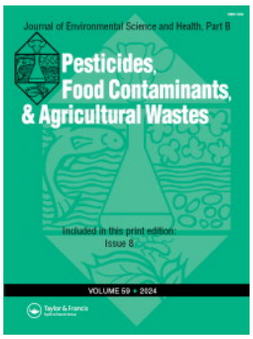

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The effect of formulation composition and adjuvant type on difenoconazole dislodgeable foliar residue

Mohamed H. Badawy[a], Darragh Murnane[a], Kathleen A. Lewis[a], and Neil Morgan[b]

[a]School of Life and Medical Sciences, University of Hertfordshire, Hatfield, Herts, UK; [b]Syngenta, Jealott's Hill International Research Centre, Bracknell, Berkshire, UK

ABSTRACT

Rigorous risk assessments for those exposed to pesticides are carried out to satisfy crop protection regulatory requirements. Non-dietary risk assessments involve estimating the amount of residue which can be transferred from plant foliage to the skin or clothes, known as dislodgeable foliar residues (DFRs). DFR data are less available than crop residue data as studies are costly and limited by seasonality. European regulatory authorities are reticent to allow extrapolation of study data to different scenarios as the contributory factors have hitherto been poorly identified. This study is the first to use a new laboratory DFR method to investigate how one such factor, pesticide formulation, may affect DFR on a variety of crops. The study used the active substance difenoconazole as both an emulsifiable concentrate (EC 10%) and a wettable powder (WP 10%) with and without adjuvants (Tween 20 and organophosphate tris(2-ethylhexyl)phosphate TEHP) on tomato, French bean and oilseed rape. A comparable DFR% was retained from the WP and EC formulation on most crops except for tomato, where lower DFR% was retained in the case of WP (39 ± 4.7%) compared to EC (60 ± 1.2%). No significant effect of adjuvant addition was observed for either formulation except when mixing TEHP (0.1% w/v) to the EC 10% on French bean, resulting in 8% DFR reduction compared to the EC formulation alone. This research demonstrates the value of a unique DFR laboratory technique in investigating the importance of the formulation and in-tank adjuvants as factors that affect DFR.

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Dislodgeable foliar residue; non-dietary risk assessment; factors that affect DFR; formulation; difenoconazole; DFR laboratory technique

Introduction

Plant protection products (PPPs) are manufactured in many different formulations due to variations in the active substances' (As) solubility, biological efficacy, and ease of handling, application parameters such as spray characteristics and spray ability, and transport.[1] Despite the importance of AIs in the formulation, there are also other vital components, sometimes referred to as "*inert ingredients*," which may range from 0% to 99.99% of the total product composition.[2] These 'inerts' often improve formulation efficacy such as for example, solvents, carriers, catalysts, synergists, adjuvants, or other compounds.[3] 'Inerts' enhance efficacy through a number of effects, for example, promoting formulation physical and chemical stability, aerosolization performance and deposition onto plant surfaces, the formation of an adherent pesticide film on the leaf surface and/or enhance penetration of the pesticide to the biological site of action.[4]

Conventional crop protection equipment atomizes the spray liquid into fine droplets so that they can be uniformly deposited on the plant's leaves. However, only a small fraction of the chemical reaches the targeted plant canopy. A large portion of the pesticide sprayed may eventually reach the ground or drift off the target influenced by many deterministic factors (i.e., method of application, crop density, meteorological conditions etc.).[5] Apart from the spray concentration or dose, the droplets size and the spread on the plant leaves could boost the effectiveness of the PPPs. Therefore, suitably formulating the product to increase the dispersion of pesticide droplets to promote the uptake of the pesticide by the crop or the pest is necessary. The droplet size and the equipment flow rate could be adjusted to achieve these results.[5,6] Thus, the application method, canopy types, droplet size and the dose are equally crucial to maximize the PPPs effectiveness.

Different types of agrochemical formulations can be produced depending on the application, customer acceptability, and regional market requirements. With the advancement in formulation science and cost implications, most agrochemical formulators attempt to develop a product that can be applied globally. Emulsion concentrates formulations (EC) have been one of the most popular and common PPP formulations for many years and represent the most significant volume of pesticide formulation consumed and demanded worldwide.[7] They tend to be an oil suspension of active substances plus emulsifiers that form an emulsion in dilution. Surfactant emulsifiers are added to the EC formulations

CONTACT Mohamed H. Badawy moh.mma@hotmail.com Department of Life and Medical Science, University of Hertfordshire, Hatfield, Herts, AL10 9AB, UK.

to ensure spontaneous emulsification with good stability properties in the spray tanks. The size of EC dispersed particles varies depending on the formulation composition but typical size ranges between 0.1- 5.0 µm.[8] This compares with WPs products which are finely ground formulations with a particle size greater than 5 µm and applied to the field after suspending in water.[9,10]

Wettable powder (WP) formulations have also been in use for many years and tend to be formulated from particles of the active substance comparably larger than that of an EC (5-40 µm). In addition, WP formulations usually contain dry surfactants as powder wetting and dispersing agents with inert carriers and fillers such as silica particles that prevent the active substance particles from fuzing and aggregating.[8] WP are usually diluted and mixed with water before application. Non-dietary exposure to PPPs could potentially affect agricultural workers, residents and bystanders who may be present during or after agriculture operations.[11,12] During regulatory risk assessments, some exposure scenarios involve exposure to PPPs through dislodgeable foliar residue (DFR), which is "the amount of residues present on leaves that can be washed from the leaf surface after the spray dries".[13] These exposure scenarios are well covered in the regulation (EC.) NO 1107/2009 and presented in the European Food Safety Authority (EFSA) guidance document and the USA agriculture reentry task force (ARTF) on the assessment of exposure of operators, workers, residents and bystanders in the risk assessment of PPPs.[12, 14,15]

In the literature, formulation type and co-formulant ingredients such as solvents, carriers, inert material, wetting agents, etc., have been reported to impact DFR, for example, by affecting coverage of, and retention on the leaf, as well as penetration of pesticide in the leaf surface.[16] Moreover, Whitmyre *et al.* (2004) and the California Department of Pesticide Regulation conducted three studies on melon, grape and peach foliage in which DFR was measured in field studies using Endosulfan EC or WP. In all the studies, the WP formulation resulted in higher DFR values. The authors related the latter finding to ingredients of the WP formulation. For example, the particulate nature of the components may mediate the full migration of the pesticide molecules into the waxy and other subsurface layers of the foliage and consequently, the pesticide retention on the surfaces for a longer time may be expressed as surface residues rather than leaf deposits". As a result, WP formulations have historically been considered, in terms of DFR, the worst-case end-product.[17,18]

Consequently, the USA Environmental Protection Agency (EPA) recommended considering the range of product formulations available for the active substance during the registration evaluation process and so data may be required for each type. In general, results from the literature are inconclusive concerning the effect of different formulations on residue deposits and the behavior of pesticides. This could be due to the difficulty in isolating other factors that may affect the residues, such as different plant species and varieties used, different adjuvants, types and concentrations of co-formulas, plant growth stages, different application methods and varied spray droplet sizes and many other factors.[19,20] For instance, plant architecture and surface roughness (waxy, hairy, smooth) have an impact on the DFR.[21]

The term 'adjuvant' is used to describe any additive to a formulation or spray tank that enhances pesticide activity through improvement of the formulation delivery to, or improving post-deposition penetration of the AI into, the plant surface.[22] Whilst there is some evidence that adjuvants may increase a pesticide's human toxicity, generally, when used correctly, they do not harm plants, remain stable, and address performance issues.[4, 23–26] These substances include surfactants, spreader stickers, crop oils, anti-foaming materials, buffering agents, and compatibility agents.[27] Adjuvants play a significant role in droplet size distributions, deposit patterns, foliar residues (both dislodgeable and penetrated), and persistence characteristics of pesticides.[28,29] Adjuvant choice depends on the physicochemical properties of the active substances and the types of formulation (EC, WP, solution, granules, etc.).[24]

Amongst the most common adjuvants are surfactants.[30] The primary function of these is to reduce the surface tension within the external surface layers of water. The lower the surface tension of a pesticide solution, the better the pesticide coverage of the deposited formulation by improved droplet spreading on leaf surfaces, thereby allowing more pesticides to reach their biological target.[31] Theoretically, this will eventually lead to more absorption and less DFR on the surface. Nonionic surfactants are the most common type available. Most adjuvants are used at concentrations in excess of their critical micellar concentration (CMC) which are usually achieved at a low concentration, about 0.1% by spray volume[31]

Further commonly-used adjuvants are "*plasticisers*" or "*accelerators*", which accelerate the mobility of active substance absorbed into the leaf *via* the lipophilic pathway.[32] An example of a plasticizing molecule is the organophosphate tris(2-ethylhexyl)phosphate (short: TEHP).[33] These phenomena affect the total absorption and retention of an active substance in the plant, which could, in return, affect DFR.[34]

In general, pesticide residues should be kept in balance with those remaining on fruits and leaves during harvest or maintenance of the crop to maintain safety and proper use. On some occasions, it has been shown that the addition of adjuvants might slightly reduce the DFR and, accordingly, will reduce the potential human dermal exposure.[35] On the contrary, the DFR in the presence of a spreader-sticker adjuvant increased.[36]

Identifying the effect of factors that could be affecting DFR in field studies conditions could be challenging especially due to the confounding effect of environmental factors (temperature, humidity, wind speed, rainfall etc.) that overlap with the effect of the spray properties and canopy features.[37] The effects of the formulation on the spray generation, droplet deposition, droplet-surface interaction and finally the surface penetration/retention ratio are crucial features to identify the effect of the formulation on the overall DFR. Therefore, the recently published DFR technique[38] that allows the study of factors that may affect DFR under controlled laboratory conditions are useful. This rapid laboratory DFR technique has been developed particularly to

generate DFR data on many targeted crops under controlled and manageable environmental conditions so that the data could be used in conjunction with the industrial experimental data generated to support PPPs registration.[38] Thus, the regulatory authorities could feasibly set accurate and more reflective DFR default values for various crop groups and pesticides. In this research paper, the DFR laboratory technique has been used to investigate the effect of different formulations (i.e., EC and WP) on the DFR of a representative PPP, difenoconazole (DFZ) on various crops (i.e., French bean, tomato and oilseed rape) with and without the addition of one of two adjuvants (Tween-20 0.1% (w/v) or TEHP 0.1% (w/v)). It is hoped that this study would shed light on the ability of laboratory DFR method to be employed for systematic product studies, that consequently help in generating data suitable to enable stakeholders to make better decisions and judgments on extrapolation and setting reasonable DFR default value for regulatory risk assessments.

Materials and methods

Three different crops were selected (i.e., French bean, tomato and oilseed rape) to provide a variety of foliage textures. A Sanyo versatile environmental growth chamber Model MLR-351 purchased from SANYO Electric Company, Sussex, UK, was used to grow the plants. The overall Laboratory DFR method followed was that described by Badawy et al. (2022), which is briefly summarized in the following descriptions.

Test systems

All plants were treated with either difenoconazole EC 10% (w/v) or WP 10% (w/v). The fungicide was selected due to its wide use on different plants to control several pests and analytical stability. Both formulations were formulated and provided by Syngenta Jealott's Hill International Research Station, UK for research purposes only. WP formulation incorporated nonionic surfactant in the formulation to ensure the diffusivity. Neither formulation is registered or commercially used. The in-use concentration was approximately (0.625 mg mL^{-1}), corresponding to the average field application rate of (125 g DFZ 200 $Litres^{-1}$ $hectare^{-1}$). The adjuvant, Tween 20, under the tradename "TWEEN 20-LQ-(CQ), was purchased from Croda France S.A.S. (France). In addition, the surfactant Tris(2-Ethylhexyl) phosphate under the tradename "DISFLAMOLL TOF", denoted hereafter as (TEHP), was purchased from LANXESS Deutschland GmbH, Industrial & Environmental Affairs (Germany). Each of these additives was added and mixed to the spray solution at a concentration of 0.01% (w/v). The final volume of the spray formulations was 5 mL.

Leaf treatment application

Treatment was performed by dispensing 40 uniform droplets (20 droplets per leaf) of 0.2 µL each onto the surface of the targeted leaves (2 leaves for each replicate). The plants were treated with DFZ concentration of approximately 0.625 mg mL^{-1}. Picus® Electronic Pipette, Single Channel model 735021 purchased from Sartorius Lab Instruments GmbH & Co. KG, Goettingen, Germany, was used. The electronic micropipette was used to generate droplets of a 0.2 µL size, the smallest reproducible volume that can be achieved by any commercially available micropipette. Thus, the amount of DFZ that is expected to be on each tested replicate (2 leaves) was 5 µg. Plants were kept stable at room temperature (22 °C) for 3 h after the treatment allowing the applied DFZ to dry on the leaf surface before cutting the treated leaves at the petiole using clean scissors and forceps. Leaves were then placed in clean and securely capped 150 mL glass bottles for assessment of DFR.

Leaf surface residue recovery

A fresh concentration of an aqueous surfactant solution of Aerosol OT 0.01% (w/v) (from ThermoFisher Scientific, Stortford, UK) was used to dislodge the pesticide residues from plant leaves following OPPTS Guidelines, EFSA guidance 2022 and prior reports.[12,13, 39] Furthermore, the validation of the required number or dislodging processes and volume of the wash-off solution needed to rinse all the residue from these selected plants was established by[38] as per the Table A1 in the Appendix. After being placed in the glass bottle, the leaves were washed in the determined Aerosol OT 0.01% volume for each crop tested. Before the chromatographic analysis, decanted residue solutions for each wash were labeled and stored at (-4 °C) in a cold dark room. The residue analysis was performed within a week of the storage.

The difenoconazole analysis followed the same analytical method with the same precision and accuracy level as performed by.[38]

Droplet microphysical characterization

Droplet microphysical characterization can be studied by investigating the Dynamic surface tension (DST). PPP formulation contains additives that reduce the surface tension within the external surface layers of water. The lower the surface tension of a pesticide solution, the better the pesticide coverage of the deposited formulation by improved droplet spreading on leaf surfaces, thereby allowing more pesticides to reach their biological target.[31] Theoretically, this will eventually lead to more absorption and less DFR on the surface. Therefore, studying DST is crucial to understand the spread ability and penetration of the PPPs into or/and onto the leaf surface

DST measurements for all formulations were taken using the bubble pressure tensiometer BP100 from Kruss GMBH (Hamburg, Germany). The maximum bubble pressure method is an easy and convenient method for measuring the surface tension. In this method, the capillary is immersed in the solution, and a gas bubble is created inside the liquid using gas with controllable pressure (Rapp, 2017). Using the tensiometer, 40 mL of formulations and water were sampled

in the measurement chamber. Single surface tension values (mN m^{-1}) were measured over a specific time period, ranging from 10 ms to 100000 ms surface age for all tested formulations. In addition, water measurements were tested up to 53000 ms surface age since the longer duration was required to achieve the equilibrium surface tension of the water. The results were interpreted as DST curves as a function of time as an indication of the response time for droplet surface indicative of surface spreading.

Statistical analysis

Raw data were analyzed using SPSS, IBM version 27.0 (BM Corp. Released 2020. IBM SPSS Statistics for Windows, Version 26.0. Armonk, NY: IBM Corp.). All collected residue data were tested using Shapiro-Wilk for normality. A significance value (P-value) ≥ 0.05 of the tests indicated normality besides ensuring that the skewness and Kurtosis values are in the acceptable range of the normal distribution (-1,1) and (-3,3), respectively (Shapiro & Wilk, 1965). One-way ANOVA (Analysis of Variance) was used to analyze the difference between the means of tested groups. Tukey's HSD was used to detect the post hoc significance between the groups in case of any significance. If the F statistic was higher than the critical value (the value of F that corresponds with alpha value (P), usually 0.05), then the difference among groups was deemed to be statistically significant (T. K. Kim, 2017). Independent T-test assuming non-equal variance between the independent samples from a population that displays a normal distribution and computes the difference between the means of the two samples at significance level of $p \leq 0.05$.

Results

In the following report of the results and elsewhere in the paper, the term DFR recovery, expressed as a percentage of the applied dose, is used as measure of the amount of active substance dislodged from the surface. In this respect, a higher percentage recovery relates to higher potential exposure to workers entering treated crops.

The results for different DFZ formulations (i.e., EC 10% (w/v) and WP 10% (w/v)) revealed no significant difference between the DFR of either formulation on French bean or oilseed rape leaves as shown in Table 1 below. Table 1 shows the descriptive statistics comparing two different formulations of the DFZ 10% (i.e., EC and WP) on French bean, tomato, and Oilseed rape. *Independent T-test assuming non-equal variance between the groups has been used and showed a significant difference between tested formulations on tomato leaves only ($p \leq 0.0005$). **data proved to be normally distributed when tested by the Shapiro-Wilk test using SPSS* where $p \geq 0.05$. RSD. % is the percentage of relative standard deviation among samples of each tested concentration level, while the SD ± is the standard deviation for the 10 determinations ($n = 10$).

The significance value of both crops was above the significance level of the independent T-test ($p = 0.08$, 0.07), respectively. However, a significant difference between formulations was observed in the case of tomato leaves with a P-value ≤0.0005. The mean DFR recovery% (± SD) in the case of the DFZ EC 10% on tomato leaves was higher (60 ± 1.2%) than the WP 10% (39 ± 4.7%).

For EC formulation the DFR recovery was the highest in case of French bean (82%) followed by tomato (60%) and the lowest recovery was observed on oilseed rape leaves (31%). The same pattern was observed in the case of WP formulation but with different residue magnitude; French bean was the highest (74%) followed by tomato (39%) and the lowest recovery on oilseed rape (37%), where there was no significant difference between the DFR for the WP formulation on tomato and oil seed rape. The DFZ EC 10% formulation was mixed with Tween 20 (0.1% (w/v)) and TEHP at two different concentrations (0.1% and 0.3% (w/v)), in order to examine the effect of adjuvant mixing on DFR from an exemplar plant, French bean. French bean leaves were chosen for this experiment for their economic value and also for ease of cultivation. The one-way analysis of variance showed that the effect of adjuvant addition was significant ($p = 0.006$) as shown in Table 2 which *elucidates the descriptive statistics of difenoconazole EC 10% with and without different adjuvants with different concentration (i.e., Tween 20 (0.1% w/v) and TEHP with both 0.1% and 0.3% (w/v)). †The mean difference is significant at the 0.05 level ($p \leq 0.05$). When tested with ANOVA, Tukey's HSD test for multiple comparisons showed a significant effect from adding TEHP 0.1% only. The data above represent the mean (±SD) of ($n = 10$) determinations. RSD. % is the percentage of relative standard deviation among samples of each tested group. **Data proved to be normally distributed when tested by the Shapiro-Wilk test using SPSS* where $p \geq 0.05$.*

Post hoc analyses using the Tukey HD post hoc test for multiple comparison significance indicated that the significance difference was in the case of the EC formulation that was mixed with TEHP (0.1% (w/v)) which had a lower DFR compared to all other EC tested formulation tested (i.e., EC

Table 1. Comparison between DFR recovery of different DFZ formulations (EC 10% and WP 10%) on French bean, tomato, and oilseed rape leaves.

	French bean		Tomato		Oilseed rape	
Descriptive statistics	EC 10%	WP 10%	EC 10%	WP 10%	EC 10%	WP 10%
N (Replicates)	10	10	10	10	10	10
Mean µg (±SD)	4.1 (±0.14)	3.7 (±0.65)	3.02 (±0.06)	1.96 (±0.23)	1.6 (±0.17)	1.8 (±0.3)
Median (µg)	4.11	3.58	3.0	1.97	1.64	1.96
RSD%	3.5 %	17%	2 %	12 %	11%	16%
DFR Recovery% Mean (±SD)	82% (±3)	74% (±13.1)	60 % (±1.2)	39% (±4.7)	31% (±3.3)	37% (±6.1)
Shapiro-Wilk Normality test (P-value) (Significance p ≤ 0.05)	0.08**	0.34**	0.38**	0.91**	0.371**	0.11**
T test (significance 2-tailed)	0.08		≤0.0005 *		0.07	

Table 2. The effect of different adjuvant addition on DFZ EC 10% DFR on French bean.

	DFZ EC 10% Formulation groups			
Descriptive statistics	DFZ EC 10%	EC 10%+Tween-20 (0.1% w/v)	EC 10% +TEHP (0.1% w/v)	EC 10%+TEHP (0.3% w/v)
N(Replicates)	10	10	10	10
Mean µg (±SD)	4.1 (±0.20)	3.9 (±0.31)	†3.7 (±0.2)	3.9 (±0.20)
Median	4.1	3.9	3.7	3.9
(RSD%)	5.1%	8.1%	5.6 %	5.5%
DFR Recovery% Mean (±SD)	82 % (±4.1)	77 % (±6.3)	74 % (±4)	78% (±4.1)
Shapiro-Wilk Normality test (P value) (Significance p = 0.05)	0.1**	0.8**	0.1**	0.6**
ANOVA Signifcance		$p = 0.006$		

Table 3. Different effects of adjuvant addition on DFZ WP 10% DFR on French bean.

	DFZ WP 10% formulation groups		
Descriptive statistics	DFZ WP 10% (w/v)	WP 10%+Tween-20 (0.1% w/v)	WP 10%+TEHP (0.1% w/v)
N (Replicates)	10	10	10
Mean µg (±SD)	3.7 (±0.65)	3.7 (±0.60)	4.0 (±0.74)
Median	3.58	3.91	3.92
Variance (RSD%)	17.7%	16.3%	18.3
DFR Recovery% Mean (±SD)	74 % (±13)	74 % (±12)	78 % (±15)
Shapiro-Wilk Normality test (P value) (Significance p = 0.05)	0.08**	0.12**	0.3**
ANOVA significance		$p = 0.44$	

10% (w/v), EC 10 + Tween-20 and EC + TEHP 0.3% (w/v)). Generally, the effect of the adjuvant addition on the degree of DFR was beneficial. It slightly decreased the percentage of DFZ residue retention in all the treated groups compared to the DFZ EC 10% without any adjuvant. The DFR mean recovery% was the highest with the EC10% formulation (82 ± 4.1%), followed by the TEHP at 0.3% and Tween-20 at 0.1% (w/v), with DFR mean recovery% of 78 ± 4.1%, 77 ± 6.3%, respectively. On the other hand, the DFR mean recovery was the lowest (74 ± 4%), with the formulation containing TEHP adjuvant at a concentration of 0.1% (w/v).

On the other hand, in the case of DFZ WP 10% formulations tested with adjuvants, the one-way analysis of variance showed no significant effect of adjuvants ($p = 0.44$). The mean DFR recovery% of WP 10% was similar to the DFZ WP 10% with the addition of Tween-20 (0.1% (w/v)) retaining (74 ± 13%) and (74 ± 12%) respectively. Despite the insignificant difference between WP 10% formulations and the WP 10% +TEHP (0.1% (w/v)), the latter DFR recovery% was slightly higher (78 ± 15%). It was noted that the variance in DFR% was higher in the case of WP formulations (16-20%CV) on French bean leaves compared to EC formulations (5-8%CV). Table 3 elucidates the descriptive statistics of difenoconazole WP 10% with and without different adjuvants (i.e., Tween −20 (0.1% w/v) and TEHP (0.1% (w/v). † The mean difference is insignificant at the 0.05 level. When tested with ANOVA, there was no significant effect from adding either Tween-20 (0.1% w/v) or THEP (0.1% w/v) to the DFZ WP 10% formulation ($p = 0.44$). The data above represent the mean (±SD) of ($n = 10$) determinations. RSD. % is the percentage of relative standard deviation among samples of each tested group. **Data proved to be normally distributed when tested by the Shapiro-Wilk test using SPSS* where $p \geq 0.05$.

Figure 1, 2 and Table 4 below are showing the dynamic surface tension (DST) values for all the DFZ formulations tested. The DST curves as a function of time ranging from 10 to 100,000 ms was measured, however, the DST for the formulations is recorded at two surface ages in Figure 1 and 2 (10 ms and 5360 ms). The initial surface age is the initial time that indicates the first formation of the bubble in the measurement while the 5360 ms was chosen to reflect the time of impaction of the droplet on the leaf surface when applied using the micropipette in the lab DFR technique. Approximately 5000 ms was the estimated time for the droplet to develop from the pipette tip till it touches the leaf surface using the controlled pipetting method.

Figure 1 shows the results of DST measurement expressed as a relation between the surface age (ms) and surface tension (mNm^{-1}). The surface age is defined as the time interval between the minimal measured pressure, identified with the bubble formation, and the maximum pressure, which marks the onset of the spontaneous bubble detachment. The surface tension value on the Y- axis corresponds to the latter moment. All DFZ EC formulations were diluted in water achieving a concentration of DFZ (0.625 mg mL^{-1}). Adjuvants (Tween 20 and TEHP) were added to the EC formulation with a concentration of 0.1% (w/v).

Figure 2 shows the results of DST measurement expressed as a relation between the surface age (ms) and surface tension (mNm^{-1}). The surface age is defined as the time interval between the minimal measured pressure, identified with the bubble formation, and the maximum pressure, which marks the onset of the spontaneous bubble detachment. The surface tension value on the Y- axis corresponds to the latter moment. All DFZ WP formulations were diluted in water achieving a concentration of DFZ (0.625 mg mL^{-1}). Adjuvants (Tween 20 and TEHP) were added to the WP formulation with a concentration of 0.1% (w/v).

Pure distilled water was used to dilute all the formulations; thus, the same was used for the control replicate. There was no decrease in the water surface tension during

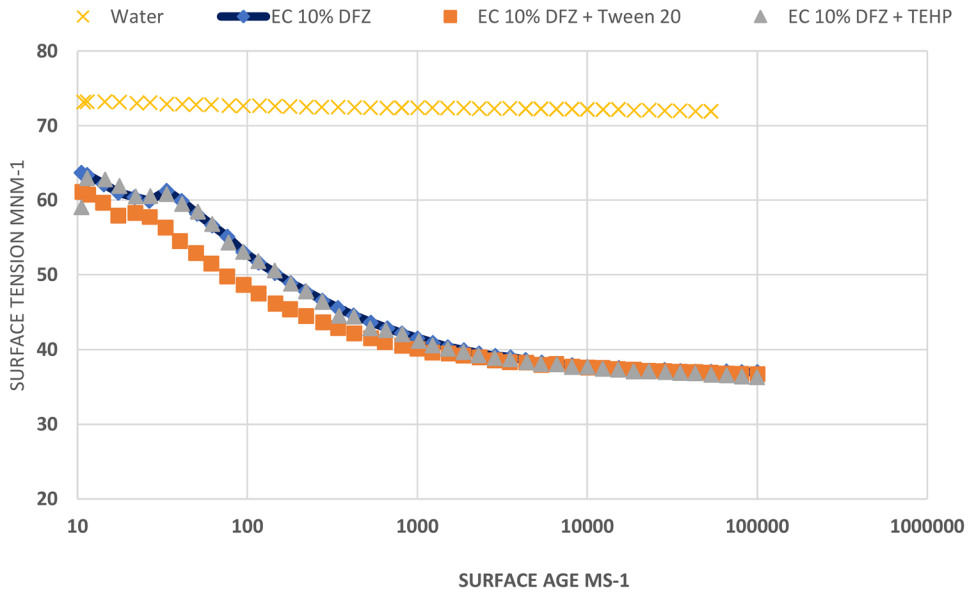

Figure 1. The results of dynamic surface tension measurements for different DFZ EC formulations.

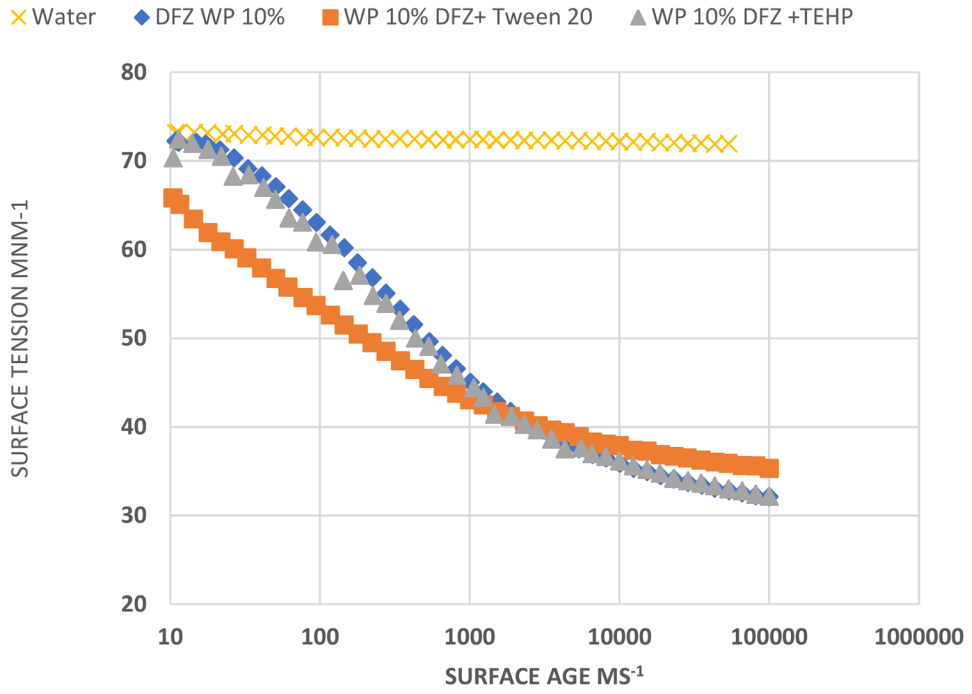

Figure 2. The results of dynamic surface tension measurements for different DFZ WP formulations.

Table 4. Dynamic surface tension vales at the initial and expected impaction time.

Formulations tested	Initial DST (mNm^{-1})	DST at 5360 surface age (ms)
Water	73	72
WP 10% (w/v)	72.3	37.5
WP 10% + Tween 20 (0.1% w/v)	66	39
WP 10% + TEHP (0.1% w/v)	71	37.7
EC 10% (w/v)	64	38
EC 10% + Tween 20 (0.1% w/v)	61	38
EC 10% +TEHP (0.1% w/v)	60	38

the first 53000 ms of the measurements. The DST of water remained constant at 72 mNm^{-1} approximately. In all DFZ formulations, the starting point or initial DST was slightly lower or equal to the water DST, but exhibited a decrease over time to reach an equilibrium surface tension indicative of microphysical changes to the droplets that would affect droplet-leaf interactions. All EC and WP formulations had the same equilibrium surface tension at 5360 ms surface age.

The DST of WP formulations declined more steeply than ECs formulations, reaching DST below 40 $mNm^{-1,}$ approximately at 5000 ms surface age, albeit from a higher starting value. WP + Tween 20 (0.1% w/v) initial DST was the lowest compared to other WP formulations (around 66 mNm^{-1}); but achieved a similar equilibrium DST to all WP and EC formulations at the same surface age (5000 ms). Table 4 shows all tested formulations' initial and contact dynamic surface tension DST values using bubble pressure tensiometer BP100 from Kruss GMBH (Hamburg, Germany). The

DST at approximately 5000 ms is the DST at droplet contact time with the targeted leaves using the electronic micropipette in the DFR developed method.

Discussion

Pesticide formulations are used to present the active substance for sale in the market, which generally includes, in addition to the active substance(s), different adjuvant(s), and other formulants combined to render the product valuable and effective for the purpose claimed. Theses formulations components are diverse and that is the likely cause of formulation effects on the residue pattern and intensity not being conclusive in the open literature.[19,20]

WP formulations have historically been considered as leading to the highest DFR of all PPP formulation types.[17,18] In this research, there were no significant differences between the DFR recovery of the DFZ WP 10% and EC 10% formulations when applied as individual droplets to the leaves of oilseed rape and French bean. The cause of this lack of difference in the current study could be due to the presence of nonionic surfactant in the WP tested formulation, which have not traditionally been used to formulate WP formulations in sufficient quantity to effect droplet spreading and film formation. Although surfactants are an essential component of EC formulations, traditional WP formulations have not included (nonionic) surfactants as inert ingredients rather dispersants, diluents, anti-foaming agents, binders, and disintegration agents.[40] Therefore, Syngenta's WP formulation could have benefited in terms of improved DFR% from the inclusion of the non-anionic surfactant in its formulation, equating to the EC formulation's effect. As a result, the active substance in this formulation would become more miscible in water than any other WP formulation lacking this nonionic surfactant. The DFR recovery % was slightly higher in the EC 10% (82 ± 3%) than the WP 10% (74 ± 13.1%) for French beans, however this did not reach statistical significance. It should also be noted that measurement of DFR in the field not only reflects the dislodgeability of residues from the leaf surface, but the initial magnitude of residues also reflects the amount of spray captured and retained. This initial residue was standardized in the laboratory to probe the specifics of formulation-leaf interactions that impact on DFR.

In general, spray deposition, adhesion, droplet coverage, and retention on leaves were found to be enhanced when nonionic surfactants are incorporated into the formulation,[41,42] and the current study has only probed adhesion, droplet wetting and retention on the leaf. Many researchers found that when surfactants are used, the foliar uptake of pesticide from droplets and biological efficacy of the active substances were improved.[42–45] In the current study, it was only in the case of tomato leaves that the previously reported trends[20, 46] of a higher DFR for EC than WP formulations as a result of better deposit retention on the leaf surface. However, there was no significant difference between EC and WP formulations for oil seed rape and French bean. Since the WP formulations contained nonionic surfactants, the addition of other adjuvants in their presence did not impact the DST of the formulations at the impaction time as shown in Figures 1 and 2. This could be due to using the right concentration of the initially incorporated adjuvant, which enabled the optimal mix possible between the active substance and the adjuvant. The data gathered by the USA ARTF proved comparable proximity of EC and WP DFR on different leaves. In this data, 75 studies involving WP pesticide spray left an average lower DFR of 0.906 µg cm^2 lb-ai acre^{-1} than 1.10 µg from the 95 studies involving EC sprays.[14]

Unlike French bean and oilseed rape, there was a significant difference ($p = 0.006$) between both EC and WP formulations when applied to tomato leaves in the current study. The DFR mean Recovery% (±SD) on tomato with WP 10% was (39 ± 4.7%) compared to (60 ± 1.2%) with the EC 10%. Besides the explanation above on the nonionic surfactant's role, tomato trichomes are known to be hydrophilic and increase the affinity of the pesticide spray to the epidermis.[47] Ultimately, the absorption of the WP formulation increased by the nonionic surfactant initially incorporated with it, leaving less DFR on the surface. Additionally, the DST results demonstrated the rapid diffusivity of the several co-formulated sufactants within the suspension particularly during the solvent evaporation phase, which would facilitate extensive absorption surface area creation for the hydrophilic aqueous suspension formulation on the hairy tomato leaf surface.

The EC formulation also incorporated surfactants that helped in the deposition and absorption. However, the emulsified system resulted in slower diffusivity of surfactant molecules as observed from the droplet surface aging. Furthermore, the presence of the hydrophobic disperse phase within the surfactant could reduce DFZ penetration into the hydrophilic tomato leaf surface, with the hydrophobic DFZ having preferential retention within the oil phase of the developing film. DFZ is classified as having a low solubility in water (15 mg L^{-1} at 20 °C) according to the Pesticide Properties Database (PPDB)[48]

Deposit behavior depends on both the characteristics of the droplet and the texture of the targeted leaves; thus, the studied leaf texture/crop (i.e., tomato) magnified the nonionic surfactant effect when applied with the DFZ WP 10% and resulted in 20% lower DFR (39 ± 4.7%) than the EC 10% (60 ± 1.2%). The effect of different adjuvant addition on the DFZ WP 10% DFR revealed no statistical effect on the French bean leaves when tested with ANOVA ($p = 0.44$). On the contrary, one-way ANOVA revealed that there was a statistically significant difference in the DFR intensity between at least two groups in the case of DFZ EC 10% when mixed with adjuvants (Tween-20 (0.1% w/v), TEHP (0.1% (w/v)), and TEHP (0.3% (w/v)). This significant difference observed was only between EC 10% group and EC 10%+TEHP (0.1% (w/v)) where ($p = 0.003$).

The adjuvants used in this research were meant to act differently to reduce the DFR recovery% when mixed with the DFZ WP or EC formulation. Tween −20 is a surfactant known to reduce the surface tension of the spray droplets, increasing the wetting and the spreading of the pesticide on the leaves. In comparison, the TEHP is a plasticizer or sometimes called a penetrator, which is known to enhance the uptake of the AI into the plant by reversibly changing the structural properties of the plant cuticle.[33] It is hypothesized that this kind of adjuvant decreases the size of the crystalline platelets in the cuticle and enhances the pesticide

fluidity by improving the diffusion coefficient.[33] From the above, the lower miscibility of the AS in the DFZ 10% WP formulation and the expected fast drying of the deposit on the leaf could be the leading cause of the poor functionality of both adjuvants tested (i.e., Tween-20 and TEHP). The proposed low miscibility of AS in the WP was therefore not promoted by the adjuvant function of either reducing the surface tension of the spray particles (Tween-20) or changing the cuticular structure (TEHP) to allow more penetration and diffusion of the DFZ into the cuticle. This was observed from the close mean DFR recovery% on French bean (74 ± 13.1%. 74 ± 12.1% and 78 ± 14.8%) in WP 10%, WP 10% +Tween (0.1% (w/v)) and WP 10% + TEHP (0.1% (w/v)) treatment groups respectively.

On the other hand, the good and homogenous miscibility of the AS in the emulsion formed from the DFZ EC10% was found to enhance the absorption of the DFZ into the French bean leaves when the DFZ EC 10% was mixed with TEHP (0.1% w/v), as evident from the reduced DFR% (74 ± 4.0%) observed in the presence of the TEHP 0.1% (w/v) compared to the DFZ EC 10% (w/v) alone (82 ± 4.1%) on the French bean leaves. It was also noticed that increasing the concentration of the TEHP from (0.1% (w/v)) to (0.3% (w/v)) did not improve the DFR recovery % or increase the absorption and penetration of the DFZ into French bean leaves. These findings align with the concept that an accelerator's efficacy depends on the type of plasticizer and its right concentration. The DFZ 10% EC formulation benefited from adding the accelerator TEHP with the appropriate typical concentration of 0.1% w/v and not 0.3% w/v, which agrees with many findings that suggest adjuvant critical micelle concentration formation is usually reached at a concentration of 0.1% of the spray volume.[31]

Despite the pressing argument that the most significant effect on leaf wettability is the surface structures, some physical tests were also considered crucial (i.e., dynamic surface tensions, contact angles etc.) to understand the droplet behavior that is of importance in droplet-leaf interactions.[49] Therefore, the DST was measured to analyze the difference in the DFZ formulations tested and reflect on the DST of each at a specific time (the time when the droplets touch the plant surface). It is hypothesized that during foliar application in the field, the majority of spray droplets impact the leaf surface after about 50 to 400 ms.[50] The interface saturation and the surface tension lowering are required to be achieved in such a small-time frame for good retention on the leaf; alternatively, an applied droplet would shatter and bounce off the target.[51]

This estimated time in the field was estimated when mobile spray equipment was used with high velocity and pressure to induce droplet travel from the nozzle to the leaf, unlike in the current experiment. The present investigation was performed in the laboratory, the droplets were generated by pressing on the micropipette and waiting for the droplet of 0.2 µL to fully develop on the pipette's tip before placing it on the leaf surface. This process was estimated to take 5 s (5000 ms). The specific value of 5360 ms was selected for further consideration from the bubble pressure measurements.

Taylor, 2011 proposed a critical DST value below 55 to 60 mNm^{-1} which would allow a full spreading and annulus formation of the droplet over targeted leaves.[49] From the generated data, water DST was constant at around 72 mNm^{-1} with no change, defined as the normal surface tension of water in the literature.[52] These results confirm no contamination in the water source used, which served as a diluent for all other formulations tested. The equilibrium surface tension was also reached immediately with water, in contrast to the dynamic behavior seen with the EC and WP formulations, which results from differential molecular mobility of dissolved surfactants and solute within the formulation. All WP and EC formulations achieved approximately the same equilibrium surface tension value, which was consistent with the broadly similar DFR values for all WP and EC formulations. However, there were differences in their DST as a function of surface age (Figures 1 and 2), which would affect the differential rates of leaf wetting and spreading by the droplets after application.[49] WP formulations possessed a higher initial DST but a more rapid rate of surface change than EC formulations. Consequently, a low equilibrium DST (equivalent to that of the EC formulations) was rapidly achieved for WP formulations, thereby compensating for the high initial DST.

The DST measurements at the impact time for the WP formulations (i.e., WP10%, WP10% +tween 20 (0.1% (w/v) and WP 10% +TEHP (0.1% (w/v)) proved to have very close DST of 37.5, 39, 37.7 mNm^{-1} respectively as shown in Table 4. The DST at the impact time was also identical (38 mNm^{-1}) in all EC formulations tested (EC 10%, EC 10% +Tween 20 (0.1% (w/v)) and EC 10%+TEHP 0.1%). The close DST value for the ECs formulation and WPs formulation around 37-38 mNm^{-1} were reflected in the DFR recovery % comparison between both formulations on French bean and oilseed rape, while the DFR recovery % was different in the case of tomato leaves. This difference was discussed earlier due to the nature of the leaf and the solubility of the formulation on this kind of leaf. This adds another piece of evidence that the effect of EC formulations has been equated to the WP formulation when adjuvants are incorporated into the formulations. In contrast, the DST did not change when adjuvants were mixed in the spray solution, and that has also been reflected in the DFR recovery % for both EC and WP formulations on French beans. The significant effect of TEHP (0.1% (w/v)) addition to the EC was not related to the surface tension reduction but to the different activity of the TEHP as a plasticizer that reversibly changes the structural properties of the plant cuticle.[33] The increased solubility of the emulsion may enhance the functionality of this adjuvant in the EC spray compared to the suspension in the WP spray.

Conclusion

The findings of this research shed light on the importance of formulation and adjuvants as factors that affect DFR. From the DFR recovery results of different DFZ formulations (EC 10% and WP 10%), it was observed that the DFZ WP formulation retained a mean DFR magnitude comparable to the EC 10% formulation on French bean and oilseed

rape leaves, but not tomato leaves. Unlike previous studies, the isolated droplet application of our laboratory DFR technique allowed examination of formulation effects on DFR that would be mediated by alterations to droplet-surface interactions and leaf penetration processes, without the confounding impacts of aerosolization and aerosol properties.

The findings in the current study demonstrated that it is not necessarily the case that the WP formulations in general retain more DFR compared to EC products, as has been historically documented for some PPPs. The DFZ WP 10% left significantly lower residue on tomato leaves compared to the EC 10%. Without any confounding aerosol behavior effects (spray capture and retention), the formulation composition was one of the main drivers of such low DFR for tomato leaf due to the enhanced interaction of a hydrophilic droplet with the hairy hydrophilic characteristics of the leaf surface.

In summary, EC formulations displayed a low initial surface tension which would promote film spreading, whereas WP formulations demonstrated a more rapid diffusivity of surfactants than EC formulations, which would compensate for the relatively higher initial surface tension, thereby promoting equivalent film spreading to EC formulations. The latter findings are consistent with the similar DFR values across WP and EC formulations.

The laboratory DFR method was suitable to demonstrate that the effect of incorporating adjuvants is chemical and formulation specific. This was observed from the different results of mixing TEHP or Tween-20 with EC formulation where for example, the DFZ 10% EC formulations benefited from the addition of TEHP as accelerator at 0.1% w/v but not higher concentrations (0.3% w/v).

These findings indicate the importance of the formulation and in-tank adjuvants as factors that affect DFR. It shows the importance of investigating these factors and the usefulness of the laboratory DFR developed method in generating and studying factors affecting DFR in standardized, controlled and robust method that can overcome the seasonal nature of DFR field studies. This could eventually help the industry and PPPs regulators in defining the influencing factors and draw a conclusion on the possibility of extrapolation between applications based on scientific evidence. Further statistical analysis of DFR field studies data submitted by PPP registrant to regulatory agencies during the registration process could help the regulators to allow DFR study extrapolations based on their formulation types. In addition to the scientific evidence that could be provided by utilizing the DFR laboratory methods to investigating such determining factor.

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Disclosure statement

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ORCID

Mohamed H. Badawy http://orcid.org/0000-0003-4625-6231

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and the Appendix.

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Appendix

Table A1. Summary of AOT 0.01% (w/v) required volume and number of washes for each DFZ formulation/crop combination tested.

Pesticide	Crops/leaves	Number of washes	Total amount of AOT 0.01% required	Surface area (two leaves double-sided) (cm2)	AOT 0.01% volume required per cm^2 leaf
DFZ EC 10%	French bean	1	30 mL	45	0.7
	Tomato	2	45 mL	58	0.8
	Oilseed rape	3	45 mL	132	0.3
DFZ WP 10%	French bean	2	45 mL	55	0.8
	Tomato	1	30 mL	53	0.6
	Oilseed rape	3	45mL	146	0.3