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Possibilities To Use Tank-Mix Adjuvants for Better Fungicide Spreading on Triticale Ears

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Tank-mix adjuvants can increase the overall performance of plant protection products. Their most important ways of action are the improved retention, spreading, wetting, and penetration of the pesticide on the target and the reduction of fine droplets. In this paper, deposition and spreading of the systemic fungicide propiconazole on triticale ears were quantified. A better deposition and spreading of fungicide on the ear may be a possible help for the *Fusarium* problem in triticale, wheat, and other cereals. Triticale ears were applied with propiconazole in combination with 11 different tank-mix adjuvants. Vegetable oil, alcohol ethoxylates, lactate ester, trisiloxanes, and an amphoteric molecule were included in this experiment. When no tank-mix adjuvant was used, the lower part of the ear was reached five times less by the propiconazole spray than the upper part of the ear. When the tank-mix adjuvant was combined with the propiconazole formulation, an increase in residue on both the upper and the lower part of the ear was observed. A higher residue on the upper half of the ear means a better deposition, while a higher residue on the lower part of the ear is related to a better downward spreading over the grains and the needles of the ear. The combination of those two observations makes it interesting to use tank-mix adjuvants for the prevention of mycotoxin-producing *Fusarium* species. The advantages are emphasized even more when cost effectiveness was calculated. The use of a proper tank-mix adjuvant can result in 40% lower cost per application per hectare.

KEYWORDS: Tank-mix adjuvants; propiconazole; triticale; *Fusarium* head blight; ear; cost effectiveness

INTRODUCTION

Fungi are estimated to be the cause of up to 30% of losses in the production of wheat, triticale, rye, and other cereals. Contact and systemic fungicides play an important role in the trial to prevent diseases and to minimize losses. Fusarium head blight on wheat is caused by several *Fusarium* species (*Fusarium graminearum*, *Fusarium culmorum*, *Fusarium poae*, *Microdochum nivale*, etc.). Fusarium head blight species receive a lot of attention because they cause not only direct economic losses but also mycotoxin contamination of grain lots. The moderate weather conditions of Northwest Europe favor Fusarium head blight, but the ratios in which they occur are very time- and location-dependent (*1–4*). When the flowering stage coincides with heavy rainfall, Fusarium head blight problems in grain production increase (*5*).

Tank-mix adjuvants improve retention, deposition, spreading, and penetration of the pesticide. The literature on adjuvants rarely addresses fungicides because researchers are mainly focused on herbicides (*6, 7*). Gent et al. concluded improved coverage and penetration of [^{14}C]azoxystrobin on onion and potato by using organosilicone/methylated seed oil-based adjuvant (*8*). Improved retention and rainfastness by using tank-mix adjuvants was observed for dithiocarbamates, for mancozeb on apple seedlings (*9*), and for maneb and mancozeb on pea and potatoes (*10*). Tank-mix adjuvants may also be combined with insecticides to give better rainfastness results (*11, 12*). Holloway and Western studied the effect of three adjuvants on the deposition of two different fungicides. They found higher residues of propiconazole when a nonylphenol ethoxylate (NPEO) or polymer was used (*13*). For triticale and lettuce, the use of the different kinds of tank-mix adjuvants showed a trend toward higher detected leaf residues of, respectively, tolylfluanid and propiconazole (*14*).

The control rate of Fusarium head blight by the best available fungicide applications is no higher than 70−80%, while laboratory experiments demonstrate that a full control may be possible (*15*). A possible reason for a less than complete control rate in the field may be a lack of spreading of the spray solution

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Table 1. Chemistry of the Tested Tank-Mix Adjuvants

tank-mix adjuvant	chemical class	supplier
Softanol 50	alcohol ethoxylate (monobranched)	INEOS, Belgium
Softanol 70	alcohol ethoxylate (monobranched)	INEOS, Belgium
Softanol 120	alcohol ethoxylate (monobranched)	INEOS, Belgium
Oil-C	vegetable oil	Belchim, Belgium
Actirob	esterified rape oil	Novance, France
Ester-A	lactate ester	Purac, The Netherlands
Amphoteric-A	amphoteric molecule	Degussa, Germany
OS-C	trisiloxane	Degussa, Germany
Softanol EP 7025	alcohol ethoxylate (branched)	INEOS, Belgium
NIS-C	inulin polymer	Orafti, Belgium
Magic Sticker	trisiloxane	Modify, The Netherlands

over grains and needles to all parts of the ear (*3*). Research about how to control Fusarium head blight has been reported; however, scientific literature about the positive effects of tank-mix adjuvants with fungicides on ear protection by means of fungicides is lacking. Therefore, an experiment was set up to detect the influence of tank-mix adjuvants on this downward spreading rate.

MATERIALS AND METHODS

Adjuvants and Fungicide. The active ingredient that was used on *X Triticosecale* is propiconazole 250 g L^{-1} EC (Tilt, Syngenta Crop Protection N.V.) 0.5 L ha^{-1}. It has a water solubility of 100 mg/L at room temperature and is lipophilic as indicated by its octanol−water partition coefficient log $K_{ow} = 3.72$ (*16*). Tilt was used in combination with 11 tank-mix adjuvants (**Table 1**). Actirob (Novance, France) is an esterified rapeseed oil that is authorized as tank-mix adjuvant in Belgium. All other tested adjuvants were experimental. Softanol 50, Softanol 70, Softanol 120, and Softanol EP7025 (Ineos, Belgium) are monobranched alcohol ethoxylates. They have, respectively, five, seven, 12, and seven ethylene oxide units with Softanol EP7025 having both ethylene oxide units and propylene oxide units. Oil-C (Protex, Belgium) is a vegetable rapeseed oil (842 g/L), Ester-A (Purac, The Netherlands) is a lactate ester, and AMP (Degussa Goldschmidt, Germany) is an amphoteric molecule and consequently has a positive charge at a low pH and a negative charge at a high pH. OS-C (Degussa Goldschmidt, Germany) is a trisiloxane molecule. NIS-C (Orafti, Belgium) is a modified inulin molecule, and Magic Sticker (Modify, The Netherlands) is a polymer adjuvant.

Plant Material and Methodology. Triticale was grown in open air according to EPPO rules. Triticale was sown on parallel fields of minimum 15 m^2 on October 28, 2005. Unsprayed ears were collected at random from the field on June 7, 2006. Ears were placed vertically in a tray with wire netting inside the barn (**Figure 1**). A number of 100−110 ears were placed per tray. This number of ears guaranteed a total plant material mass that was high enough for a reliable residue analysis. The trays were sprayed at a rate of 0.5 L ha^{-1}, the spray volume was 300 L ha^{-1} with a Teejet XR80015-VS sprayboom equipped with nozzles, and application rates of the adjuvants were 0.3 L ha^{-1}. All 12 applications were replicated three times. After spraying, triticale ears were cut in two halves. Because of the vertical position of the ears, the upper half was expected to have received more of the sprayed propiconazole than the lower half. Per application, both upper halves and lower halves were collected separately and extracted.

Extraction and Chemical Analysis. Propiconazole had a relative apolar character with a log K_{ow} of 3.72 and a solubility in hexane of more than 5 g/L. Propiconazole was extracted from the two portions of each ear. Fresh triticale ears were homogenized by means of Moulinette (Moulinex). Fifty grams of the homogenized plant material was mixed (DuPont Instruments Sorvall Omni-Mixer) with 200 mL of acetone/hexane (1:1). This was filtered over a Buchner filter and washed with 50 mL of acetone/hexane. The filtrate was shaken by hand for 90 s with 200 mL of water and 25 mL of saturated NaCl solution. The water layer was removed, and this procedure of shaking with water and NaCl solution was repeated. The hexane fraction was dried over Na_2SO_4. Gas chromatographic analysis was performed with an Agilent 6890 GC equipped with a 5973 inert MSD. A HP-5MS capillary column (30m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, United States) was used, and the oven program was as follows: 70 °C for 2 min as the initial temperature, a 25 °C/min ramp to 150 °C, a 3 °C/min ramp to 200 °C, an 8 °C/min ramp to 280 °C, and 10 min at 280 °C. A split/splitless injector was used in the splitless mode (2 min of purge time, 50 mL/min purge flow). The carrier gas was helium with a constant column head pressure of 137 kPa. The injector and transfer line temperatures were 280 and 250 °C, respectively. One microliter of sample was injected. Mass detection was performed in the single ion monitoring (SIM) mode after a solvent delay of 15 min (ionization energy for electron impact was 70 eV). The selected ions used for detection and quantification are shown in **Table 2**. The ions were selected from the fragments with the highest *m/z* values and strongest signals, which are highly specific for each compound. To quantify the pesticide residues, both a surrogate and an internal standard were used. Phenanthrene-d_{10} was used as a surrogate to calculate the extraction recovery. When phenanthrene-d_{10} recoveries were outside the range of 70−130%, the sample was re-extracted. Mirex was chosen as the internal standard to make a correct quantification. The calibration curve was the result of the ratio [area compound/area mirex] on the ordinate and the concentration on the abscissa. In this way, machine-dependent variations were canceled out. The extraction method achieved a recovery of more than 90%.

Figure 1. Experimental setup for quantifying spreading of propiconazole on triticale ears.

Table 2. Selected Ions Used for Detection and Quantification

compound	retention time (min)	quantifier (*m/z*)	qualifier (*m/z*)
phenanthrene-d_{10} (surrogate)	13.68	188	189
propiconazole	26.91	173	259
mirex (internal standard)	29.81	344	345

Statistical Analysis. Results of residues were expressed as mg/kg fresh weight and were the means of three replicates, with standard deviations indicated. The statistical package SPSS 12.0 was used to determine if residues were significantly different from the control application without adjuvants. The independent sample *t* test (5% level) was used to detect significant differences.

RESULTS AND DISCUSSION

Rationale. Because of the vertical position of the ears and the presence of grains and needles in the ear, the upper half was expected to receive more of the sprayed propiconazole than the lower half. **Figure 2** shows that for all applications this supposition is correct. In some applications, the deposition on the lower half is only 20% of the upper half deposition.

Quantification of Differences in Spreading. Effective tank-mix adjuvants increase the residues on both lower and upper halves of the ears (**Figure 2**). On the upper halves of the ears where the tank-mix included Softanol 50, Softanol 120, oil-C, and ester-A, the fungicide residues were up to 1.8 times higher

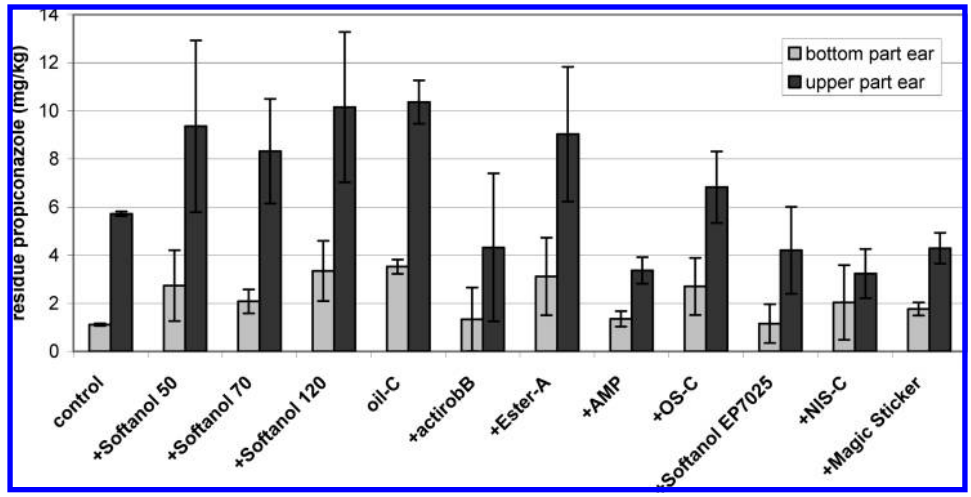

Figure 2. Propiconazole residue on upper and lower halves of the ears.

than the control application (**Figure 2**). A higher deposition on the upper part of the ear may be related to reduced droplet bouncing off the ear. This means that the initial contact ear droplet is improved.

The adjuvants clearly influence the physicochemical properties of the spray solution. Bergeron describes the droplet impactation phenomenon in detail (*17*). For most plant surfaces, it is a combination of repulsive chemical interactions and physical morphology of ear or leaf that together create a surface capable of efficiently repelling the water and generating astonishing hydrophobic behavior. In the most extreme cases, these surfaces are referred to as super water-repellent surfaces. Because the fungicide application is water-based, a solution has been found by applying adjuvants. In this study, the vegetable oil-C, known for its sticking properties, gave good results, as well as the branched alcohol ethoxylate and the ester molecule, which are well-performing surface-active agents. When tank-mix adjuvants are added, residues on the lower half of the ear can be increased. A residue of 1.1 mg/kg was found in the case of the control application, while residues that are significantly higher, even above 3.0 mg/kg, were found for Softanol 120, oil-C, and ester-A. This might imply a better spreading over the grains and needles to the lower part of the ear.

Quantification of Economical Consequences. A significant higher propiconazole deposition on both upper and lower halves of the ears was observed by using Softanol 120, oil-C, and ester-A. The effect of higher deposition on the upper half of the ear was used to calculate a decreased amount of pesticide formulation needed. The price of the reduced amount of a.i. has to be adjusted with the price of tank-mix adjuvant. Prices in March 2007 were 71.7 Euros per L propiconazole formulation (Tilt) and an average of 5.0 Euros per L tank-mix adjuvant.

Figure 3 shows the cost per application per hectare relative to the full-dose control application. For the control application, the price of 0.5 L Tilt ha^{-1} was taken into account. Consequently, the 100% price was 35.85 Euros. When an increased deposition on the upper half of the ear was observed, a lower dose can be used. **Figure 3** shows that for combinations with Softanol 120 and oil-C, the reduced price is 40% lower in comparison to the full-dose control application price. When these tank-mix adjuvants are used, an equal amount of propiconazole is deposited on the ear with a lower input of the a.i. propiconazole.

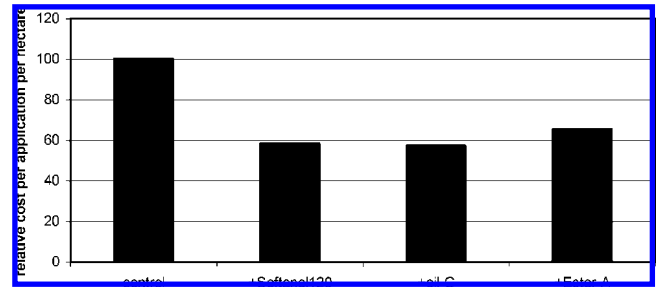

Figure 3. Relative cost per application per hectare of the three best-scoring tank-mix adjuvants, based on the deposition on the upper part of the ear.

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