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Pelargonic Acid and Caraway Essential Oil Efficacy on Barnyardgrass (*Echinochloa crus-galli* (L.) P.Beauv.) and Johnsongrass (*Sorghum halepense* (L.) Pers.)

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Abstract: Bioherbicides are naturally originated products posing alternatives to synthetic herbicides for weed control. The objective of this study was to evaluate the efficacy of pelargonic acid and microencapsulated caraway essential oil on barnyardgrass (*Echinochloa crus-galli* (L.) P.Beauv.) and johnsongrass (*Sorghum halepense* (L.) Pers.). Two separate pot experiments were conducted at the Agricultural University of Athens (spring 2021), arranged in a completely randomized design (CRD) with six weed control treatments replicated four times. Treatments included the applications of: microencapsulated caraway essential oil at 50 g L^{-1} (CAR), CAR plus a commercial adjuvant (CAR + adj), i.e., alcohol ethoxylate at 1.8 g L^{-1}, pelargonic acid at 36.3 g L^{-1} (PA), PA plus a commercial adjuvant (PA + adj), i.e., alcohol ethoxylate at 1.8 g L^{-1}, and a tank mixture of pelargonic acid at 64 g L^{-1} plus microencapsulated caraway essential oil at 50 g L^{-1} (PA + CAR). An untreated control (CON) was also included. The results of the current research confirmed the knock-down effect of pelargonic acid against both barnyardgrass and johnsongrass and demonstrated the low efficacy of caraway microcapsules. The addition of a commercial adjuvant improved the efficacy of caraway essential oil but did not appear to affect the performance of pelargonic acid. No synergistic effects were observed between pelargonic acid and microencapsulated caraway essential oil. Further research is needed to optimize the use of these and other natural herbicides for weed control in agriculture and as components of sustainable integrated weed management (IWM) systems.

Keywords: natural herbicides; bioherbicides; adjuvant; NDVI; canopy cover; knock-down effect

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1. Introduction

Bioherbicides are naturally originated products derived from plant extracts, microorganisms, and insects that can be used for weed control [1]. These natural products have great potential in the field of weed management and pose an alternative, nonchemical, environmentally friendly alternative to synthetic herbicides. Of a variety of bioherbicides, there is a growing research interest in the use of products based on pelargonic acid and various plant essential oils that can facilitate weed control [1,2].

Pelargonic acid ($CH_3(CH_2)_7CO_2H$) is a saturated fatty acid with nine carbon atoms in the structural formula (C9:0) and is naturally synthesized as esters in the essential oil of *Pelargonium* spp. It can also be isolated from tissues of various plant species [3]. Pelargonic acid and its salts are used as active ingredients in emulsifiable concentrate formulations as natural nonselective contact herbicides; pelargonic acid-based products are increasingly being evaluated for their potential to control annual broadleaved and grass weeds [4].

Burndown applications of pelargonic acid affect cell membranes in treated plant tissues, causing cell leakage followed by degradation of membrane acyl lipids [5]. The applications lead to stripping of cuticular waxes, resulting in rapid desiccation of the foliage [6]. Injury begins within 15–60 min after application, with symptoms of phytotoxicity intensifying within 1–3 h and gradually leading to plant breakdown [4]. The intercalation of pelargonic acid into the lipid bilayer leads to light-independent destabilization of membranes as well as light-dependent membrane peroxidation by radicals derived from photosensitized chlorophyll displaced from thylakoid membranes [7]. Pelargonic acid can also cause the degradation of linolenic acid in thylakoid membranes [8].

Essential oils are natural volatile compounds extracted from plant leaves, roots, flowers, seeds, and other plant parts [9]. Phytotoxicity symptoms following essential oil application generally include chlorosis, leaf burning, and reduction in plant growth, as well as inhibition of mitosis, membrane depolarization, reduction in chlorophyll content, cellular respiration, and oxidative damage [1]. The phytotoxic potential of essential oils is attributed to their major constituents known as terpenoids (mainly mono- and 14 sesquiterpenes), which occur in the form of hydrocarbons, alcohols, aldehydes, ketones, ethers, esters, peroxides, and phenols [10]. Terpenoids, at least those capable of affecting mitosis, can be considered as a class of mitotic disrupter bioherbicides [11]. Among a variety of plant species whose essential oils are suitable for the development of bioherbicides, the essential oil of caraway (*Carum carvi* L.) has been highlighted as another promising candidate species for this purpose in the temperate climate zone of Europe [12–14]. The essential oil of caraway is rich in oxygenated monoterpenes, and its main components are carvone and limonene [15,16]. Among the monoterpenes contained in the essential oil of caraway, limonene is considered one of the most phytotoxic [14].

At this point, although the performance of plant essential oils looks promising under controlled laboratory conditions, their practical use for weed control under field conditions remains limited, mainly due to their low water solubility and high volatility [10,12]. To overcome these drawbacks and improve the performance of essential oils, researchers propose to use essential oils as solid emulsions to prevent the loss of biological properties of essential oil components [14,17]. This method mainly uses microencapsulates in which a microdroplet of an essential oil is enclosed by a carrier shell that forms a functional barrier [17,18]. The matrix wall isolates the active ingredients from the environment, allowing for their gradual release in response to external environmental conditions [18]. One of the most promising natural and synthetic polymers that can be used as a carrier envelope for microencapsulation of essential oils is maltodextrin, a polysaccharide with high water solubility [14]. There is recent evidence that the application of caraway essential oil microencapsulated with maltodextrin provides good control of barnyardgrass (*Echinochloa crus-galli* (L.) P.Beauv.) and that the efficacy of the above bioherbicide can be further improved when combined with a commercial adjuvant [14]. The use of surfactants has been suggested as a recommended practice to improve the performance of essential oils as bioherbicides [12]. It can also be assumed that the addition of adjuvants can lead to better adhesion and uniform coating of the applied bioherbicide on the leaf surface of weeds. This is also possible for the latter bioherbicide included in the current study, pelargonic acid. In addition, combinations between pelargonic acid and essential oils should be further investigated to determine if there are synergistic relationships between the above different groups of bioherbicides, as shown in the recent study by Travlos et al. [4].

The objective of this study was to evaluate the efficacy of pelargonic acid and microencapsulated caraway essential oil on two cosmopolitan summer weeds of high agronomic importance, namely barnyardgrass and johnsongrass (*Sorghum halepense* (L.) Pers.). Another objective was to evaluate the role of adjuvant addition on the efficacy of the two bioherbicides on the target weed species. The weed control potential of the mixture of the above bioherbicides was also evaluated.

2. Materials and Methods

2.1. Plant Material

From March to May 2021, two separate pot experiments were conducted in the Laboratory of Agronomy at the Agricultural University of Athens. The species studied in the first experiment was barnyard grass. Johnsongrass was the species studied in the second experiment. Two experimental runs were conducted for each experiment. Barnyardgrass seeds were collected from a rice field (*Oryza sativa* L.) in the Chalastra region, Thessaloniki, Greece (40.635° N, 22.736° E). Johnsongrass seeds were collected from a maize (*Zea mays* L.) field in Pyrgos, Elis, Greece (37.639° N., 21.476° E). At each site, seeds were harvested in September 2019 after crop harvest. The collected seeds were then air-dried, threshed, packed in paper bags, transported to the Agronomy Laboratory of the Agricultural University of Athens and stored at room temperature to be used in the subsequent experimental runs.

2.2. General Experimental Procedures

In the first experiment, 30 seeds of barnyardgrass were sown per pot on 12 March and 26 April 2021 for the first and second experimental runs, respectively. In the second trial, 40 seeds of johnsongrass were sown per pot on 9 April and 27 April 2021 for the first and second experimental runs, respectively. In both experiments, weed seeds were sown in pots with an outer diameter of 26 cm, a height of 24 cm, and a capacity of 9.5 L at a sowing depth of 2−3 cm. All pots had been filled with a mixture of herbicide-free soil from the experimental field of the Agricultural University of Athens and peat at a ratio of 1:1 (v/v). The soil properties were as follows: clay loam (CL) with a pH of 7.15%, 15.46% $CaCO_3$ and 2.28% organic matter. In addition, the concentrations of NO_3^-, P (Olsen) and Na^+ were 101.3, 9.87 and 113 ppm, respectively. After sowing, all pots were adequately watered and then placed outdoors. Precipitation height was 28.5 mm in April and 23.2 mm in May (Table 1).

Table 1. Mean, maximum, and minimum monthly temperature (°C) and monthly total precipitation (mm) prevailed during the experimental period.

Month	Weather Parameter			
	Mean Temperature (°C)	Maximum Temperature (°C)	Minimum Temperature (°C)	Monthly Precipitation (mm)
March	11.3	16.0	7.3	41.8
April	15.3	20.3	9.9	28.5
May	21.0	26.2	12.1	23.2

In both experiments, weeds were thinned to five plants per pot. To prevent any water stress, all pots were regularly irrigated during the whole experimental period, according to plant needs and the frequency of rainfall events.

2.3. Experimental Design and Treatments

First, the commercial products used in this research are presented. Beloukha Garden (Belchim Crop Protection NV/SA, Technologielaan 7, 1840 Londerzeel, Belgium) was the commercial product containing pelargonic acid at a concentration of 68% (w/v). Caraway essential oil (EO) was purchased from Avicenna Oil (Wrocław, PL). It was applied after being microencapsulated with maltodextrin. Microencapsulates were prepared on an industrial scale by the Hoffmann Aroma company (Zamysłowo, PL) in the process of nozzle spraying (in a mixer with a spray function) using silicon dioxide E 551 (SD) as a carrier [18]. The resulting microcapsules contained 6.55% (w/v) caraway oil, composed of 15.2% of limonene and 79.9% of carvone, and the whole chemical composition of the essential oil was as in previous studies by Synowiec et al. (2019). Trend 90 SL (E.I. DuPont de Nemours & Co Inc., Wilmington, DE, USA) was the commercial product used in two of six treatments. The active ingredient of this commercial product is isodecyl alcohol ethoxylate at a concentration of 90% (w/v). The treatment list was identical in the two separate experiments. Both experiments were conducted in a completely randomized design (CRD) with six weed control treatments replicated four times (Table 2).

Table 2. Definition of the six different weed control treatments that were applied in both experiments.

Treatment	Active Substance Concentration ($g\ L^{-1}$)	Abbreviation
Untreated Control	–	CON
Caraway EO [1]	50	CAR
Caraway EO + Adjuvant [2]	50 + 1.8	CAR + ADJ
Pelargonic Acid	36.3	PA
Pelargonic Acid + Adjuvant	36.3 + 1.8	PA + ADJ
Pelargonic Acid + Caraway EO	64 + 50	PA + CAR

[1] EO; essential oil. [2] As for the two bioherbicide products, the concentration of the active substance (i.e., alcohol ethoxylate) is also presented for the adjuvant.

Weed control treatments included the application of: (i) caraway essential oil, (ii) caraway essential oil tank mixed with an adjuvant, (iii) pelargonic acid, (iv) pelargonic acid tank mixed with an adjuvant, and (v) pelargonic acid tank mixed with caraway essential oil. An untreated control was also included. In the barnyardgrass experiment, the bioherbicides were applied on 14 April 2021 in the first experimental run and on 18 May 2021 in the second experimental run, when the plants had reached the phenological stage of 3–4 true leaves (BBCH: 13–14). In the johnsongrass experiment, the bioherbicides were applied in the first and second experimental runs on 27 April and 18 May 2021, respectively, when the plants had reached the phenological stage of 2–3 true leaves (BBCH: 12–13). Applications were carried out with a hand-held pressurized sprayer (Venus 2, Viopsec Kalimeris S.A., Athens, Greece) equipped with a ceramic hollow cone nozzle (HCI 80, Albuz, Évreux, France). Spraying was performed at a pressure of 300 kPa and a spray angle of 80°. The height between the nozzle and pots was 40 cm, and the spray head was set to move over the plants at 1.5 km h^{-1}. The apparatus was calibrated to deliver the equivalent of 200 L ha^{-1}. The leaves of the weed plants were oriented vertically at the time of spraying. All pots remained outdoors until the end of each experimental run.

2.4. Evaluations

To evaluate bioherbicide efficacy, fresh weed biomass, NDVI, weed canopy cover, and maximum quantum yield of photosystem II (F_v/F_m ratio) were measured at 1, 5 and 10 DAT. To measure fresh weed biomass, plants were clipped by scissors at 0.5 cm height. Two plants were sampled at each measurement. Weed fresh weight was measured using a digital balance (KF–H2, Zenith S.A., Athens, Greece). NDVI was measured using a Trimble® GreenSeeker® hand-held optoelectronic sensor (Trimble Agriculture Division, Westminster, CO, USA). The sensor unit has self-contained illumination in both red and near infrared bands and measures reflectance in the red and near infrared (NIR) regions of the electromagnetic spectrum [19] according to Equation (1):

$$NDVI = \frac{NIR - Red}{NIR + Red} \tag{1}$$

where $NIR - Red$ and $NIR + RED$ are the spectral reflectances in the near-infrared (NIR) and red (Red) wavebands, respectively. NDVI evaluations were performed by passing the sensor at approximately 30 cm above weed canopy for 5 s. As shown in previous studies, because of the way NDVI is calculated, deterioration in vegetation health can be detected by reduced NDVI values [20–22]. Canopeo (Division of Agricultural Sciences and Natural Resources, the OSU App 160 Center and Oklahoma State University) was the application used for weed canopy measurements. Canopeo (available on Google Play) is used to accurately determine the percent of green canopy cover, through downward-facing photos taken from a mobile phone device in real time. It is an image-analysis tool that classifies all pixels in the image, and the result of the analysis is a binary image, where white pixels correspond to the pixels that satisfy the selection criteria (green canopy), and black pixels correspond to the pixels that do not meet the selection criteria (not green canopy). Fractional green canopy cover ranges from 0 (no green canopy cover) to 1 (100% green canopy cover).

Moreover, FluorPen FP 110, a portable, battery-powered fluorometer (Photon Systems Instruments, Drásov, Czech Republic) was used for evaluating the effects of bioherbicide application on some physiological parameters of the targeted weeds. FluorPen FP 110 enables quick and precise measurement of chlorophyll fluorescence parameters in the laboratory, greenhouse or field. To use measurements of chlorophyll fluorescence to analyze photosynthesis, researchers must distinguish between photochemical quenching and nonphotochemical quenching. This is achieved by stopping photochemistry, which allows researchers to measure fluorescence in the presence of nonphotochemical quenching alone. In our experiments, pots were covered with a thick black plastic bag for 30 min to stop photochemistry. With FluorPen FP 110, the physiological parameter F_v/F_m or maximum quantum yield of photosystem II was measured at 1, 5 and 10 DAT. The assessment period was not longer than 10 DAT since the current experiment was focused on evaluating the knockdown effect of the natural herbicides on each one of the studied weed species.

2.5. Statistical Analysis

For each experiment, weed canopy cover, fresh weed biomass and plant height data were expressed as percentages (%) of the corresponding values recorded for the untreated control plants. No transformation was performed for NDVI and QY values. Assumptions of normality and homoscedasticity were tested by performing Shapiro−Wilk [23] and Levene tests [24], respectively. Then, all data were first subjected to two-way analysis of variance (ANOVA). Treatments and experimental runs were considered fixed effects, whereas replications were considered random effects. In both experiments, the effects of experimental runs on all parameters were not significant (p value ≥ 0.05). Therefore, data were pooled over experimental runs and analyzed again by one−way ANOVA. Means were separated using Fischer's least significant difference (LSD) test at a confidence interval of $a = 0.05$. Statgraphics Centurion XVI (Statgraphics Technologies, Inc., P.O. Box 134, The Plains, VA 20198, USA) was the statistical package used for all analyses.

3. Results

3.1. Effects of Bioherbicide Application on Barnyardgrass (Echinochloa crus-galli (L.) P.Beauv.)

Weed control treatments affected barnyardgrass fresh weight in all evaluations (p value ≤ 0.001). One day after treatment, CAR + ADJ resulted in a 30% reduction in barnyardgrass fresh weight compared to CON. Pelargonic acid-based treatments (PA, PA +ADJ) were even more effective since they reduced barnyardgrass fresh weight by approximately 75%. Similar was the performance of the mixture between pelargonic acid and microencapsulated caraway essential oil (PA + CAR). CAR was the least effective treatment, providing no significant reduction in barnyardgrass biomass compared to the untreated (CON). At 5 DAT, the lowest fresh weight values corresponded again to PA, PA + adj, and PA + CAR. CAR + adj resulted in 45% lower barnyardgrass biomass compared to CON, and CAR still did not show any effect on the target weed. The above results were also confirmed at 10 DAT (Figure 1a).

The effects of bioherbicide application on barnyardgrass NDVI were significant in all evaluations (p value ≤ 0.001). Based on NDVI measurements conducted at 1 DAT, all treatments including pelargonic acid resulted in low NDVI values ranging between 0.18 and 0.22. CAR + adj reduced barnyardgrass NDVI by 33% compared to CON. CAR

NDVI was not statistically different to the values recorded for the untreated plants (CON). At 5 DAT, CAR + adj NDVI was further reduced, having no significant differences with PA, PA + adj, and PA + CAR. In the final measurement conducted at 10 DAT, the highest NDVI corresponded to CON and CAR. Plants treated with pelargonic acid (PA) and the mixture of pelargonic acid and microencapsulated caraway essential oil (PA + CAR) seemed to recover since increased NDVI values were recorded. The same is noted for CAR treatment. NDVI remained low (0.22) for PA treatment (Figure 1b).

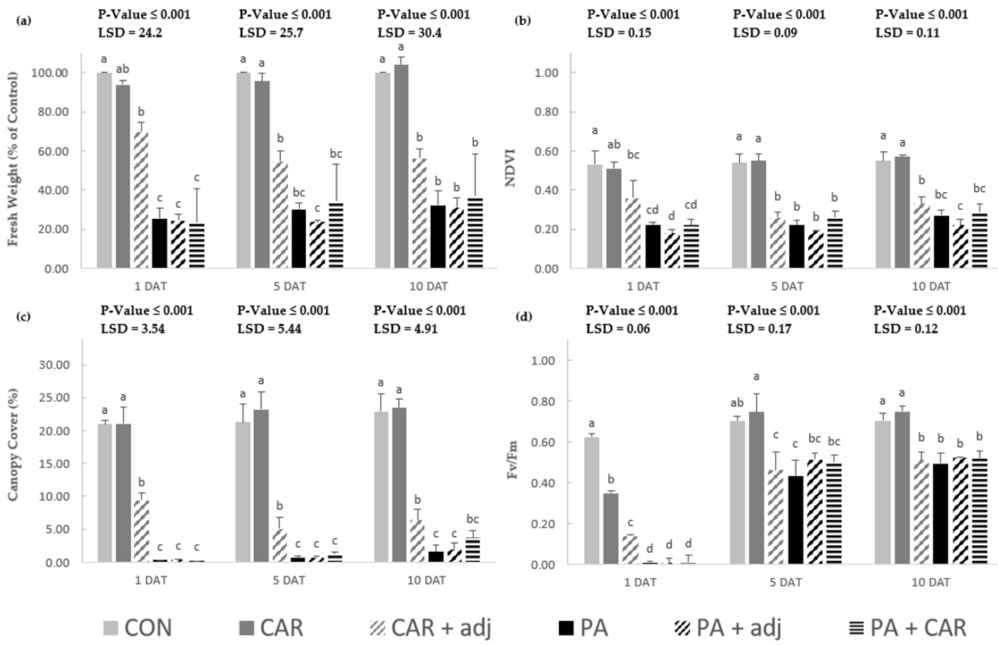

Figure 1. Barnyardgrass (*Echinochloa crus-galli* (L.) P.Beauv.) (**a**) fresh weight (% of control), (**b**) NDVI, (**c**) canopy cover (%), and (**d**) maximum quantum yield of photosystem II (F_v/F_m). Data are shown as pooled over experimental runs and reanalyzed by one-way ANOVA. Treatment means were separated according to Fischer's least significant difference (LSD test) at a confidence interval of $a = 0.05$. For each measurement, different lowercase letters indicate significant differences between treatments. Vertical bars indicate standard errors.

In all measurements, weed control treatments exerted a strong influence on barnyardgrass canopy cover and maximum quantum yield of photosystem II (F_v/F_m) (p-Value ≤ 0.001). A common observation across 1, 5, and 10 DAT was that PA, PA + adj, and PA + CAR provided the highest reduction of weed canopy cover, while intermediate values were obtained for CAR + adj. In addition, barnyardgrass canopy cover was highest for CON and CAR treatments (Figure 1c). At 1 DAT, the F_v/F_m ratio was 60% and 78% lower for CAR + adj compared to CAR and the untreated control (CON), respectively. Pelargonic acid-based treatments (PA, PA + adj, and PA + CAR) resulted in low F_v/F_m values. At 5 DAT, differences between treatments became lower. Specifically, PA + adj reduced F_v/F_m by 27% and 30% compared to CON and CAR, respectively. This treatment did not differ significantly to PA + CAR. CAR + adj and PA resulted in slightly lower F_v/F_m compared to the above two treatments (0.43−0.46). Similar results were observed at 10 DAT where CAR + adj, PA, PA + adj, and PA + CAR caused significant F_v/F_m in comparison to CON and CAR. These four treatments did not differ at a significant point (Figure 1d).

3.2. *Effects of Bioherbicide Application on Johnsongrass (Sorghum halepense (L.) Pers.)*

Bioherbicide effects on the fresh biomass of johnsongrass were significant in all three measurements (p value ≤ 0.001). At 1 DAT, CAR and PA + CAR reduced johnsongrass fresh weight by 42% and 50% compared to the untreated (CON), respectively. PA and PA + adj resulted in lower johnsongrass biomass than PA + CAR. Moreover, CAR + adj provided an 80% reduction in johnsongrass biomass compared to CON (Figure 2a).

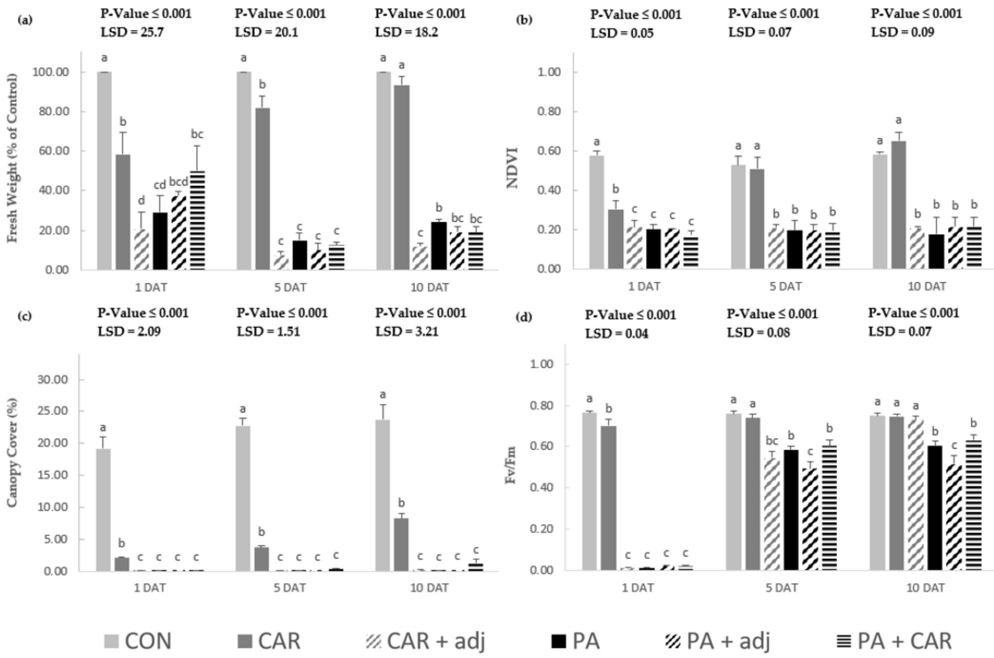

Figure 2. Johnsongrass (*Sorghum halepense* (L.) Pers.) (**a**) fresh weight (% of control), (**b**) NDVI, (**c**) canopy cover (%), and (**d**) maximum quantum yield of photosystem II (F_v/F_m). Data are shown as pooled over experimental runs and reanalyzed by one-way ANOVA. Treatment means were separated according to Fischer's least significant difference (LSD test) at a confidence interval of a = 0.05. For each measurement, different lowercase letters indicate significant differences between treatments. Vertical bars indicate standard errors.

In the second measurement (5 DAT), CAR + adj, PA, PA + adj, and PA + CAR showed similar efficacy in reducing johnsongrass fresh weight by 85−92% in comparison to the untreated control (CON). Weed fresh weight differed only 20% between CAR and CON. In the final measurement conducted at 10 DAT, johnsongrass fresh weight per plant was 76% lower after treatment with microencapsulated caraway essential oil with the addition of the adjuvant (CAR + adj) compared to the value recorded for the untreated plants (CON). PA + adj and PA + CAR further reduced johnsongrass fresh weight, while PA resulted in 89% lower weed biomass compared to CON (Figure 2a).

Johnsongrass NDVI was influenced by weed control treatments in all evaluations as well (p value $\leq$ 0.001). In the initial evaluation (1 DAT), highest NDVI values corresponded to CON, whereas CAR reduced NDVI by almost 50% compared to CON. All four treatments resulted in low NDVI values ranging from 0.17 to 0.21. At 5 DAT, NDVI was similar to 1 DAT for CAR + adj, PA, PA + adj, and PA + CAR. NDVI increased for CAR and did not differ with the value recorded for CON. Similar were the observations made at 10 DAT (Figure 2b). In all evaluations (1, 5, and 10 DAT), CAR + adj, PA, PA + adj, and PA + CAR resulted in low canopy cover values for johnsongrass. CAR reduced canopy cover for johnsongrass by 98%, 97% and 92% at 1, 5, and 10 DAT, respectively, compared to the untreated control (CON). For this treatment (CAR), canopy cover was slightly higher compared to CAR + adj, PA, PA + adj, and PA + CAR (Figure 2c).

The maximum quantum yield of photosystem II (F_v/F_m) was also affected by bioherbicide treatments as observed at 1, 5, and 10 DAT (p-Value $\leq$ 0.001). In the first evaluation (1 DAT), F_v/F_m did not differ between CON and CAR. The other four treatments (i.e., CAR + adj, PA, PA + adj, and PA + CAR) provided a substantial reduction of johnsongrass maximum quantum yield of photosystem II. At 5 DAT, the F_v/F_m ratio increased for all the above treatments but remained significantly lower than the values for CAR and CON. PA + adj was the treatment resulting in the lowest F_v/F_m values out of all weed control treatments. At 10 DAT, PA and PA + CAR reduced johnsongrass maximum quantum yield of photosystem II compared to CON, CAR, and CAR + adj. In addition, PA + adj reduced the value of F_v/F_m ratio by 15%, 20%, and 30% PA, PA + CAR, and CAR + adj. F_v/F_m did not differ significantly between CAR + adj, CAR and CON treatments (Figure 2d).

4. Discussion

The results of the present study indicate that both target weeds appear to be particularly susceptible to pelargonic acid, with extensive phytotoxic symptoms. These results are in full agreement with previous studies showing that pelargonic acid can achieve sufficient levels of weed control when applied at early weed growth stages [4,25]. Fukuda et al. [6] also confirmed the knockdown effect of pelargonic acid at 3 DAT following the visually perceived weed damage a few hours after treatment. Our results are consistent with those of Muñoz et al. [5], who highlighted the high phytotoxic potential of pelargonic acid formulations even after 7 days after treatment.

Unlike annual johnsongrass plants grown from seed, barnyardgrass plants gradually recovered from the applied pelargonic acid-based formulations from 5 DAT and onward. This observation is confirmed by the literature and represents an additional challenge that needs to be addressed to improve pelargonic acid potential for weed control. This contact, nonselective foliar herbicide lacks any systemic activity and does not cause damage to the basal meristems from which the development of new shoots can be observed. To overcome these challenges, repeated applications of pelargonic acid at short time intervals at high concentrations targeting small and younger weeds is a prerequisite for effective and long-term weed control [26–29]. This is especially noted when applications are conducted under real-field conditions, as revealed in the recent study by Kanatas et al. [20]. These authors found that applying pelargonic acid twice within a two-week interval can improve the herbicidal effects on barnyardgrass and common broadleaved weed species such as common lambsquarters (*Chenopodium album* L.), black nightshade (*Solanum nigrum* L.), redroot pigweed (*Amaranthus retroflexus* L.), and annual mercury (*Mercurialis annua* L.). Therefore, pelargonic acid is also a promising alternative herbicide that can be implemented in integrated weed management (IWM) systems and can be combined with the use of other practices. For instance, Kanatas et al. [30] demonstrated that the adoption of stale seedbed technique along with the pelargonic acid application in soybean crop remarkably reduced the density of annual weeds in comparison to normal seedbed lacking pelargonic acid burndown treatment before sowing. Such practices can also contribute to the development of more environmentally friendly weed management strategies, the reduction of herbicide inputs in agriculture so as to catch European Green Deal's goals, and the management of weed biotypes that have developed resistance to synthetic herbicides [31–34].

The addition of the commercial adjuvant used in the preparation of the spray solution did not contribute to a further increase in the efficacy of pelargonic acid on the target weeds. Our results differ from those of Coleman and Penner [35] who claimed that the addition of diammonium succinate and succinic acid improved the efficacy of a pelargonic acid formulation from 117% to 200% under greenhouse conditions. In another study by Webber et al. [29], natural adjuvants such as garlic extracts (at a concentration of 30%) and yucca extracts (at a concentration of 60%) improved the efficacy of pelargonic acid. Similar results were also reported by Webber et al. [25]. The lack of improved efficacy of pelargonic acid in the present study may possibly be attributed to the unsuitability of alcohol ethoxylate as an adjuvant for the preparation of tank mixtures containing pelargonic acid. It may also be a matter of the application rate of the adjuvant or may have been influenced by other external factors. In any case, considering the potential of adjuvants to improve the herbicidal potential of pelargonic acid, further adjuvants should be evaluated by conducting additional pot and field trials repeated in space and time.

At the same time, our study showed that pelargonic acid does not seem to have a synergistic effect when applied in the form of a mixture with microcapsules containing caraway essential oil. These results differ from those of Travlos et al. [4], where pelargonic acid showed synergistic effects with manuka (*Leptospermum scoparium* J.R.Forst. & G.Forst.) essential oil. Therefore, it can be concluded that natural herbicides should be evaluated as an alternative to caraway essential oil to produce effective bioherbicide tank mixtures with pelargonic acid. Another finding was that the use of microencapsulated caraway essential oil as a bioherbicide should be combined with the use of an adjuvant to achieve a higher level of weed control. In the current study, this treatment resulted in lower values for weed biomass, NDVI, canopy cover, and maximum quantum yield of photosystem II (Fv/Fm) for the target weed species in most evaluations compared to the application of caraway essential oil alone without the addition of an adjuvant. These results agree with those of Synowiec and Drozdek [36], who observed that the addition of adjuvants improved the injury effects of caraway oil on the leaf area of treated weeds. Similar results are also reported by Synowiec et al. [14], who found that the application of microencapsulated caraway essential oil together with the addition of an adjuvant reduced the biomass of barnyardgrass and affected the Fv/Fm ratio and other fluorescence parameters of this species.

Although the herbicidal potential of pelargonic acid and microencapsulated caraway essential oil cannot be ignored, there are some challenges in optimizing their use in agriculture. Apart from the lack of adequate crop selectivity, systemic activity, and high production costs, the potential fate of these compounds in the soil and their impact on the soil microbiome is a major concern. Since monoterpenoids and pelargonic acid affect membranes, effects on soil organism biodiversity are likely. In the absence of experiments directed at this important question, future research should also investigate the short- and long-term effects of pelargonic acid and caraway essential oil on soil microbiomes, community structures, and biodiversity.

5. Conclusions

The results of the current research confirmed the knock-down effect of pelargonic acid against both barnyardgrass and johnsongrass and demonstrated the low efficacy of caraway microcapsules. The addition of a commercial adjuvant improved the efficacy of caraway essential oil but did not appear to affect the performance of pelargonic acid. No synergistic effects were detected between pelargonic acid and microencapsulated caraway essential oil. Further research is needed to optimize the use of these and other natural herbicides for weed control in agriculture and as components of sustainable integrated weed management (IWM) systems.

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