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Quantitative determination of the influence of adjuvants on foliar fungicide residues

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Abstract

The correct use of adjuvants can increase the overall performance of plant protection products significantly. 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 which counters the problem of spray drift. The increase in efficiency of the pesticide application may cause an increased impact on the environment. This is possible in two ways: firstly, because of the presence of the adjuvant molecule in the environment and secondly because of the influence of the adjuvant on the plant permeability and consequently the pesticide residue. In the present work, the latter problem is studied on *Triticale* and lettuce. Propiconazole was applied on *Triticale* at its maximum approved rate. On lettuce tolylfluanid was applied. The applications on *Triticale* and lettuce were combined with four and six different types of adjuvants, respectively. Two of them, Trend90 and Actirob B, are authorized tank-mix adjuvants in Belgium. The other tested adjuvants are in experimental stage: two polymers, one organosilicone, an amphoteric molecule and two mono-branched alcohol ethoxylates. The influence of these different adjuvants on the residue of the applied pesticides was monitored several weeks. For both *Triticale* and lettuce, the use of the different kinds of adjuvants showed a trend towards higher detected residues on the leafs. Nevertheless, the degradation rates of the applications with adjuvants were comparable to that of the control.

Keywords: Tank-mix adjuvants; Propiconazole; Tolylfluanid; *Triticale*; Lettuce; Gas chromatography with mass selective detection (GC-MS)

1. Introduction

Triticale and lettuce are crops that can suffer from serious losses through fungal infections. Prominent diseases in *Triticale* are caused by *Septoria* spp., while in lettuce *Sclerotinia* (spp. *minor* and *sclerotiorum*) is a major threat (Tomlin, 2003). The main strategy against infection with these pathogens is preharvest treatment with chemical fungicides. Propiconazole is a systemic fungicide that acts by inhibiting the synthesis of ergosterol to prevent fungal mycelium development. Its acceptable daily intake (ADI) is 0.04 mg/kg day and its maximum residue limit (MRL) is 5 mg/kg (Tomlin, 2003). Tolylfluanid is a non-systemic fungicide that inhibits the germination of fungal spores and blocks fungal respiration. Its ADI is 0.079 mg/kg day and its MRL 5 mg/kg (Tomlin, 2003). Fungicide residue research requires determination of their degradation curves. In this way exceeding established maximum limits can be prevented. The fungicide degradation curves may be influenced by tank-mix adjuvants. These chemical compounds can improve the retention, spreading and penetration of foliage-applied sprays of many plant protection products, thus improving the overall protection of the plant. However, side effects such as a higher residue of the fungicides and a decreasing degradation rate may occur. The most important reason for an altering degradation rate is the change of permeability of the plant cuticle and the increased penetration of the pesticide molecule. Residue studies in crop protection are done very frequently; however, little information can be found on the effect of adjuvants on pesticide residues. Holloway and Western

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(2003) studied the effect of three adjuvants on the degradation rates and developed a model system. They found higher residues of propiconazole and diclofop-methyl when a nonylphenol ethoxylate (NPEO) or polymer was used. In this work, we study the NPEO alternatives since they are being phased out in the European Union. The main purpose is to compare the degradation rates of the different applications with the control application of propiconazole on *Triticale* (one preharvest application) and tolylfluanid on lettuce (both one and two applications).

2. Material and methods

2.1. Plant material, spray applications and sampling procedures

Triticale (*X Triticosecale*) and lettuce (*Lactuca sativa var. capitata*) were both grown and sprayed in open air according to EPPO rules. Two cultivars of the winter cereal *Triticale* were sown on three parallel fields of minimum 15 m^2 on 28/10/04. They were sprayed at Zadoks growth stage 59 (GS 59) (Tottman and Broad, 1987) on 27/05/05. Lettuce was planted on four parallel fields on 25/08/05. They were sprayed on 26/09/05 (one application) or 26/09/05 and 03/10/05 (two applications). Table 1 shows the different cultivars, spray conditions and application rates for both crops. The collection of the samples were done arbitrary, without using the outer plants of the field. In case of lettuce, five heads were taken per sample, for *Triticale* 100 leafs were used per sample.

2.2. Adjuvants and fungicides

The active ingredient used on *X Triticosecale* was propiconazole 250 g/l EC (Tilt) 0.5 l/ha. This fungicide was purchased from Syngenta Crop Protection N.V. and combined with Trend90, Actirob, Zipper and Softanol 70. Trend90 (Du Pont de Nemours) is an isodecyl alcohol ethoxylate, Actirob (Novance N.V.) is an esterified oil, Zipper (Modify B.V., Holland) is an organo modified trisiloxane in experimental stage and Softanol 70 (Ineos, Belgium) is a mono-branched alcohol ethoxylate with seven ethylene oxide units in experimental stage. The active ingredient used on *Lactuca sativa* var. *capitata* was tolylfluanid 50% WG (Euparen multi) 25 g are^{-1}, purchased from Bayer Crop Science N.V. and combined with the authorized Trend 90 and Actirob and with the experimental Full Stop, Magic Sticker, AMP and Softanol 50. Full Stop (Modify B.V., Holland) and Magic Sticker (Modify B.V., Holland) are blends of polymers with organo modified trisiloxanes, AMP (Degussa Goldschmidt, GmbH, Industrial Specialties, Essen, Germany) is an amphoteric molecule and Softanol 50 (Ineos, Belgium) is a mono-branched alcohol ethoxylate with five ethylene oxide units.

2.3. Extraction and chemical analysis

Propiconazole and tolylfluanid are pesticides with a relative apolar character. The $\log K_{ow}$ for propiconazole is 3.72; for tolylfluanid this is 3.90. Their solubility in hexane is more than 5 g/l for both compounds. The following extraction method achieved a recovery of both pesticides of more than 90%: the fresh lettuce was homogenized by means of a Scharfen cutter (D 5810 Witten, West-Germany); the fresh *Triticale* was homogenized by means of Moulinette (Moulinex). About 50 g of the homogenized plant material was mixed (DuPont Instruments Sorvall Omni-Mixer) with 200 ml of acetone/hexane (1:1). This was filtrated over a Buchner filter and washed with 50 ml 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 at Agilent 6890 GC equipped with a 5973 inert MSD. A HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, USA) was used and the oven program was as follows: 70 °C during 2 min as 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 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 were highly specific for each compound. To quantify the pesticide residues, both a surrogate and an internal standard were used. Phenanthrene-d10 was used as surrogate to calculate the extraction recovery. When phenanthrene-d10 recoveries were outside the range of 70–130%, the sample was re-extracted. Mirex was chosen as 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 cancelled out.

2.4. Statistical processing of the data

The degradation of pesticide residues is fitted to classical first-order kinetics (Thorstensen and Lode, 2001; Ma et al., 2001; Morton et al., 2001). The statistical package S+ 7.0 is used to quantify a good fit to a general linear model. An Anova fixed model was built with the logarithmated residue as dependent variable, the application and time as independent variables and an interaction effect between