Very-low volume application and attendant suspension concentrate formulation design

By ANDREW C CHAPPLE and MALCOLM A FAERS

Bayer AG, Alfred Nobel Str. 50, 40789 Monheim, Germany
Corresponding Author Email: andrew.chapple@bayer.com

Summary

Recently, unmanned aerial systems (UAS or drones) are emerging, especially rapidly in Asia Pacific, as alternative and potentially disruptive methods to apply plant protection products more sustainably. However, limited carrying capacity for the spray liquid results in spray volumes being reduced down to ~8–30 L ha^{-1} from the more typical 100–1000 L ha^{-1}). Similarly, spray boom application volumes are moving below 100 L ha^{-1}. At these very-low spray volumes (VLV: 5–50 L ha^{-1}), the much lower number of spray droplets (typically in the range VMD 100 to 250 µm) will affect spray deposition and coverage and this can result in reduced efficacy (Wang *et al.*, 2019). This creates interesting opportunities for formulation design where the higher concentration of active substance (a.s.), surfactants and other formulants in the spray droplets can be utilised to enhance wetting, spreading and biodelivery of the a.s. to the target, in particular, suspension concentrates (SCs) of low water solubility. This paper constitutes a *precis* of the work addressing this subject given in much greater detail in Faers *et al.* (2023) as well as a discussion of the opportunities afforded by VLV formulation technology.

At very-low spray volumes, SC formulations containing relatively low doses (g ha^{-1}) of formulants (adjuvants) that enhance spreading on the leaf surface and/or uptake up the active ingredient(s) can thus maintain good spreading, uptake and biological efficacy, thus overcoming the coverage limitations of reference SC formulations (Fig. 1). This result is unexpected and surprising when the relatively low dose of formulants (adjuvants) used (g ha^{-1}) is considered. Examples of processes driving both the spreading of deposits and uptake of a.s. through such mechanisms as Wenzel and Cassie-Baxter wetting regimes and 'coffee rings' are shown along with the interaction between deposits and leaf surface structure. Spreading and uptake are just two facets of VLV formulations: there are also opportunities for reduction in environmental exposure to PPPs through the addition of rain-fast /anti-washoff and anti-bounce adjuvants as well as drift reducing adjuvants. Making large changes to the behaviour of an a.s. through formulation effects means that registration processes will have to address these changes and be adapted.

Key words: Formulations; very-low volume; spraying; adjuvants

Introduction

This paper is a *precis* of recent formulation work covered more extensively in Faers *et al.* (2023) where a great more detail is given along with the supporting references and more examples than are provided here. The reader is encouraged to refer to this paper directly and, if referenced, should fully reference Faers *et al.* (2023: https://doi.org/10.1002/ps.7707). Where Faers *et al.* (2023) deal with the formulation processes and consequences, this paper outlines some of that work and highlights the potential advantages of formulation design that could create new opportunities for future VLV applications, both from drones and boom sprayers.

The use of plant protection products (PPPs) in arable crops has typically meant using low volume applications (LV: 50–200 L ha^{-1}) and sometimes much higher (*e.g.*, horticulture and glasshouse crops), using various machinery from the humble knapsack up to modern 40 m booms on self-propelled sprayers. Recently, UAS such as drones have brought niche application systems such as the Yamaha R50 unmanned aerial vehicle (UAV) – a mono-rotor small scale helicopter – into mainstream use. These have taken application volumes into the realm of VLV (5–50 L ha^{-1}) and as a result, have led to a reassessment of the effects of formulation components on activity of the PPPs applied to crops. Moving to VLV, especially to the lower end of the range, crop cover begins to be an issue. At the same time, there is also a worldwide emphasis on reducing spray drift and this has usually meant using larger droplet spectra (although other methods of reducing drift are available) with the result that with VLV, the number of droplets reaching a canopy decreases rapidly compared with conventional application methods and volumes. This did not especially matter when application volumes were in the 100s L ha^{-1}. A second issue is the momentum of the spray cloud. When an arable boom is used to spray 20 L ha^{-1} as opposed to 200 L ha^{-1}, there is just 10% of the momentum available to distribute the PPP into and through the canopy. Drones do not suffer from this problem, although the reverse can occur: too much momentum is imparted to the spray cloud and the drops 'bounce' out of the sprayed area and can be released in to the air as drift.

The effect on efficacy of reducing cover has been addressed by Wang *et al.* (2019) who evaluated the effects on fungal and insect pest control of changing spray volumes from LV (225 and 450 L ha^{-1}) to VLV (9.0, 16.8, and 28.1 L ha^{-1}). They found that efficacy clearly decreased with application volume. However, they were unable to separate the conflation of spray volume and drop size. It was also clear where the concentration of the methylated crop oil adjuvants mattered most: 9 L ha^{-1} at 1% concentration gave lower efficacy that 18 L ha^{-1} at 1% concentration as the amount of oil adjuvant available at the leaf surface in the deposits doubled. Example data is given in Fig.1, where Wang *et al.*'s (2019) data has been normalised to the 450 L ha^{-1} application (100% efficacy). In all cases, efficacy decreases with decreasing application volume, with a greater rate of decline at around 20 L ha^{-1}. The most likely explanation is the reduction in cover afforded by the low volume applications, especially as the formulations used do not appear to contain adjuvants that would improve spreading or uptake.

Leaving aside drones (application volumes typically 5–20 L ha^{-1}), arable crop applications start at around approximately 100 L ha^{-1} and go up to as high as a 1000 L ha^{-1}. Droplets generated generally provide high enough coverage to deliver the relevant efficacy, with the added contribution of coalescence of droplets at very high application volumes as well as the momentum generated to reach into the canopy. However, as application volumes fall, coalescence becomes rarer and the deposit density and distribution is more directly related to the application parameters chosen (*e.g.*, nozzle size, application volume). Clearly, for a given nozzle, halving application volume halves the number of droplets but doubles the concentration of active ingredient and adjuvants in the deposits. This self-evident interaction is not normally considered in formulation design: the application volumes are sufficiently high to give decent cover and by extension, efficacy. The interesting question then arises: where is the lower limit (the combination of drop size and application volume) and can formulation design bring the efficacy loss under control (Fig. 1).

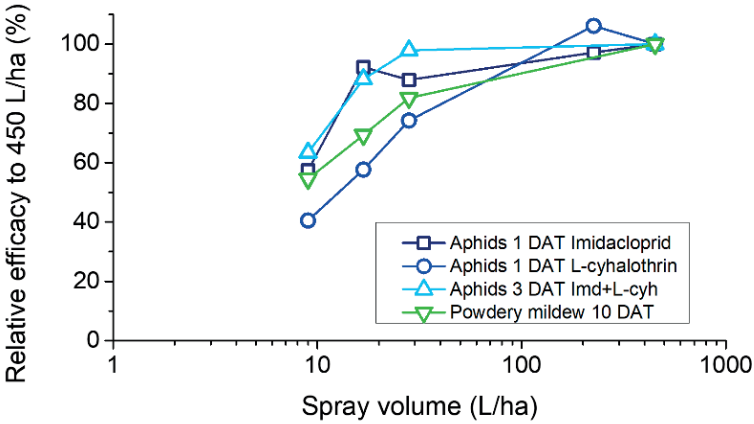

Fig. 1 Field efficacy replotted from Wang *et al.* (2019) for a range of products applied to wheat with the efficacy at 450 L ha^{-1} taken as the 100% reference value. Spray volumes 450 and 225 L ha^{-1} applied by backpack sprayer, 28.1, 16.8 and 9.0 L ha^{-1} applied by UAS. Insecticide tests □, ○, △, fungal disease test▽. (From Faers *et al.* 2023).

Lastly, leaf surfaces differ in their surface properties. This is a combination of the type of waxes of which they are made and the surface micro-structures made from these waxes (Fig. 2), with the added complications of growth stage and weathering (Holloway, 1969; Taylor, 2011).

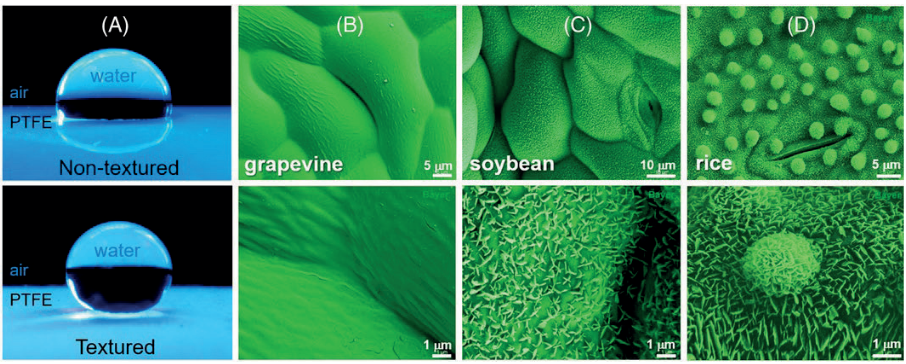

Fig. 2. Different wetting behaviours of a water droplet on smooth non-textured PTFE film and micro-roughened textured PTFE film (a). SEM images (colored) of adaxial grapevine (b), soybean (c) and rice (d) leaf surfaces illustrating the different micro-textures that exist. (From Faers *et al.*, 2023).

Formulation effects

Of the various formulation effects that can be driven by concentration in the deposit, two formulation mechanisms are considered here: superspreading and uptake enhancement. There is, however, very little published data on *formulation* effects at VLV, for UAS or boom sprayers. (Wash-off, rain-fastness, drift reduction are not directly dealt with here.)

The below draws heavily from Faers *et al*. (2023) where the reader may find more extensive information on modes of action and the supporting references as well as the formulation recipes. In general, this century has seen little work on the consequences of application effects: for herbicides, one must go back to a review of application effects by Knoche, (1994) that shows the importance of application volume and drop size which is not simple, as is also shown in the review by Combellack, (1984). For equivalent work with fungicides, one must go all the way back to Frick, (1970) for indications of the effects of deposit size, distribution, and application volume.

1. Organo-silicone high-spreading surfactant studies

Water as a carrier liquid has poor wetting and spray retention properties, mainly caused by epicuticular leaf structure (principally wax crystals: Fig. 2). Adjuvants are well known as being able to overcome this limitation. Organo-silicone (trisiloxane) based surfactants are known for their high spreading effects, especially at low spray volumes (Stevens, 1993; Venzmer, 2021). In general, lower application volumes gave either greater efficacy or capture, but the risk of increasing run-off is real (Gaskin *et al.*, 2004) and needs to be borne in mind.

2. Uptake adjuvant studies

Spreading may improve cover but an alternative route to maintaining efficacy at low application volumes is to increase uptake (*e.g.*, various oils and certain non-ionic surfactants). At low surfactant concentrations, particulate a.s. become pinned at the edge of the evaporating deposit whereas adjuvants continue to flow through the volume of the evaporating liquid, driven by an effect known as Marangoni flows from surface tension gradients at the air-water interface (Deegan *et al.*, 1997; Faers, 2007; Faers and Pontzen, 2008). As the deposit dries, the AS become concentrated at the edge of the deposit due to the greater evaporation occurring there whereas the adjuvant, if it is for example a less dense oil, continues to move with the Marangoni flows with the result that it predominantly collects at the centre of the deposit. Here the lower association between the a.s. particles and oil adjuvant results in reduced a.s. uptake into the plant. However, as the concentration of the surfactants reach the critical micelle concentration, the surface of the drying deposit becomes saturated with the surfactant and the Marangoni flows cease, with the result that a greater proportion of the oil adjuvant can now collect at the edge with the consequential higher association resulting in enhanced a.s. uptake into the plant. This enhanced association between the a.s. particles and the uptake enhancing adjuvant can especially occur at decreasing spray volumes, where both the coalescence of the spray droplets on the plant surface decreases and the concentration of the a.s. and adjuvant increases. The resulting distribution of a.s. and solid components at the edge of the deposit is known as coffee rings (see Fig. 4, apple). By this process, both the SC formulation design and spray volume can affect the level of uptake into the target plants.

Published work has addressed the effects of uptake adjuvants on efficacy (see Faers *et al.*, 2023 therein). The general conclusions to be reached are that for poorly water soluble crystalline lipophilic AS, a solubilised active has greater uptake into leaf cuticles than the discrete particles. However, little work has been done at very-low application volumes. When this has been done (*e.g.*, Faers and Pontzen, 2008), coffee ring deposit microstructures have shown enhanced uptake, with the interesting corollary that a.s. surface concentration in the deposits was more important than deposit area coverage.

Experimental work

The above leads to an important question: what formulation solutions are available to overcome the limitations imposed by very-low volume applications on coverage and or bio-delivery? As a summary of the work of Faers *et al.* (2023), two components are considered:

leaf spreading and wetting surfactants (*e.g.*, Silwet® 408 and 806,); and uptake promoting nonionic adjuvants (*e.g.*, Crovol® CR-70G, Alkamuls® A, and Lucramol® HOT 5902). All work was done in the laboratory and glasshouse, for a range of actives (all SCs: reported here isoflucypram but also penflufen, tebuconazole, fluopicolide, inpyrfluxam, and bixafen in the main document).

Application in the field was done using an adapted knapsack sprayer into paddy rice, approximately 0.8 m high. For volumes of 600 and 1200 L ha^{-1} a TX-8 (TeeJet, US) nozzle was used; for emulation of VLV spraying, a Conejet® TX-2 (TeeJet, US) was used. Both were applied at 3 bar and 0.4 m above the canopy. Deposition was assessed under UV-light and leaves collected for individual image analysis (ImageJ software). In the laboratory, 1.4 µL (approximately 1390 µm diameter.) drops were applied to greenhouse grown rice and apple leaves, and spreading measured. (Exact details can be found in Faers *et al.* (2023)).

Cuticle penetration studies were done according to the method of Schoenherr and Baur (1996).

Greenhouse efficacy studies reported here considered efficacy of various SC formulations against *Puccinia recondita* (L.; brown rust) on potted indoor grown wheat using a track sprayer applying ether 200 L ha^{-1} or 10 (or 15) L ha^{-1}, through a TP8002E TeeJet nozzle at 2 bar. VLV was reached using a Lechler PWM system at 30 Hz (8% to 100% to achieve the relevant application volumes). Plants were inoculated 1 day after application and assessed visually for disease development.

Results

The effects of reducing application volume from 600 L ha^{-1} down to 4 L ha^{-1} on the deposition on field grown rice plants is shown in Fig. 3, for the reference SC formulation (non-adjuvanted). Where coverage is a component of efficacy, clearly such sparse distributions will have an effect.

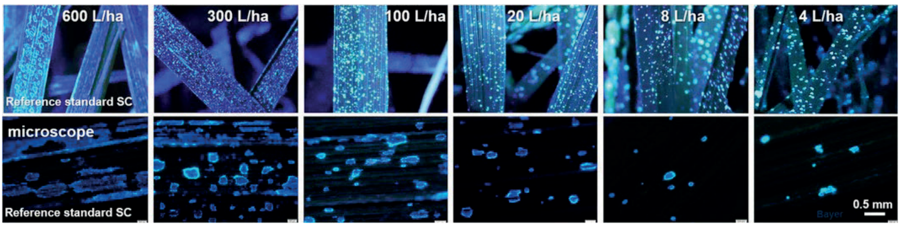

Fig. 3. Images of leaf deposits from hand spray application of the reference SC on rice plants for high and low spray volumes. Top row is at a low magnification showing whole leaf areas (in the field), bottom row is at high magnification in a microscope showing individual spray deposits (…SC Dose rate = 1 L ha^{-1}). (From Faers *et al.*, 2023).

However, the texture of the leaf itself (see Fig. 2) will also affect how spreading will take place. Fig. 4 shows the effects of a high spreading formulation on the deposit structure for two leaf surfaces (rice and apple): just applied on the left, dried down on the right. 'Coffee rings' are also visible around the apple deposits. The only variable altered is the concentration corresponding to the different application volumes: all other components remain the same. What is clear is that the target surface and formulation components both have to be taken into account. One can also see the production of coffee rings with some of the apple deposits.

In Fig. 5, spray deposits are shown on rice leaves derived from more realistic drop sizes generated using a knapsack sprayer as described above. These can be compared to Fig. 3 (non-adjuvanted formulation).

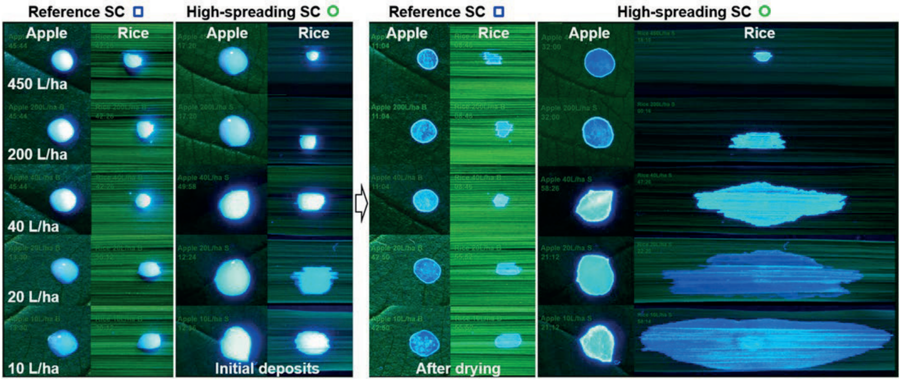

Fig. 4. Coverage before (left) and after dry-down (right) of reference SC (unadjuvanted) and high-spreading + enhanced uptake SC at concentrations corresponding to medium and very-low spray volumes (450 to 10 L ha^{-1}) applied as 1.4 µL droplets (pipette) to the adaxial surface of apple and rice leaves (SC dose rate = 1 L ha^{-1}). (From Faers *et al.*, 2023).

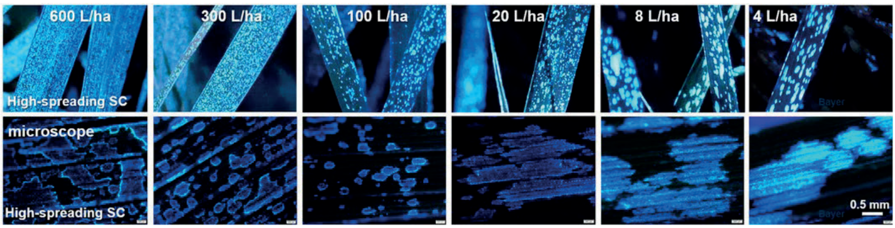

Fig. 5. Macroscopic and microscopic images of leaf deposits from hand spray application of a high spreading on rice plants for different spray volumes (application rate = 1 L ha^{-1}). (From Faers *et al.*, 2023).

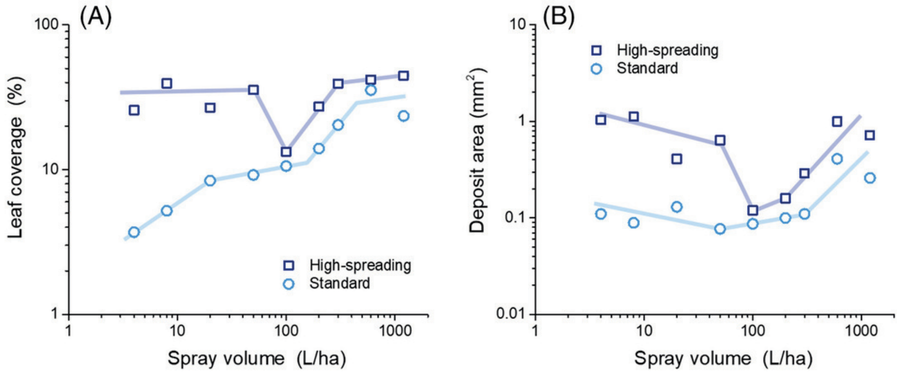

Fig. 6. Leaf coverage A and mean deposit area B for the reference SC (○) and a high-spreading SC (□) from hand/backpack spray application on rice plants for a wide range of spray volumes. Lines drawn for guidance. (From Faers *et al.*, 2023).

Coverage results from data in Figs. 3 and 5 are plotted in Fig. 6. Of interest is that the leaf coverage is maintained below approximately 40 L ha^{-1}. Deposit area and leaf coverage both decline for adjuvanted and non-adjuvanted formulations but at a certain concentration, the spreading characteristics of the adjuvanted formulation counterbalance the reduction in cover caused by the reduction in the number of droplets available and leaf coverage and deposit area recover to the original levels.

Fig. 7 shows the penetration profiles for two formulations, an unadjuvanted SC and an SC designed for uptake promotion. Uptake is improved for both 10 and 200 L ha^{-1}, but dramatically so for the 10 L ha^{-1} application volume. In general, uptake promoting agents have little effect on spreading, so this improvement would appear to be driven mainly by the concentration effect on the uptake enhancer.

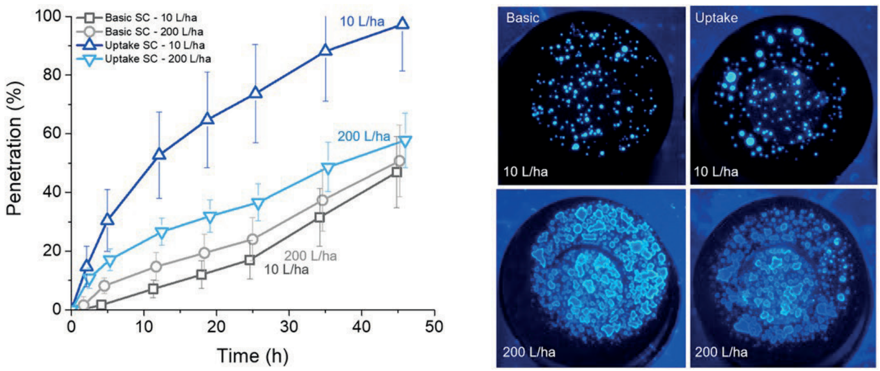

Fig. 7. Left: Cuticle penetration results for inpyrfluxam SC (reference SC) and an uptake promoting formulation after spray application at 200 and 10 L ha^{-1} spray volumes (application rate = 0.5 L ha^{-1}). Right: Representative spray deposit images on cuticle measurement cells showing the different depositions at 10 and 200 L ha^{-1}. Error bars are standard deviations. Basic SC @ 10 L ha^{-1} □ and 200 L ha^{-1} ○; Uptake SC @ 10 L ha^{-1} △ and 200 L ha^{-1}▽. (From Faers *et al.*, 2023).

When the above components of spreading and uptake are considered in terms of efficacy, the physical effects observed translate to biological outcomes. Fig. 8. shows the effects of different formulation types – unadjuvanted, spreading, uptake, and spreading+uptake – on the control of rust on wheat. The standard SC can be improved dramatically using spreading and uptake adjuvants. However, at 10 L ha^{-1}, not only is efficacy improved by uptake adjuvants alone, but efficacy is the same or higher at lower dose rates. Similar effects on efficacy – especially due to surface spreading – have been shown for inpyrfluxam and bixafen (Faers *et al.*, 2023).

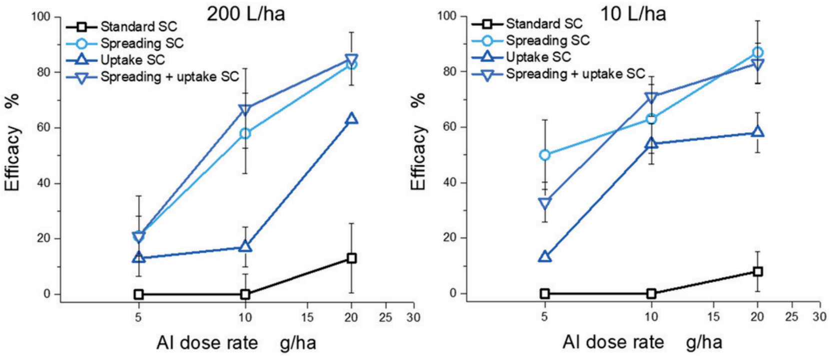

Fig. 8. Curative efficacy (%) of isoflucypram SC formulations applied at different active ingredient dose rates (g ha^{-1}) on greenhouse grown wheat plants against *Puccinia recondite* infection at spray volumes of 200 and 10 L ha^{-1} (SC application rates 1, 0.5 and 0.25 L ha^{-1}). Error bars are standard deviations. Standard SC □, Spreading SC ○, Uptake SC △, Spreading + uptake SC ▽. (From Faers *et al.* (2023).

Discussion

A limiting factor to VLV sprays is the reduction of coverage, especially below about 40 L ha^{-1}, as has been demonstrated by Wang *et al.* (2019). This is particularly relevant for drone applications. The work of Faers *et al.* (2023) shows that the loss of coverage can be offset with formulation adjuvants once a threshold of concentration has been reached. Obviously, this varies with adjuvant and there is a need to consider the interaction between leaf structure and the various formulation components (Fig. 2). However, improved penetration is also part of the equation for maintaining efficacy of a.s. at low application volumes and low plant coverage (Fig. 7). Where spreading alone cannot maintain efficacy, uptake can be an alternative approach. From Fig. 8, it can be seen that the uptake component can contribute in the same deposit structure as spreading: the two are not exclusive, nor do they necessarily work against each other. However, it must be stressed that the balance between what are two competing if not antagonistic effects must be carefully designed, as shown in Fig. 8. Not only will it be important to get the correct balance between application volume (and therefore the concentration of a.s and adjuvants) and the ratios of the adjuvant concentrations, but a tailored recommendation for spray application taking into account the crop (and growth stage?) as well as which nozzle, pressure, and application volume ranges will need to be met in order to realise the benefits that exist at the formulation-application interface and for the formulations to work as designed.

The advantages of increasing concentrations of adjuvants in spray volumes do not stop at maintaining efficacy at reduced coverage. At conventional application volumes, the efficacy of rain-fast (RFA) / anti-washoff additives are also driven by concentration of the adjuvant and this is likely to be true for VLV. The exact mechanism has yet to be fully investigated: for example, how important is the ratio of a.s. to RFAs and is this more important than the concentration of the RFA in the droplet? Changing the adherence properties of a formulation and increasing uptake into the leaf all mean that more of the a.s. stays on the leaf and does not move to the soil beneath the canopy: thus the a.s is not available for pathways to run-off, drainage, and groundwater contamination. Half-lives of a.s. and metabolites on foliage are roughly an order of magnitude shorter than in soil and this is key. Likewise, the efficacy of drift reducing adjuvants are largely concentration driven. Extrapolating from the limited experimental understanding available at the moment, VLV formulations thus have the potential to drive sustainability of PPPs in agriculture: delivering more of the a.s to the target site and having less available for off-crop movement (to soil and the off-crop). Surfactants and adjuvants can be leveraged to a much greater extent than with LV applications, and this opens doors to a variety of application technology / formulation technology interfaces that will be of value not just to the farmer. However, such large changes in the performance of an a.s. mean that registration of products aimed at VLV will require a rethink: the assessment of the risk to the environment in particular will have to consider both the positive (*e.g.*, less a.s. reaching the soil) and negative (*e.g.*, more a.s. available as dislodgeable foliar residues). Formulation performance may then be as important as a.s. properties in determining the possible effects on environmental and human safety. Thus, formulations for very-low volume application, from aerial or ground-based systems, have a variety of benefits and will be an interesting addition to the tools being developed for precision agriculture.

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