The Effect of Adjuvant on Leaf Wetting and Uptake of Fluid Foliar P Fertilizers for Wheat

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INTRODUCTION

The ability of foliar sprays to stick to leaves is essential to enable uptake of nutrients. Many plant species including wheat have been shown to have low wettability due to leaf surface roughness which is caused by waxes and hairs (trichomes) (de Ruiter et al. 1990). To overcome this issue, surfactants are often added to adjuvants to improve spreading and sticking of the fertilizer on the leaf surface and increase the amount of leaf interacting with the fertilizer (Fernández and Eichert 2009). A large number of adjuvants are commercially available for use in combination with agrochemicals, however their effectiveness with foliar applied fertilizers is often unknown. There is potential for incompatibility between phosphorus (P)-containing components and adjuvants in the formulation. In particular the low pH of phosphoric acid (an effective foliar formulation) may negatively interact with some adjuvants.

It has been suggested that improved wetting of foliar fertilizer on leaves (i.e. a small contact angle measured between the leaf-fertilizer interface), will increase the rate of uptake of foliar-applied fertilizers (Fernández and Eichert 2009). It follows that poorer wetting (higher contact angles) will result in lower uptake rates of the fertilizer formulation. This study aims to identify how three selected adjuvants (two commercial and one laboratory grade) in combination with foliar P fertilizers influence the wetting of wheat leaves and the subsequent short-term uptake and translocation of foliar-applied P.

MATERIALS AND METHODS

<u>Wheat growth conditions</u>

Plants were grown in pots of 10 cm diameter and 17 cm depth that were not free-draining and held a total of 1.7 kg soil pot^{-1}. Before sowing, the soil was wetted to 15% of field capacity and the following basal nutrients were mixed through the soil: potassium as K_2SO_4 at 80 mg K pot^{-1}, magnesium as $MgSO_4.7H_2O$ at 20 mg Mg pot^{-1}, zinc as $ZnSO_4.7H_2O$ at 12 mg Zn pot^{-1}, copper as $CuSO_4.5H_2O$ at 9.6 mg Cu pot^{-1}, manganese as $MnCl_2$ at 1.6 mg Mn pot^{-1} and the total sulfur applied in these reagents equated to 70 mg S pot^{-1}. The soil was watered to 70% field capacity and P and nitrogen (N) were added to the soil as a band 2 cm beneath the seed at a rate of 5.8 mg P pot^{-1} (approx. 14.7 lb P_2O_5 acre^{-1}) as phosphoric acid and 60 mg N pot^{-1} as urea before sowing. At 24 days after sowing (DAS) an additional 20 mg N pot^{-1} as urea was applied in solution to the soil surface and watered in.

Four pre-germinated seeds of wheat (*Triticum aestivum* cv. Axe) were sown in each pot at 1 cm depth and thinned at the two-leaf growth stage by leaving the two most uniform seedlings per pot. Immediately after sowing, the surface of the pot was covered with 50 g of alkathene granules to minimise evaporation from the soil. Pots were watered every 2 days to maintain 80% field capacity before increasing watering frequency to every day from early booting. Plants were grown in a controlled environment room (20 °C/15 °C day/night cycle of 12 h each) and their positions randomised every week.

<u>Adjuvants</u>

The three adjuvants analysed in this study were LI 700®, Agral® and Genapol® X-080. LI 700® is an acidifying and penetrating surfactant with 35 % w v^{-1} propionic acid (CAS No. 79-09-4), 35 % w v^{-1} soyal phospholipids (CAS No. 8002-43-5) and 10-30% w w^{-1} surfactant. Agral® is a spray additive with 63 % w v^{-1} nonyl phenol ethylene oxide condensate (CAS No. 9016-45-9). Genapol® X-080 is a pure surfactant of polyethylene glycol monoalkyl ether (CAS No. 9043-30-5).

<u>Contact angle measurements</u>

Static advancing contact angle measurements of fertilizers were made on the adaxial (top) side of leaves from wheat plants at early booting (Zadoks 40, Feekes 9) to early ear emergence (Zadoks 50, Feekes 10.1). Measurements were made using the sessile drop method as described in Forsberg et al. (2010). All contact angle measurements were made on the mid-section (length-wise) of the second leaf down on the main stem between the leaf edge and mid-vein. Before contact angles were measured for fertilizer formulations, the static advancing and receding contact angle for pure water was measured on the leaf surface to ensure leaf surface wettability did not differ between these growth stages. The static advancing and receding contact angles of the fertilizers (containing 1.5% P w v^{-1} + adjuvant at 0.01 to 0.3% w v^{-1}) were measured in the same way as the contact angle of water except the droplets were allowed to relax for 20 s before images were taken. For fertilizers on leaves, the receding contact angle could not be measured as the droplet was not observed to recede from the leaf surface. Contact angle values reported for fertilizers are the average of 20 measurements taken over 2 leaves from different pots and contact angle values for water are the average of 150 measurements taken over 30 leaf sections from 15 different pots.

<u>Foliar uptake and translocation</u>

One concentration of each of the adjuvants was chosen for the foliar uptake and translocation experiment. The 3 foliar fertilizer treatments were applied to the leaves at mid to late booting (GS 45-47, Feekes 10, 36 DAS) replicated 3 times to give a total of 9 pots. The rate of foliar applied P for all three treatments was 1.85% P w v^{-1} as phosphoric acid equivalent to 3.78 lb P_2O_5 $acre^{-1}$ (approx. based on pot surface area). The three adjuvants used were Agral® at 0.1% w v^{-1} (label rate), Genapol® X-080 at 0.1% w v^{-1} and LI 700® at 0.3% w v^{-1} (label rate). Each foliar fertilizer was labelled with ^{33}P in the orthophosphate form to give a known specific activity for each treatment. The foliar fertilizers were applied mid-morning to the second and third leaf down on the main stem with a micropipette in a dose split between the 4 leaves with 5 drops $leaf^{-1}$ (approximately 4 µL $drop^{-1}$).

Plants were harvested 7 days after foliar application when plants were between growth stages corresponding to ear ¾ emerged and early anthesis (Zadoks 56-60, Feekes 10.4-10.51). Plant parts were harvested and divided into the following sections before washing: treated leaves, main stem and tillers. After washing, treated leaves were separated into the treated area, leaf tip and leaf base. The ear was also separated from the rest of the main stem. All parts were dried in an oven at 60 °C for 72 h. Plant parts were weighed, ground and digested in boiling nitric acid and analysed for P by inductively coupled plasma - atomic emission spectroscopy (ICP-AES) (Zarcinas et al. 1987). A 2 mL sample of the digest was added to a vial with 10 mL of scintillation fluid (EcoScint) and counted on a Perkin Elmer Quanta Smart liquid scintillation analyser (Model Tri-Carb B3110TR). All counts were corrected for decay to a single time point (harvest).

RESULTS AND DISCUSSION

The static advancing contact angle of water on these leaves was 159 ± 6 ° (Figure 1) and the receding contact angle was 149 ± 10 °. These high contact angles with only a small difference between the advancing and receding contact angle are due to the presence of trichomes and waxes on the leaves (Figure 2) which influence the interaction between the drop and the leaf.

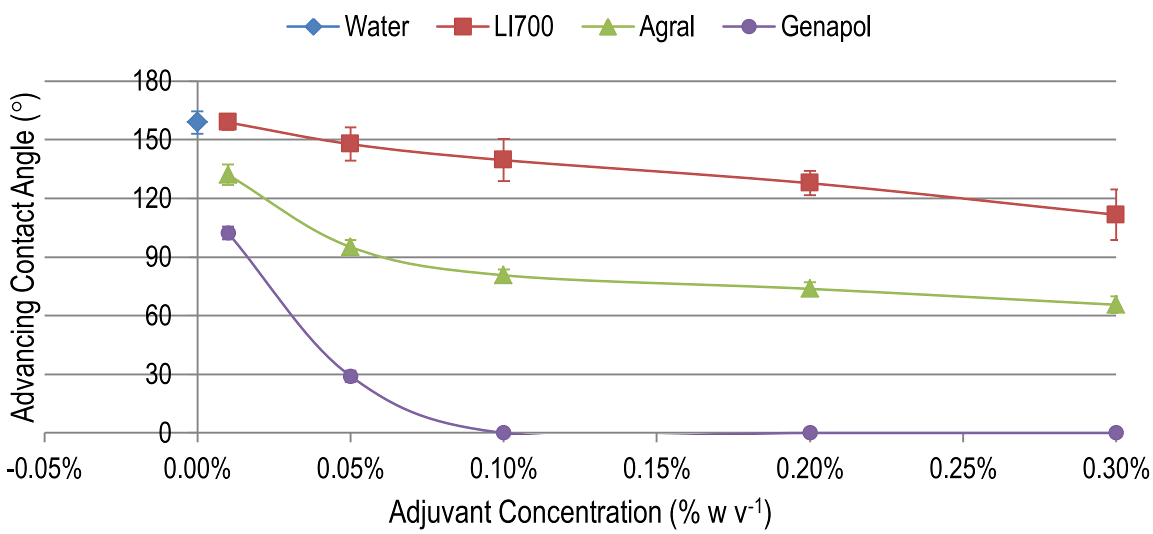

Figure 1. Advancing contact angles for the 3 adjuvants at varying concentrations (% w v^{-1}) in a formulation with 1.85% P w v^{-1} (measurements made at t= 20 s).

Measurements of the contact angle between leaves and phosphoric acid at concentrations ranging from 1-2 % w v^{-1} were also tested and found to be the same as for water (data not shown). The high contact angles with a small difference between advancing and receding drops observed for water and fertilizer droplets demonstrated that the wheat leaves are indeed superhydrophobic when surfactants are not present and as the droplets rest on top of the structure, the leaf-fertilizer contact area is small (Cassie state wetting (Lafuma and Quere 2003)). The low adhesion of sprayed droplets to the leaf surface would lead to significant run-off, making the foliar fertilizer ineffective due to fertilizer losses to the soil and small leaf-solution contact areas. In contrast, once a surfactant was added, the static receding contact angle dropped to effectively 0° meaning that once the fertilizer was deposited on the leaf it could not be removed (data not shown).

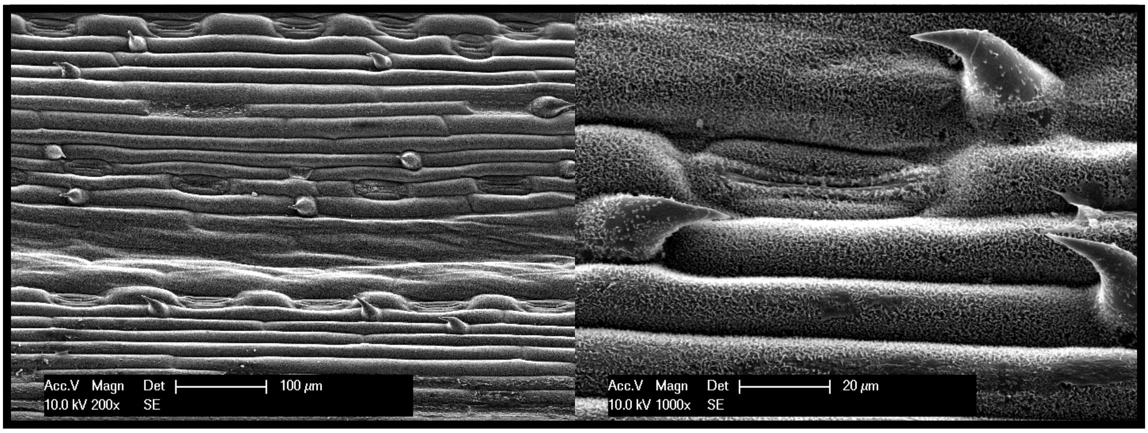

Figure 2. Scanning Electron Microscope images of the adaxial side of wheat leaves at early booting showing the presence of trichomes, stomata and waxes.

The static advancing contact angle of the fertilizers behaved differently as the adjuvant concentration was increased (Figure 1). At low LI 700® concentration (0.01% w v^{-1}), the static advancing contact angle was similar to that for water and decreased with increasing concentration over the full range of concentrations tested to 112˚ at 0.3% w v^{-1} LI 700®. The static advancing contact angle of Agral® decreased rapidly with increasing adjuvant concentration, until a concentration of 0.1% w v^{-1} where the contact angle was 81˚, with very little change for higher concentrations. The relative contact angle differences between Agral® and LI 700® have also been reported for field bean, pea and barley leaves by Holloway et al. (2000) who found the leaf coverage by sprays to be higher for Agral® (at 0.1% v v^{-1}) than LI 700® (at 0.5% v v^{-1}). Genapol® showed the sharpest decrease in contact angle as concentrations increased with complete spreading (formation of a thin film of fertilizer) on the leaf surface at a concentration of 0.1% w v^{-1}.

For the plant uptake and translocation experiment, the label rates of LI 700® (0.3% w v^{-1}) and Agral® (0.1% w v^{-1}) were used and Genapol® was used at a rate of 0.1% w v^{-1} which was known to result in complete leaf wetting. This ensured we had 3 contrasting contact angles for our 3 treatments with an expectation that different uptake rates would be found. There was however no difference between the foliar uptake of the 3 treatments and an average 94% of the fertilizer applied was measured in the shoot biomass after washing (Table 1). Less than 3% of the foliar fertilizer was washed off after harvest with only a small proportion (< 3% of P applied) unaccounted for. Since none of the fertilizers dripped off the leaves, this unaccounted for proportion is likely to have been translocated to the roots which were not analysed.

Table 1. Uptake and translocation of foliar applied P as a percentage of foliar P applied per pot. The translocation is the percentage of foliar P applied that was recovered in plant parts other than the treated leaf.

	Agral®	**Genapol®**	**LI 700®**
Total Foliar Uptake (% of applied)	91 ± 10	92 ± 6	98 ± 6
Total Translocation (% of applied recovered in other plant parts)	60 ± 4	73 ± 8	71 ± 6

Although the total translocation of foliar-applied P out of the treated area of the leaf to other plant parts was not different between the treatments, there was a difference in the final P sink. For Genapol®, which had the lowest contact angle and therefore highest leaf coverage by the fertilizer, more foliar-applied P was translocated to the ear on the main stem (15%) compared to LI 700 (5%) but less to the tiller leaves (7% for Genapol® compared to 12% for LI 700®) (data not shown). The recovery measured here is likely to be higher than in the field where spray delivery may be affected by splash upon droplet impact or accumulation of droplets which could lead to dripping from the leaf and loss to the soil. Losses may be more likely for Genapol® because the surface coverage per unit volume was high and leaves will quickly be covered by a complete film of liquid leading to dripping. In contrast, discrete droplets (which are more likely at higher contact angles; Agral® and LI 700®) are expected to strongly adhere to the leaf and prevent droplet run-off giving a higher volume per unit area of leaf and, therefore, better uptake. Differences in wetting for the 3 adjuvants may also affect the time-to-drying, which will be reduced for a thin film when compared with discrete droplets. Consequently, the period of time available for uptake by Genapol® will be reduced because the fertilizers must be in solution for uptake (Fernández and Eichert 2009). The competition between increasing leaf coverage and decreasing time-to-drying for decreasing contact angle may be responsible, at least in part, for the similar uptake observed for the 3 fertilizer solutions used in this study.

CONCLUSIONS

We have studied the effect of adjuvant and adjuvant concentration on the wettability of wheat leaves and foliar P uptake. Although there was a significant difference in the static advancing contact angle for the adjuvant treatments, the foliar uptake of P was not different and more than 90% uptake for all treatments. This suggests that as long as the fertilizer remains adhered to the leaf, foliar uptake will occur. It is possible that any improvement of uptake due to increased leaf-solution contact area is off-set by shorter time-to-drying with decreasing contact angle, and may help to explain the results from this study. Further studies are required to investigate the effect of time-to-drying on foliar uptake and the influence of adjuvants on long-term translocation.

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REFERENCES

de Ruiter H, Uffing A J M, Meinen E and Prins A 1990 Influence of surfactants and plant species on leaf retention of spray solutions. Weed Sci. 38, 567-572.

Fernández V and Eichert T 2009 Uptake of hydrophilic solutes through plant leaves: Current state of knowledge and perspectives of foliar fertilization. Crit. Rev. Plant Sci. 28, 36-68.

Forsberg P S H, Priest C, Brinkmann M, Sedev R and Ralston J 2010 Contact Line Pinning on Microstructured Surfaces for Liquids in the Wenzel State. Langmuir 26, 860-865.

Holloway P J, Butler Ellis M C, Webb D A, Western N M, Tuck C R, Hayes A L and Miller P C H 2000 Effects of some agricultural tank-mix adjuvants on the deposition efficiency of aqueous sprays on foliage. Crop Prot. 19, 27-37.

Lafuma A and Quere D 2003 Superhydrophobic states. Nat Mater 2, 457-460.

Zarcinas B A, Cartwright B and Spouncer L R 1987 Nitric acid digestion and multi-element analysis of plant material by inductively coupled plasma spectrometry. Commun. Soil Sci. Plant Anal. 18, 131-146.