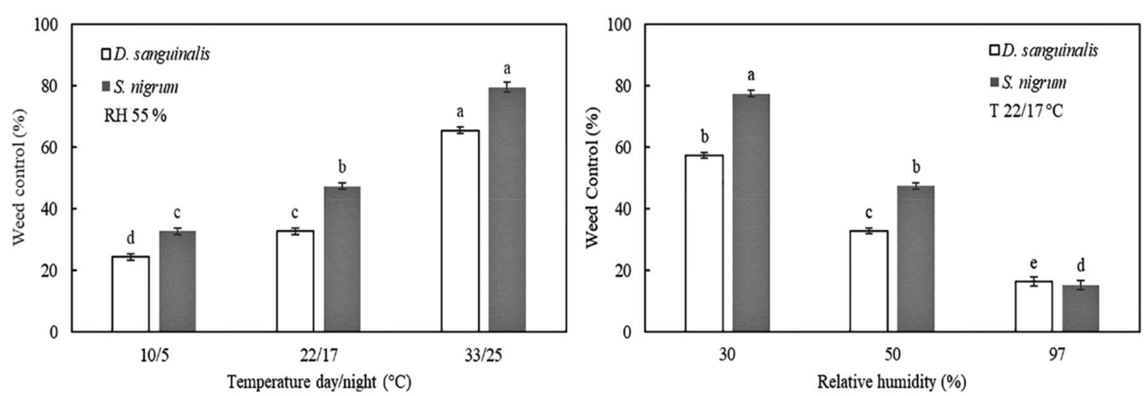

Fig. 3 Effect of temperature and relative humidity on *Digitaria sanguinalis* and *Solanum nigrum* control with PA-MPEG at 5.1 kg ae ha^{-1} in a spray volume of 200 L. Values within each weed species with the same letters are not significantly different ($p \leq 0.5$, Tukey's test). Bars represent standard errors

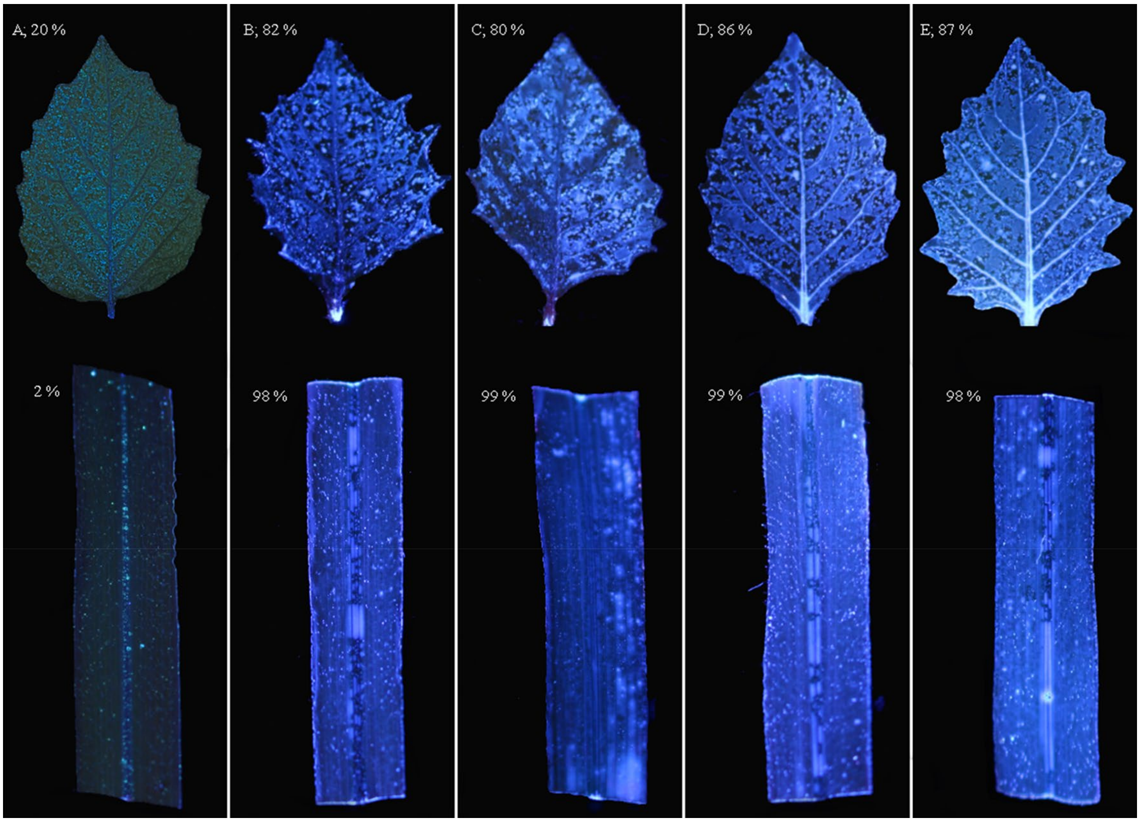

Fig. 4 Spray coverage on individual leaves of *Digitaria sanguinalis* and *Solanum nigrum* with PA-MPEG at a rate of 5.1 kg ae ha^{-1} in a spray volume of 200 L ha^{-1} through different tip nozzles and spray pressures. The blue colour represents the leaf area covered by the spray, denoted as a percentage (%). **A** water, LU-120–02 tip nozzle at 300 kPa; **B** PA-MPEG, LU-120–02 tip nozzle at 100 kPa; **C** PA-MPEG, LU-120–02 tip nozzle at 200 kPa; **D** PA-MPEG, LU-120–02 tip nozzle at 300 kPa; and **E** PA-MPEG, ID-120–02 tip nozzle at 300 kPa

Table 4 Droplet size distribution of pelargonic acid ester methyl polyethylene glycol (PA-MPEG) at 5.1 kg ae ha^{-1} in 200 L ha^{-1}

	Nozzle	Pressure (kPa)	$D_{v0.1}$[a]	$D_{v0.5}$[a]	$D_{v0.9}$[a]	V < 90[b]	V < 105[b]	V < 150[b]	V < 210[b]	RS[c]
Water	LU-120–02	200	76	156	327	16.1	23.9	47.4	70.0	1.6
Water	LU-120–02	300	70	146	323	19.5	28.0	51.8	72.9	1.7
Water	ID-120–02	300	209	629	1370	1.6	2.5	5.7	10.1	1.8
PA-MPEG	LU-120–02	200	77	419	1302	13.2	17.1	27.5	36.5	2,9
PA-MPEG	LU-120–02	300	65	319	1199	18.9	24.0	36.3	45.8	3.6
PA-MPEG	ID-120–02	300	98	348	1073	8.7	11.3	19.6	30.4	2.8

[a]Values represent droplet diameter

[b]Percentages of spray volume contained in droplets less than 105, 150, and 210 µm

[c]RS is the relative span of the spray droplet spectrum

Discussion

Pelargonic acid ester of methylated polyethylene glycol (PA-MPEG) is a new active ingredient not depending on formation and thus different from PA. However, both active substances, PA-MPEG and PA, cause similar symptoms on the treated plant and have the same MoA, which is still unclear (Campos et al. 2021, 2022). While PA-MPEG contains 340 g of PA acid equivalent (ae) per litre, PA-MPEG is neither a new formulation nor a pre-drug of PA that is hydrolysed to PA again. Results on hydrolysis stability have shown that PA-MPEG is hydrolytically stable at different pH (data not shown). Furthermore, other FA ester

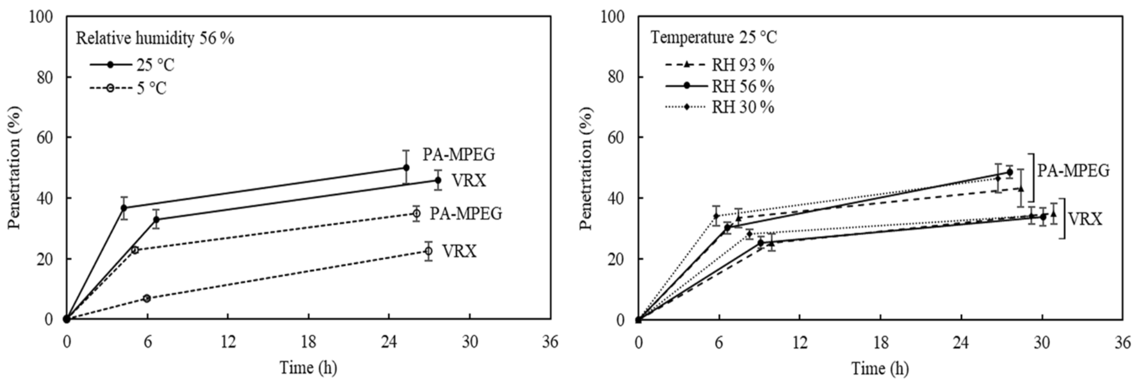

Fig. 5 Effect of temperature and relative humidity on the penetration of PA-MPEG and a commercial formulation of PA (VRX) at 25 g ae L^{-1} across leaf cuticle membrane of *Malus domestica* (apple)

derivatives did not show herbicidal activity (Campos et al. 2021). This novel active ingredient, which can be directly diluted in water and applied, has been previously reported as a fast-acting contact herbicide with equal or even better weed control than PA herbicide at lower or equal rates (Baur et al. 2019). More importantly, PA-MPEG does not have the disadvantages of PA, such as the need for a complex formulation, combinability with other actives, high volatility, and the unpleasant smell (Campos et al. 2021). With these properties, PA-MPEG is a better alternative to conventional contact herbicides than PA. However, PA-MPEG use rates are still high, and consequently, further efforts and research on reducing them are needed.

Weed size has a significant impact on foliar applied herbicides efficacy (Eure et al. 2013). Post-emergence herbicides achieve maximum weed control when applications are made on plants in early growth stages (up to 10 cm high; BBCH 10–14) (Bayer Cropscience 2019; Pintar et al. 2021). For contact herbicides like PA, weed size is even more relevant due to the need for maximum coverage and thus total plant area. Crmaric et al. (2018) and Webber and Shrefler (2006) observed higher PA efficacy on younger weeds. Accordingly, the trials reported here were done with medium-sized weeds (18–20 cm height) for better differentiation of factors of influence on PA-MPEG efficacy. As the effect of PA-MPEG and PA is a very rapid non-selective contact activity, practically not depending on the metabolism of specific weeds (Baur et al. 2019; Muñoz et al. 2020), only *D. sanguinalis* and *S. nigrum* were sufficient in the context of this research. Both plants are representative monocot and dicot weeds of difficult control, particularly *D. sanguinalis* in corn and *S. nigrum* in potatoes fields (Kraehmer and Baur 2013). Moreover, these weeds are also commonly used in studies.

PA-MPEG and PA efficacy depend first on the dose (Muñoz et al. 2020; Travlos et al. 2020) and second on the spray volume, which gives the maximum plant coverage. For example, PA-MPEG applied at a rate of 4.3 kg ae ha^{-1} in a spray volume of 500 L ha^{-1} did not perform well and was not at all effective, neither did PA-MPEG at 17 kg ae ha^{-1} in a spray volume of 100 L ha^{-1}. There is an interaction (dose–spray volume) that needs careful use recommendations with these types of herbicides (Crmaric et al. 2018; Webber and Shrefler 2006; Webber et al. 2014).

From the results with *D. sanguinalis* and *S. nigrum,* PA-MPEG applied at a rate of 12.8 kg ae ha^{-1} in 500 L ha^{-1} spray volume is the most efficient and optimum application rate. This dose allows reducing the PA by 13.9 kg and water volume by 420 L per hectare compared to the commercial standard (VRX) recommendation. The significant reduction is partly due to the superior wetting properties of PA-MPEG, which improve weed coverage and canopy penetration despite the spray volume reduction, particularly on monocot weeds. The dynamic surface tension of straight PA-MPEG is below 45 mN m^{-1} at 200 ms, which guarantees excellent spray retention and capillarity spreading (Baur and Pontzen 2007), the latter giving even better coverage with the monocot (Fig. 4).

The maximum burndown effect was observed 2 days after application (Coleman and Penner 2008) with no significant differences in weed control even after 7 days, like in previous studies (Campos et al. 2021, 2022). The efficacy of a single application of PA-MPEG at 12.8 kg ae ha^{-1} in a spray volume of 500 L ha^{-1} was higher than 80%, which could provide long-lasting weed control. Thus, the second application in a short time interval (15 days) might not be needed. This differs from Krauss et al. (2020) and Webber et al. (2014), who suggested repeated PA applications to achieve sufficient weed control. However, the regrowth of the weed under field conditions needs observation to determine if a second application is required (Travlos et al. 2020).

PA-MPEG (5.1 kg ae ha^{-1}) at lower spray volumes (200 L ha^{-1}) resulted in full coverage only on individual leaves (Fig. 4) and caused rapid necrotic symptoms of these leaves (data not shown). However, the control of complete plants of *D. sanguinalis* and *S. nigrum* with PA-MPEG was poor, even weaker than expected from a study with other weeds by Muñoz et al. (2020). From Fig. 2, we concluded that PA-MPEG applied at 5.1 kg ae ha^{-1} in a spray volume of 200 L ha^{-1} showed better performance than BLK at label recommendation (10.9 kg ae ha^{-1} in 200 L ha^{-1}spray volume), though on an insufficient control level around 40%. The poor weed control observed might be due to insufficient spray penetration into the weed canopy at the lower spray volumes. PA-MPEG and PA were applied on medium-sized plants (18–20 cm height), in contrast to other studies where smaller weeds were used (Muñoz et al. 2020; Travlos et al. 2020).

There are notable differences between PA-MPEG and PA-based contact herbicides and systemic ones. With systemic herbicides, an increase in concentration by reducing carrier volume often results in better weed control and often due to the several advantageous effects of higher concentration. It reduces the dynamic surface tension and increases spray coverage, and for glyphosate, a more concentrated spray deposit also increases cuticular penetration possibly via reducing dissociation (Creech et al. 2015; Knoche 1994; Schönherr and Baur, 1994;). This interaction on weed control was not observed with PA-MPEG and PA, where coverage effects are relevant (Fig. 1) and required for excellent weed control with the FA-based herbicides (Crmaric et al. 2018).

At a spray volume of 200 L per hectare, commonly used for herbicides in broadacre agriculture, higher dose rates of PA-MPEG did not cause a significant enhancement in *D. sanguinalis* and *S. nigrum* control. PA-MPEG achieved an efficacy between 40 to 50% on medium-sized plants. Application parameters like adjuvants or weed size can impact PA efficacy (Coleman and Penner 2008; Webber and Shrefler 2006). With PA-MPEG, the adjuvant functionalities are already included with a liquid physical state above zero °C and excellent wetting properties. A low dynamic surface tension compensates differences of nozzles, which was also observed with PA-MPEG, where related differences in mean drop size or driftable fines had no impact but driftable fines, e.g. also did not vary much. Although the optimal boom height depends on the mounted tip nozzles, PA-MPEG efficacy was increased when boom height was adjusted to 10 and 25 cm above the target. This finding could be a valuable insight in order to reduce PA-MPEG and PA use rates. While the application with a boom height of 50 cm could have provided a greater spray coverage at the top of the weeds than at lower boom heights, other effects have had a higher impact on PA-MPEG performance. One possible effect is a larger fraction of spray liquid collecting in the leaf axils. It has been found in previous single droplet studies that locally high concentrations at the axil and similarly also on the leaf petiole or stem, respectively, showed higher damage (de Ruiter et al. 1999) and caused the death of the leaf organ, even with low direct damage of the leaf blade (data not shown). We recently suggested that the effect of PA-MPEG and PA might be related to the interruption of capillary water flow in the apoplast in the presence of high amounts of the surfactant or acid and lipids from membrane disintegration (Campos et al. 2022). Another effect could be a higher fraction of stomatal penetration into the leaf of the two weeds that are both amphistomatic.

Weather conditions like light, temperature, or humidity have a significant impact on the success of weed control (Kudsk and Kristensen 1992; Zimdahl 2018). For example, light conditions impact both, the development of the plant midterm and the plants' immediate response to herbicides (Kudsk and Kristensen 1992; Larcher 2003). More importantly, several active ingredients like the contact herbicide glufosinate-ammonium are significantly better penetrating at high relative humidity, mainly due to better hydration of spray deposits which increases the driving force across the cuticle, achieving higher weed control (Anderson et al. 1993; Baur 1998, 1999). For PA herbicides, the label recommendation is to apply during sunny days, but Dayan and Watson (2011) and Lederer et al. (2004) reported that PA action was not light dependent. We think that light could also have a direct effect as transpiration, which is at least tenfold higher with open stomata, and imbalanced water loss is the main MoA of PA-MPEG and PA (Campos et al. 2022). Weed control at constant light and relative humidity (55%) increased with temperature for both the monocot and dicot weed species (Fig. 3). Higher control was also observed in PA field trials during the warmer season (Kanatas et al. 2021). This can have two different causes. Cuticular penetration studies showed that both PA-MPEG and PA penetrate at a significantly slower rate and to a lower level within one day at 5 °C (Fig. 5). The penetration of PA-MPEG at low temperature is higher than with PA and notably, weed control at low temperature was always found to be better with PA-MPEG (data not shown). PA-MPEG is related to fatty alcohol ethoxylates, which are good penetration enhancers but still show temperature-dependent penetration and effect on the penetration of other actives (Baur 1999). Another reason for the observed temperature dependence is that low temperature also slows plant growth and the water requirement by the plant (Larcher 2003). So, the plant could be less affected by the discontinuity of the water flow in the cell walls and xylem, and thus not facing water shortage. There was even a more pronounced antagonistic effect of high relative humidity on PA-MPEG efficacy, suggesting that the temperature below 10 °C combined with more than 75% RH could cause even lower activity of PA-MPEG, while the temperature of 20 °C or more and relative humidities below 60% are beneficial (Fig. 3). To our knowledge, there are no references in the literature considering the humidity for FA herbicides' efficacy. The high humidity could also increase the penetration of these herbicides by likely extending droplet evaporation time or accessing the stomatal route (Baur 1998). However, this was not relevant for PA-MPEG penetration. PA-MPEG and PA performed better at the lowest relative humidity (Fig. 5), opposed to other contact herbicides like glufosinate-ammonium (Anderson et al. 1993). As a liquid and moderately lipophilic PA-MPEG solute penetration was not better at higher relative humidity but similar at 55 and 93% RH and slightly better at 30% RH. At this relative humidity, hydration of the ethoxy chain is reduced, which increases solubility and thus penetration across the cuticle (Baur 1999). PA-MPEG has a closer number of ethylene oxide (EO) than the fatty alcohol ethoxylate Genapol C 050, about 6 EO. Both PA-MPEG and Genapol C 050 showed similar results on penetration, depending only slightly on the humidity in contrast to higher ethoxylates with 8–17 EO units (Baur 1999). Thus, the low weed control cannot be explained by a low PA-MPEG penetration.

Cuticular transpiration rate does not have a vital role in PA-MPEG efficacy (Campos et al. 2022), and stomatal transpiration measurement after application of the high rates of PA and PA-MPEG does not give a clear response. As mentioned above, the saturated atmosphere could reduce the transpiration by a decreased gradient of water potential and PA-MPEG and PA also via shortage in supply (flow) of water via cell walls. Therefore, the combination of reduced damage at suboptimal used rates and the reduction in water loss due to climate conditions (cold temperature and/or high humidity) could maintain leaf vitality eventually with the healing of weak injuries (Georgieva et al. 2010).

In conclusion, PA-MPEG efficacy depends on its used concentration. However, maximum spray coverage and penetration into the weed canopy, which are given by high spray volumes, are also key factors for high efficacy with PA-MPEG as well as with PA. This work shows the most efficient PA-MPEG dose rate that provides better weed control than PA benchmarks at different spray volumes and also presents the most suitable spray volume for achieving good weed control on medium-sized weeds. Applications made outside the recommended arrangement of parameters can lead to possible decreases in weed control. However, boom height, weed size, or adequate climate conditions could decrease product rates while maintaining efficacy. Nevertheless, rates are high compared to conventional herbicides, and further research should be carry out to solve this problem for PA-MPEG, e.g. using synergists and particularly co-formulations with synthetic active ingredients or biological control agents.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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