

Non-hazardous rapeseed oil spray adjuvants do not improve the rainfastness or effectiveness of glyphosate for *Rhododendron ponticum* shrub control

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Abstract

Rhododendron ponticum (L.) is a highly invasive, non-native woody shrub that prevents tree regeneration and kills native flora. Achieving successful control of rhododendron can be difficult due to its thick waxy leaf surfaces, which discourage the absorption of foliar-applied herbicides. The spray adjuvant Mixture B NF® has therefore been used for many years to improve the efficacy, absorption, and rainfastness of foliar applications of glyphosate. We established an experiment to test if alternative non-hazardous adjuvants could be equally effective. Treatments were applied as foliar sprays and then subjected to artificial rainfall to examine rainfastness. We found that the non-hazardous adjuvants Codacide Oil® and Toil® (both based on rapeseed oil), and also SU Wett®, offered little or no benefit to the efficacy or rainfastness of glyphosate applications to rhododendron. However, further research using these adjuvants on other weed species is recommended. The only treatment in our study that showed acceptable levels of rhododendron control was glyphosate plus Mixture B NF®. Current recommendations for the control of rhododendron are therefore still valid. When foliar sprays of rhododendron bushes are required, apply 2.88–3.60 kg a.i. ha⁻¹ glyphosate and add Mixture B NF® adjuvant at a rate of 2 per cent of final spray volume. A minimum rain-free period of 6 h should occur after application of glyphosate products to any weed type, but if there is a risk of rainfall occurring earlier than this, and the application cannot be delayed, the use of Mixture B NF® is likely to improve rainfastness, reduce run-off and improve control.

Keywords Herbicide · Forest · Invasive weeds · Additives

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Introduction

Rhododendron ponticum (L.) (hereafter referred to as 'rhododendron') is a highly competitive, non-native invasive woody shrub species that is naturalised throughout much of Europe (CABI 2019). It is particularly widespread throughout the UK and Ireland, and in woodlands wherever it is present it prevents tree regeneration and shades out and destroys native flora (Edwards 2006). Rhododendron also acts as a sporulating host for the fungallike pathogens Phytophthora ramorum (Werres) and P. kernoviae (Brasier). Infected rhododendron leaves and shoots generate a large number of spores, often spreading the pathogens to nearby Japanese larch (Larix kaempferi (Lamb.) Carr.), which normally results in potentially lethal stem cankers and makes the infection of other susceptible tree species more likely (Webber et al. 2010). Removal of rhododendron has therefore become an important part of sustainable forest management in the UK and Ireland (Edwards 2006), but this is often both difficult to accomplish, and very expensive. For example, the cost of clearing rhododendron infestations across 2,000 ha of the Snowdonia National Park alone have been estimated as over US\$35 million (CABI 2019). Achieving effective control is difficult due to rhododendron's vigorous growth habit, its thick, waxy leaf surfaces which discourage the absorption of foliar-acting herbicides, and because even once they are absorbed, herbicides are often poorly translocated through the plant. The current recommended best practice for controlling rhododendron in UK forests is therefore to cut and remove all above ground growth, and then to spray the freshly cut stumps with glyphosate, with the alternative option of stem injection of uncut stems if Phytophthora is not present (Edwards 2006; Willoughby et al. 2017). However, even when best practice is followed it is common to get regrowth from treated stumps. To control this unwanted regrowth, follow up foliar applications of glyphosate are necessary which, due to the characteristics of rhododendron described above, are not always fully effective. Other herbicides such as triclopyr or imazapyr that can be equally or more effective than glyphosate in controlling regrowth (Tyler et al. 2006) are no longer approved in the UK (Willoughby et al. 2015).

Adjuvants are a type of pesticide additive that can improve the efficacy of herbicide applications by a variety of methods, such as improving wetting, spreading and penetration of leaves, reducing drift, or enhancing spray retention on plant surfaces (Hunsche 2006; Castro et al. 2014). Over 170 different adjuvant products are currently approved for use in forests in the UK by the Health and Safety Executive, whose primary role is to ensure human and environmental safety. However, unlike under the regulatory regime for pesticides, for adjuvants, manufacturers do not have to provide any evidence of efficacy or crop safety to obtain approval (Health and Safety Executive 2021). This lack of evidence led to the commissioning of research by forest management organisations to independently test claims made about the efficacy of particular adjuvants (Willoughby and Stokes, 2015).

In the case of rhododendron control, the most promising adjuvants are probably nonionic surfactants (non-electrically charged, surface acting agents). These are chemicals that reduce the surface tension of the spray deposition on leaves and improve the wetting and spreading properties of herbicides. With plants such as rhododendron that have a thick waxy leaf surface, they can help increase uptake and penetration of systemic herbicides, and ultimately help to improve the effectiveness of foliar sprays (Willoughby 1997; Eşen et al. 2006a, b; Willoughby and Stokes, 2015). Adjuvants that increase the rate of herbicide uptake in addition improve rainfastness (here taken to mean both chemical not available to run-off due to it being taken up by the plant; and also remaining spray deposits being fixed more effectively to leaves), which in turn also helps to reduce wash-off onto the forest floor (Thompson et al. 2000).

The adjuvant Mixture B NF® (AmegA, 2016) is a mixture of hydrophilic (water soluble) and hydrophobic (oil soluble) non-ionic alkoxylated alcohol surfactants, which was originally developed by the Weed Research Organisation for the GB Forestry Commission. It is thought to act both as a wetter and spreader, is an effective penetrant of leaf waxes, and has been used for many years in mixture with glyphosate and other herbicides to improve uptake and efficacy on various difficult to kill forest weed species (Lawrie and Clay 1993; Willoughby 1997). Rainfall can significantly reduce the efficacy of glyphosate, and it is recommended that a rain-free period of at least 6 h, and preferably 24 h, occurs after application (Monsanto 2016), particularly when treating species such as rhododendron where herbicide uptake into the plant is relatively slow (Edwards 2006). Mixture B NF® has been shown to increase the rainfastness of glyphosate, consistently outperforming other approved adjuvants tested (Clay and Lawrie, 1990; Willoughby 1997; Willoughby and Stokes, 2015), and it is therefore also commonly used by forest managers in the UK if precipitation is anticipated within 24 h of spraying.

Based on the safety data submitted to the UK Health and Safety Executive (HSE), the approved product label indicates that, if it were to be misused, Mixture B NF®:- is potentially harmful if swallowed; causes skin irritation and serious eye damage; and is very toxic to aquatic life (AmegA, 2016). By comparison, some glyphosate products approved for use in the UK are non-hazardous (e.g. Roundup ProActive® (Monsanto 2016). However, if Mixture B NF® is mixed with these non-hazardous glyphosate formations to increase their efficacy, the resulting spray mix takes on the characteristics of the more toxic adjuvant product. Although any unacceptable risk of harm to operators or the environment from such mixes can be avoided through the use of normal, good forestry practices as described in the UK Forestry Standard (Forestry Commission 2017), there may be some situations where this is not possible (such as, for example, where applications need to take place in or near water). It would be advantageous to identify an adjuvant that provides a similar level of efficacy enhancement to glyphosate as Mixture B NF®, but that achieves this without increasing the overall hazard rating of the resulting spray mix. In the study reported here we therefore reviewed the list of adjuvants approved for use in UK forestry (Health and Safety Executive 2021), and identified three potential types of non-hazardous products that warranted further research.

Oil ethoxylates and methylates produced from rapeseed have been developed with the aim of replacing less environmentally friendly adjuvants such as those based on alky-phenol-ethoxylates. These oil ethoxylates and methylates are thought to improve the efficacy of herbicide applications by spreading the spray mix on the leaf surface and reducing droplet surface tension and contact angle compared to water alone (Hunsche 2006). In addition, ethoxylation and methylation is thought to improve the ability of the rapeseed oil to penetrate leaves and hence improve rainfastness of the herbicide it is mixed with, by making leaf cuticles more permeable, and by solubilizing and humectifying leaf waxes (Sharma and Singh 2000; Hunsche 2006). However, oils are generally thought to be less effective than conventional wetters such as ethoxylated tallow amines (Gauvrit et al. 2007). Several oil-based spray adjuvants are approved for use in the UK. Toil® is an example of an adjuvant that contains methylated rapeseed oil, and the approved product label indicates that it is non-hazardous to humans and the wider environment (Interagro 2015). It is already used in forestry situations in conjunction with the selective graminicide cycloxydim (Willoughby and Forster 2022) as a wetter and spreader on grasses, but before the work reported here Toil® does not appear to have been tested for potential use in enhancing the efficacy of glyphosate on rhododendron.

Codacide Oil® is an adjuvant comprised primarily of unmodified (i.e. not methylated or ethoxylated), food grade rapeseed oil, with added plant-based emulsifiers, and the approved product label indicates that it has non-hazardous to humans and the wider environment (Microcide 2014). It is thought to work by reducing droplet tension, therefore acting as a better wetter and spreader of the herbicide mix than water alone. Some authors have reported that Codacide Oil® can improve the efficacy and rainfastness of glyphosate when it is used on herbaceous vegetation, but it appears to be less beneficial on grasses (Wells 1989; Clay and Lawrie 1990; Combellack et al. 2001), and in a study on rhododendron, Lawrie and Clay (1993) found minimal or even antagonistic effects.

A third type of non-hazardous adjuvant we identified was SU Wett®, which is a non-oil based, non-ionic wetter and penetrant containing ethylene oxide-propylene oxide copolymers (GAC 2016). Although it is approved for use with glyphosate in forestry, it was primarily developed to aid the speed of uptake of sulphonyl urea herbicides.

In the work reported here, we tested what effect the adjuvants Mixture B NF®, Toil®, Codacide Oil®, and SU Wett® had on the rainfastness and efficacy of glyphosate applied as a foliar spray with the aim of controlling young rhododendron plants.

Materials and methods

Site description

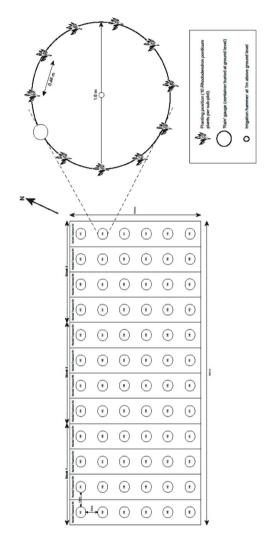
The experiment was established at Headley Research Enclosure, Hampshire, Southern England (51° 08′ 05″ N, 00° 50′ 42″ W). Headley Research Enclosure is 85 m above sea level, receives a mean annual rainfall of 705 mm, has an accumulated temperature (growing degree days > 5 °C) of 1840, and its soil is a humo-ferric podzol (i.e. it is a well-drained, very acid, sandy soil). The site is enclosed by deer and rabbit fencing, and regularly cultivated and kept weed free. Based on the results from annual soil analysis it is fertilized regularly to treat any deficiencies in phosphorus and copper, raise soil pH and supply magnesium and calcium.

Experimental design and establishment

The experiment utilized a randomized split-plot design with three replicate blocks. Each block contained four randomized, simulated rainfall treatments forming the main-plots. Each rainfall treatment main-plot contained 6 randomized herbicide treatments as the sub-plots (Fig. 1), giving 72 sub-plots in total in the experiment.

Each sub-plot contained ten rhododendron plants planted at 0.46 m spacing around the circumference of a circle with a diameter of 1.6 m, centred on a spray irrigation point, with sufficient buffer space between rainfall main plots to prevent overlap of irrigation treatments. A container buried to ground level occupied an eleventh planting space on the cir-







cle's circumference, acting as a rain gauge to allow an estimate of the amount of irrigation received by each plant to be made (Figs. 1 and 2).

The rhododendron were planted in late March 2018 into weed-free, rotovated ground, that immediately before cultivation had received an application of 28 kg ha⁻¹ of Granupotasse® 0-0-41 fertilizer (https://www.tessenderlokerley.com), providing an equivalent of approximately 11.5 kg ha⁻¹ of potassium. The plants, which were obtained from La Serra Exclusive Plants (http://www.laserra.nl), were 30–40 cm tall at the time of establishment and had been grown in 5 l pots. They were irrigated regularly after planting to prevent water deficits. Herbicides (1.44 kg a.i. ha⁻¹ glyphosate; 1.5 kg a.i. ha⁻¹ propyzamide; and 0.25 kg a.i. ha⁻¹ isoxaben) were applied as necessary during the first and second growing seasons, as carefully directed treatments avoiding overspraying any rhododendron foliage, to supress weed vegetation.

Herbicide / adjuvant treatment application

The herbicide / adjuvant combinations that were tested on the rhododendron plants are described in Table 1. They were applied to dry foliage on August 1st 2018, whilst the weather was warm (~25 °C), sunny, and with no breeze. There was no natural rainfall for at least 24 h after treatment. Applications were made on a block by block basis, using Coupler Pegler or Berthoud knapsack sprayers. A test application using water was made in the week prior to the treatment, to allow accurate calibration. Applications were made such that all parts of each plant were covered, including the undersides of leaves, to the point before significant run-off occurred, at a product rate of 3.6 kg a.i. ha⁻¹ glyphosate, using FulcoTip FCX02 (Yellow) full cone nozzles at 100 kPa pressure delivering 0.74 l min⁻¹ as a medium quality spray. This gave an equivalent volume rate of 3,500 l ha⁻¹.

Artificial rainfall treatment application

Artificial rainfall treatments were applied at the main plot level by a combination of handheld hosepipes and fixed overhead irrigation drippers, and they commenced at three different timings after the herbicide applications had been completed:- R1=no delay; R2=1 h delay; R3=3 h delay after spraying (see Table 1). The rainfall treatment consisted of a total of 26.9 mm of irrigation. Firstly, 17.5 mm of rainfall was applied by a hosepipe fitted with a fine rose, using mains pressure water, to deliver an initial 4 min deluge of artificial rain (an equivalent intensity of 263 mm hour⁻¹). This was followed by 9.4 mm of water applied over a further 60 min, via static overhead irrigation (with nozzles set at approximately 1 m in height above ground level in the centre of each sub plot). A test application determined the time required to deliver the necessary amount of irrigation, given the water pressure. This same water pressure was used each time the irrigation was applied. The equivalent total average rainfall intensity was 25.2 mm hour⁻¹.

The flour pellet method was used to determine the droplet mass distributions created by both the hosepipe rose and overhead irrigation (Kohl 1974; Navas et al. 1990). White flour was sifted into shallow trays of $2 \times 17 \times 26$ cm, levelled off and exposed to the spray from these applicators for a period between 0.5 and 4 s depending on the intensity. The trays of flour were then baked for 24 h at 100 °C, and the resulting flour pellets graded by passing the mixture through 3.55, 2.50, 2.00, 1.60, 1.00 and 0.5 mm sieves. Flour pellet mass was



 $\ensuremath{\text{Fig. 2}}$ A view of the sub-plots, with the overhead irrigation points visible in the centre of the circle of rhododendron plants

Table 1 Experimental treatments	Treatment code	Description			
	Herbicide / adjuvant treatments				
	H0	Control – water only applied			
	H1	3.6 kg a.i. ha ⁻¹ glyphosate ¹			
Notes ¹ As 10 1 ha ⁻¹ Roundup ProActive [®] (360 g l ⁻¹ glyphosate) (Monsanto 2016) ² 42.5% w/w polyoxyethylene (3EO) C12–C15 primary alcohol and 38.25% w/w polyoxyethylene (7EO) C12– C15 primary alcohol (AmegA, 2016) ³ 95% w/w rapeseed oil (food grade Canola oil, rapeseed triglycerides) and 5% polyethoxylated ester emulsifier ⁴ 95% w/w methylated rapeseed oil ⁵ 57.0% w/w ethylene oxide- propylene oxide copolymers ⁶ Artificial rainfall consisted of 26.9 mm of irrigation applied over a 64 min period, an equivalent total average artificial rainfall intensity of 25.2 mm hour ⁻¹	H2	3.6 kg a.i. ha ⁻¹ glyphosate ¹ + Mixture B NF® ² adjuvant @ 2% of final spray volume			
	Н3	3.6 kg a.i. ha ⁻¹ glyphosate ¹ +Codacide® ³ adjuvant @ 12.5% of final spray volume			
	H4	3.6 kg a.i. ha ⁻¹ glyphosate ¹ +Toil® ⁴ adjuvant @ 0.75% of final spray volume			
	Н5	3.6 kg a.i. ha ⁻¹ glyphosate ¹ + SU Wett ^{®5} adjuvant @ 0.5% of final spray volume			
	Rainfall treatments				
	R0	No artificial or natural rainfall for at least 12 h after herbicide spraying			
	R1	Artificial rainfall ⁶ applied imme- diately after herbicide spraying			
	R2	Artificial rainfall ⁶ applied 1 h after herbicide spraying			
	R3	Artificial rainfall ⁶ applied 3 h after herbicide spraying			

converted to raindrop diameter following Kohl (1974), and kinetic energy Ke (Jm⁻² mm⁻¹) was calculated using (Navas et al. 1990):-

$$Ke = 1/2m^*v^2$$

Where m is mass (kg) and v is water velocity (ms⁻¹).

The Volumetric Median Diameter (VMD) of the droplets created by the initial artificial rainfall deluge from the hosepipe rose was found to be between 2 and 3 mm, and for the overhead irrigation it was between 0.5 and 1 mm. The kinetic energy of the initial deluge was calculated to be $1.82 \text{ Jm}^{-2} \text{ mm}^{-1}$. Droplet sizes of <0.815 mm are thought to contribute very little to the kinetic energy of rainfall (Navas et al. 1990); for this reason, the kinetic energy of the subsequent overhead irrigation was judged to be negligible.

Assessments

Rhododendron health was assessed at the end of the first (October 2018) and second (November 2019) growing seasons using a subjective 1–5 visual scoring scale, where:-1=healthy; 2=approximately 25% of foliage discoloured or dead or died back; 3=approximately 50%; 4=approximately 75%; 5=dead (100%). In addition, in November 2019 after the final health score had taken place, all above ground live biomass in each sub-plot was harvested and immediately weighed with a spring balance. For each sub-plot a sub-sample

was then taken, weighed, and then dried in an oven at 70 $^{\circ}$ C for 3–4 days until a constant final 'dry' weight was reached. The ratio between the fresh and dry weights of the sub-sample allowed the equivalent total dry weight of live, above ground biomass to be calculated for each sub-plot.

Statistical analysis

Analysis was conducted in R (version 3.5.1; R Core Team 2018). Initial analysis of health scores using ordinal / multinomial logistic mixed effects models were dropped as sample size prevented an adequate model fit. Instead, health score data were analysed by "cutting" the data to make these responses binomial (2 (1) v 3/4/5 (0). This allowed the application of generalised linear mixed effects models (GLMM, lme4 package; Bates et al. 2015) with binomial errors with logit link function. Fixed effects were included for block and the interaction between adjuvant and rainfall; and adjuvant treatment nested within rainfall treatment, nested within block, was included as a random effect. Model fit was assessed using scaled residuals by simulating from the model (Hartig 2019). The significance of fixed effects were determined using ANOVA (Chi square tests, Fox and Weisberg, 2011), with non-significant treatment effects dropped from the final model. Post hoc tests (Tukey's Highly Significant Difference (HSD) with adjustments for multiple comparisons; Lenth 2019) were used to determine pairwise comparisons and presented as proportions.

Above ground live dry weight data were analysed using linear mixed effects models (LMM, lme4 package; Bates et al. 2015). Fixed effects were included for block and the interaction between adjuvant and rainfall. As results were bulked at the plot level, random effects were included for rainfall treatment nested within block (with adjuvant treatment having a single plot-level value). The significance of fixed effects were determined using ANOVA (F tests with Kenward-Roger denominator degrees of freedom; Kuznetsova et al. 2017), with post hoc tests (Tukey's HSD with adjustments for multiple comparisons; Lenth 2019) again used to determine pairwise comparisons.

Results

In October 2018, at the end of the first growing season after application, there were significant differences in rhododendron health (p < 0.05) as a result of the herbicide / adjuvant treatments, but not due to artificial rainfall treatments, nor were there any significant interactions between the two (p>0.05) (Table 2). All of the herbicide / adjuvant treatments

Table 2 Results from the Analysis of Variance (ANOVA) showing the significance of main effects and interactions for the health of rhododendron one growing season after treatment, October 2018	Source	Chi- square value	Degrees of freedom	Significance (Probabili- ty>Chi-square; p value)
	Block	2.567	2	0.277
	Rainfall treatment	4.896	6	0.557
	Adjuvant / Herbicide treatment	63.359	8	< 0.001
	Rainfall x Adjuvant / Herbicide treatment interaction	6.333	15	0.974

significantly (p < 0.05) worsened the health of the rhododendron compared to the untreated control (H0) (Fig. 3). Glyphosate+Mixture B NF® (H2), and glyphosate+SU Wett® (H5) reduced health more than glyphosate+Codacide Oil® (H3), but there were no significant differences (p > 0.05) between any of the other treatments. By the end of the second growing season in November 2019 no significant differences (p < 0.05) between treatments could be discerned, probably because of the high proportion of health scores of 4 across the site (data not presented).

Two growing seasons after spraying, there were significant differences (p<0.05) in above ground live dry weight due to the effects of the artificial rainfall and herbicide / adjuvant treatments, and there were also significant (p<0.05) interactions between the two (Table 3). Sub-plots where artificial rainfall started immediately after spraying (R1) resulted in significantly (p<0.05) more live biomass than those where there was no artificial rainfall (R0). Glyphosate+Mixture B NF® (H2) gave significantly (p<0.05) better efficacy (lower live dry biomass) than any of the other herbicide / adjuvant treatments (H1, H3, H4, H5), and was the only treatment significantly (p<0.05) different from the untreated control (H0).

Figure 4 shows the interactions between herbicide / adjuvant type and artificial rainfall treatment. The glyphosate+Mixture B NF® treatment (H2) only reduced above ground growth (live dry weight) compared to the untreated control (H0) under scenarios of no artificial rainfall (H2 R0), or where artificial rainfall commenced 3 h after application (H2 R3). When rainfall occurred immediately after spraying (R1), or after 1 h (R2), the glyphosate+Mixture B NF® (H2) was not significantly different (p>0.05) from the untreated controls (H0). No other herbicide / adjuvant combination gave any significant (p<0.05) reduction in rhododendron growth when there was artificial rainfall (R1-3).

In the initial analysis, where there was no rainfall (R0), only glyphosate + Mixture B NF® (H2 R0) gave any reduction in rhododendron growth compared to the untreated control (H0

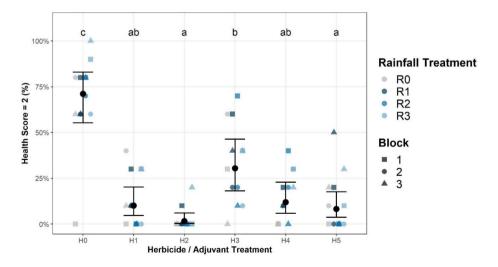


Fig. 3 Health of rhododendron one growing season after treatment, October 2018. Notes: The percentage of plants with a health score of 2 versus 3/4/5 are shown on the y axis. Transparent data points show proportions grouped by rainfall treatment / block; solid black data points show estimated marginal means, with unadjusted 95% confidence intervals, by adjuvant treatment. Herbicide / adjuvant treatments not sharing the same letter (a-c) are significantly different (p<0.05)

Table 3 Results from the Analysis of Variance (ANOVA) showing the significance of main effects and interactions for weight of above ground live dry biomass of rhododendron, two growing seasons after treatment, November 2019	Source	Sum of squares	Mean square	De- grees of freedom	F value	Signif- icance (p value)
	Block	95,524	47,762	6	0.881	0.462
	Rainfall treatment	793,027	264,342	6	4.877	0.048
	Adjuvant / Herbicide treatment	9,891,519	1,978,303	40	36.496	< 0.001
	Rainfall x Adjuvant / Herbicide treatment interaction	1,622,195	108,146	40	1.995	0.041

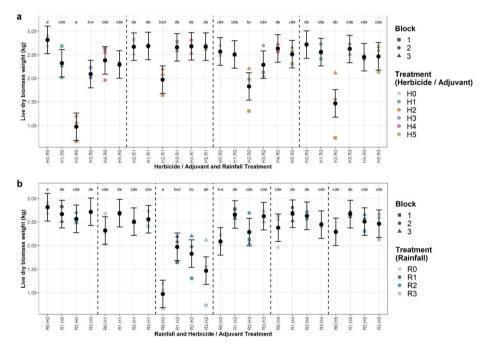


Fig. 4 Above ground live dry biomass (kg) of rhododendron, two growing seasons after treatment, November 2019:- (**a**) adjuvant by rainfall treatment interaction; (**b**) rainfall by adjuvant treatment interaction. Notes: Transparent data points show total dry weight data grouped by block; solid black data points show estimated marginal means, with unadjusted 95% confidence intervals, by treatment. Lettering shows significant differences by rainfall and adjuvant treatment (p<0.05, Tukey's HSD correction for multiple comparisons). Within each Fig. (4a or 4b), treatments not sharing the same letter (a-e) are significantly different (p<0.05)

R0). However, the effects of glyphosate+Codacide Oil® with no rainfall (H3 R0) was only marginally non-significant (p=0.06), and when a further, single level contrast analysis was undertaken, using this less conservative approach glyphosate+Codacide Oil® (H3 R0) was also found to significantly (p<0.05) reduce growth compared to the untreated sub-plots (H0

R0), although it was not as effective as glyphosate+Mixture B NF® (H2 R0). Glyphosate by itself (H1), or with the adjuvants Toil® (H4) or SU Wett® (H5), had no significant effect on the growth of rhododendron, even when there was no rainfall (R0).

Discussion

Overall, control of rhododendron was relatively poor. Although all of the herbicide / adjuvants had some initial effect on the health of the plants, any impacts on growth proved to be largely transitory, and by the end of the second growing season only one treatment, glyphosate+Mixture B NF®, gave acceptable levels of control. Applying glyphosate by itself was ineffective, even without rainfall, demonstrating again the importance of adding the adjuvant Mixture B NF® to achieve affective control from foliar sprays of rhododendron, and corroborating the results reported in other trials (Clay and Lawrie, 1990; Willoughby 1997; Willoughby and Stokes, 2015).

The artificial rainfall treatment was designed to be relatively intense, as previous field experiments have often shown only fairly minor impacts when lower quantities of overhead irrigation were applied (Willoughby 1997; Willoughby and Stokes, 2015), and because it was important to simulate a robust test of rainfastness in field conditions. When examining how realistic a simulation of natural rainfall our artificial irrigation was, in addition to the intensity of the application, droplet size and kinetic energy also need to be considered.

The Volumetric Median Diameter (VMD) of the droplets created by the initial artificial rainfall deluge from the hosepipe rose of between 2 and 3 mm is analogous to that of natural rainfall (Hudson 1993). However, whilst the intensity of this application was extremely high at 263 mm hour⁻¹ (equivalent to violent rainfall from an extreme thunderstorm), the velocity and therefore kinetic energy (1.82 Jm⁻² mm⁻¹) of the spray was very low in comparison to natural rainfall; according to Hudson (1993) rainfall of this intensity typically has a kinetic energy of around 28 Jm⁻² mm⁻¹, with lower intensities giving rise to kinetic energies from 12 Jm⁻² mm⁻¹ upwards. With a Volumetric Median Diameter of between 0.5 and 1 mm, and an intensity of 9.4 mm hour⁻¹, the subsequent overhead irrigation could be classed as 'heavy' rainfall, but again the velocity will have been much lower than natural rain so the kinetic energy is likely to be extremely low.

The artificial irrigation treatments applied were therefore probably not a highly accurate simulation of natural rainfall, and in one instance had the side effect of increasing rhododendron growth, probably due to an irrigation effect. On the other hand, the treatments were successful in applying sufficient water in the field to test herbicide rainfastness, and achieved the aim of applying a heavier intensity than in previous trials. For a more accurate simulation of natural rainfall, it would probably be necessary to undertake the research in more controlled conditions, using a purpose built indoor rainfall simulator.

The only adjuvant to improve the rainfastness of glyphosate, when applied to rhododendron, was Mixture B NF®. This was as expected, and similar benefits have been reported elsewhere (Willoughby and Stokes, 2014). This suggests that the adjuvant facilitated more rapid uptake of the glyphosate, meaning less was available to be washed off leaves by the rainfall. None of the other, non-hazardous, adjuvants provided any improvement to rainfastness of glyphosate.

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Although glyphosate + Mixture B NF® was the only combination that provided acceptable levels of control, where there was no rainfall the adjuvant Codacide Oil® did marginally improve glyphosate efficacy. It is possible that on less difficult to kill weeds, that are nevertheless problematic enough to warrant the use of an adjuvant to improve glyphosate control levels, Codacide Oil® may be of more benefit. It is therefore recommended that further research takes place into the potential of Codacide Oil®, and Toil®, for improving the efficacy of glyphosate on difficult to kill weeds such as bramble (*Rubus fruticosus* agg. L.) and bracken (*Pteridium aquilinum* (L.) Kuhn). In addition, adjuvant oils such as Codacide Oil® or Toil® might still prove to be useful in helping to reduce spray drift, even if they do not improve glyphosate efficacy.

Conclusions

When an adjuvant is required to improve the rainfastness of glyphosate, or enhance its efficacy on difficult to kill weeds such as rhododendron, then Mixture B NF® should be used. Non-hazardous adjuvants such as Codacide Oil®, Toil®, or SU Wett® offer little or no benefit to glyphosate efficacy or rainfastness on rhododendron. However, further research on other weed species is recommended.

Current recommendations for the control of rhododendron are therefore still valid (Edwards 2006) - when foliar sprays of rhododendron bushes are required, apply 2.88– $3.60 \text{ kg a.i. ha}^{-1}$ glyphosate (e.g. as $8-10 \text{ l ha}^{-1}$ Roundup ProActive®) and add Mixture B NF® adjuvant at a rate of 2 per cent of final spray volume. A minimum rain-free period of 6 h should occur after application of glyphosate products to any weed type, but if there is a risk of rainfall occurring earlier than this, and the application cannot be delayed, the use of Mixture B NF® is likely to improve rainfastness, reduce run-off and improve control.

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Author contributions Ian Willoughby conceived and designed the research, interpreted the results, and wrote the main manuscript text. Jack Forster carried out the statistical analysis. Rob Coventry contributed to the design of the research and assessments. All authors reviewed and approved the manuscript.

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Declarations

Competing interests The authors declare no competing interests.

References

AmegA (2016) Mixture B NF product label. https://www.nomixenviro.co.uk/

- Bates D, M\u00e4chler M, Bolker B, Walker S (2015) Fitting linear mixed-effects models using lme4. J Stat Softw 67(1):1–48. https://doi.org/10.18637/jss.v067.i0
- CABI (2019) Rhododendron ponticum (rhododendron). CABI Compendium. CABI Int. https://doi. org/10.1079/cabicompendium.47272
- Castro MJL, Ojeda C, Cirelli AF (2014) Advances in surfactants for agrochemicals. Environ Chem Lett 12:85–95. https://doi.org/10.1007/s10311-013-0432-4
- Clay DV, Lawrie J (1990) Effects of additives on the activity and rainfastness of glyphosate on perennial grass weeds of forestry. *Proceedings Crop Protection in Northern Britain*, 181–186
- Combellack H, Pritchard G, Illingworth J (2001) Effect of simulated rainfall and selected adjuvants on the herbicidal performance of glyphosate. Proceedings of the 6th International Symposium on Adjuvants for Agrochemicals, 13–17 August 2001, Amsterdam, Netherlands, 525–530
- Edwards C (2006) Managing and controlling invasive rhododendron. *Forestry Commission Practice Guide* 17. Forestry Commission. http://www.forestry.gov.uk/publications
- Eşen D, Jackson ML, Zedaker SM (2006a) Foliar absorption and translocation of herbicides with different surfactants in *Rhododendron maximum* L. In *Floriculture, Ornamental and Plant Biotechnology: Advances and Topical Issues.* 1st Edition, Chap. 44, Volume III. Teixeira da Silva, J.A. (eds). Global Science Books, pp. 422–430
- Eşen D, Yildiz O, Kulac S, Sarginci M (2006b) Controlling rhododendron spp. in the turkish Black Sea region. Forestry 79:177–184
- Forestry Commission (2017) The UK Forestry Standard. Forestry Commission, Edinburgh, p 232. www. forestresearch.gov.uk
- Fox J, Weisberg S (2011) An {R} companion to applied regression, second edition. Thousand Oaks CA: Sage. http://socserv.socsci.mcmaster.ca/jfox/Books/Companion
- GAC (2016) SU Wett product label. http://www.global-adjuvants.com
- Gauvrit C, Müller T, Milius A, Trouvé G (2007) Ethoxylated rapeseed oil derivatives as non-ionic adjuvants for glyphosate. Pest Manag Sci 63(7):707–713
- Hartig F (2019) DHARMa: Residual diagnostics for hierarchical (multi-level / mixed) regression models. R package version 0.2.4. https://CRAN.R-project.org/package=DHARMa
- Health and Safety Executive (2021) Adjuvants, list entries and the official list of adjuvants (webpage)https:// www.hse.gov.uk/pesticides/pesticides-registration/applicant-guide/the-applicant-guide-adjuvan.htm (accessed 6th January 2021)
- Hudson NW (1993) FAO Soils Bulletin 68. Food and Agriculture Organisation of the United Nations. http:// www.fao.org/docrep/T0848E/T0848E00.htm Field Measurement of Soil Erosion and Runoff
- Hunsche M (2006) Rainfastness of selected agrochemicals as affected by leaf surface characteristics and environmental factors. PhD dissertation
- Interagro (2015) Toil product label. https://www.interagro.co.uk
- Kohl RA (1974) Drop size distribution from medium-sized agricultural sprinklers. Trans Am Soc Agricultural Eng 17(4):690–693
- Kuznetsova A, Brockhoff PB, Christensen RHB (2017) ImerTest package: tests in linear mixed effects models. J Stat Softw 82(13):1–26. https://doi.org/10.18637/jss.v082.i13
- Lawrie J, Clay DV (1993) Effects of herbicide mixtures and additives on *Rhododendron ponticum*. Weed Res 33:25–34
- Lenth R (2019) emmeans: Estimated marginal means, aka least-squares means. *R package version 1.3.3* https:// CRAN.R-project.org/package=emmeans
- Microcide (2014) Codacide Oil product label. http://microcide.co.uk
- Monsanto (2016) Roundup ProActive product label. https://www.nomixenviro.co.uk/

- R Core Team (2018) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/
- Sharma SD, Singh M (2000) Optimizing foliar activity of glyphosate on *Bidens frondosa* and *Panicum maximum* with different adjuvant types. Weed Res 40(6):523–533
- Thompson DG, Pitt DG, Buscarini TM, Staznik B, Thomas DR (2000) Comparative fate of glyphosate and triclopyr in the forest floor and mineral soil of an Acadian forest regeneration site. Can J for Res 30:1808–1816
- Tyler C, Pullin AS, Stewart GB (2006) Effectiveness of management interventions to control invasion by *Rhododendron ponticum*. Environ Manage 37:513–522
- Webber JF, Mullet M, Brasier CM (2010) Dieback and mortality of plantation japanese larch (*Larix kaemp-feri*) associated with infection by *Phytophthora ramorum*. New Disease Reports 22:19
- Wells AJ (1989) Adjuvants, glyphosate efficacy and post spraying rainfall. Plant Prot Q 4(4):158-163
- Willoughby I (1997) Glyphosate rainfastness. Q J Forestry 91:203-210

Navas A, Alberto F, Machín FJ, Galán A (1990) Design and operation of a rainfall simulator for field studies of runoff and soil erosion. Soil Technol 3(4):385–397. https://doi.org/10.1016/0933-3630(90)90019-Y

- Willoughby IH, Forster J (2022) The herbicide cycloxydim is an effective alternative to propyzamide or glyphosate for the control of the forest grass weeds *Molinia caerulea*, *Calamagrostis epigejos*, *Deschampsia flexuosa* and *Holcus lanatus*. Forestry: An International Journal of Forest Research 95(2):274– 286. https://doi.org/10.1093/forestry/cpab035
- Willoughby IH, Stokes VJ (2015) Mixture B New Formulation adjuvant increases the rainfastness and hence effectiveness of glyphosate for rhododendron control. Forestry 88(2):172–179. https://doi.org/10.1093/ forestry/cpu041
- Willoughby IH, Seier MK, Stokes VJ, Thomas SE, Varia S (2015) Synthetic herbicides were more effective than a bioherbicide based on *Chondrostereum purpureum* in reducing resprouting of *Rhododendron ponticum*, a host of *Phytophthora ramorum* in the UK. Forestry 88(3):336–344. https://doi.org/10.1093/ forestry/cpv004
- Willoughby IH, Stokes VJ, Edwards C (2017) Ecoplugs containing glyphosate can be effective in preventing regrowth from *Rhododendron ponticum* stumps. Scott Forestry 71(3):33–39

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