

Effects of adjuvants on herbicidal action. II. Effects of a mixture of adjuvants on isoproturon retention and penetration in wheat and ryegrass

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Summary — A mixture of adjuvants composed of a liquid nitrogenous fertilizer, oil, solvent and surfactant increases isoproturon efficacy against ryegrass (*Lolium multiflorum* Lam) at application volumes of 300 and 500 l·ha⁻¹ by 67 and 64%, respectively. At application volumes of 75 and 150 l·ha⁻¹ it has no significant effect. The mixture only slightly affects spray retention on ryegrass (whatever the applied volume), but increases it on wheat by 32 to 45%. Isoproturon penetration is low in wheat (less than 4% in 3 days) as well as in ryegrass (less than 2.5%). The mixture greatly increases herbicide penetration in both species: 4 to 5 times in ryegrass and 7 to 10 times in wheat, according to application volume. When adjuvants are added individually to isoproturon suspension, only liquid nitrogenous fertilizer noticeably increases herbicide penetration. Combined effects on retention and penetration lead to an increase in herbicide uptake into the plants. The increase is about 2.5 times greater in wheat than in ryegrass. It appears that the mixture of adjuvants increases isoproturon penetration into ryegrass and its herbicidal activity. However, it tends to diminish selectivity as does a reduction in application volume.

isoproturon / adjuvant / retention / penetration / efficacy

Résumé — Effet des adjuvants sur l'action herbicide. II. Effet d'un mélange d'adjuvants sur la rétention et la pénétration de l'isoproturon chez le blé et le ray-grass. Un mélange d'adjuvants contenant de l'engrais azoté liquide, une huile, un solvant et un mouillant améliore l'efficacité de l'isoproturon sur ray-grass (*Lolium multiflorum* Lam) aux volumes d'application 300 et 500 l·ha⁻¹ (fig 1). Il est sans effet significatif à 75 et 150 l·ha⁻¹. Le mélange d'adjuvants affecte peu la rétention de la pulvérisation sur ray-grass, quel que soit le volume d'application, par contre, sur blé il l'augmente de 32 à 45% (fig 2). L'isoproturon pénètre mal chez le blé (moins de 4% en 3 j) (fig 3B) ainsi que chez le ray-grass (moins de 2,5%) (fig 3A). Le mélange d'adjuvants stimule fortement la pénétration de l'herbicide dans les 2 plantes, d'un facteur 4–5 chez le ray-grass et 7–10 chez le blé, selon le volume appliqué (fig 3). Lorsqu'on ajoute les adjuvants isolément à la suspension d'isoproturon, seul l'engrais azoté liquide augmente de manière notable la pénétration de l'herbicide (fig 4). Les effets combinés sur la rétention et la pénétration ont pour résultat une augmentation de la quantité d'herbicide entrant dans les plantes. Cet accroissement est environ 2,5 fois plus important chez le blé que chez le ray-grass. En conclusion :

– l'apport d'adjuvants extemporanés stimule fortement la pénétration de l'isoproturon chez le ray-grass et augmente son activité biologique;

– cependant, l'apport de ces adjuvants (ainsi que la diminution du volume d'application) tend à diminuer la sélectivité de l'herbicide.

isoproturon / adjuvant / rétention / pénétration / efficacité

INTRODUCTION

In a previous study (Gauvrit and Dufour, 1990) we found that a mixture of adjuvants composed of liquid nitrogenous fertilizer, oil, solvent and wetting agent increased diclofop-methyl efficacy against ryegrass. It slightly affected spray retention on ryegrass but doubled it on wheat. Herbicide penetration was increased greatly in both species, and the combined effects on retention and penetration led to an increase in herbicide entry into the plants, which was 3 to 4 times greater in wheat than in ryegrass. Even though diclofop-methyl has some persistence in soil and can be taken up by roots, foliar uptake is the predominant route of entry (Duke and Kenyon, 1988). Hence, adjuvants do not basically modify the absorption pattern of this herbicide, they merely reinforce foliar uptake. By contrast, in this study, we wanted to see what the effect was of the same mixture of adjuvants when applied with isoproturon, a herbicide whose action occurs mainly *via* root uptake (Blair, 1978): if the mixture of adjuvants increased foliar penetration, the usual routes of entry into the plant would change. We determined which effect the mixture of adjuvants had on two important efficacy parameters, namely retention and penetration, when isoproturon was applied to ryegrass and wheat, a weed control situation commonly encountered in France.

MATERIALS AND METHODS

Plant material

Wheat (*Triticum sativum* L, cv Pernel) and ryegrass (*Lolium multiflorum*, Lam, cv Adret) seeds were germinated at 25 °C then sown in a clay loam soil: sand mixture (1:1). Ryegrass plants were then placed in a growth cabinet at 14/9°C (day/night), 14 h photoperiod and 65/95% relative humidity. Wheat plants were placed under the same conditions except for day temperature: 17°C. All experiments were performed when the third leaf was 1 to 3 cm long.

Isoproturon efficacy on ryegrass

Isoproturon was prepared as a flowable suspension in water by Rhône Poulenc Spécialités Chimiques (Geronazzo) with the following composition: 50% isoproturon, 0.5% Soprofor BC10 (nonyl phenol with 10 ethyleneoxy groups), 3% Soprofor FL (triethanolamine salt

of phosphatetritylphenol with 16 ethyleneoxy groups), 5% methylglycol and 0.12% Rhodopol 23 (xanthan gum) as a thickening agent. Treatments were performed by means of an indoor sprayer consisting of a movable boom with two "Albuz" 110° nozzles positioned 50 cm apart: grey nozzle operated at 4.0 bars for 300 and 500 l·ha⁻¹, blue nozzle operated at 3.0 bars for 150 l·ha⁻¹, red nozzle operated at 2.0 bars for 75 l·ha⁻¹. Plants were placed 48 cm under the nozzles and were sprayed at 150 g·ha⁻¹ isoproturon. Among the mixture compositions commonly used by farmers, we chose the following: solvent: 0.5 l·ha⁻¹ isophorone (Prolabo); surfactant (non-ionic): 0.1 l·ha⁻¹ Citowett (100% alkyl-aryl phenol polyglycol ether (5 ethylene oxide; BASF Co); oil: 0.5 l·ha⁻¹ Végélux (84% emulsifiable mineral oil; CCL Co); 5 l·ha⁻¹ liquid nitrogenous fertilizer (39% ammonium nitrate, 39% urea in water). As a control, the oil emulsifier (chemical composition not given) was sometimes tested at a 0.12 l·ha⁻¹ dose.

At the stage defined, plants were sprayed at the chosen volume and dosage, with or without the mixture of adjuvants. Nine repetitions with 8 plants each were carried out for each treatment and after 14 d under the growth conditions described the shoots were cut off at ground level and placed at 80°C for 24 h for dry weight determination.

Retention measurements

Plants were sprayed under the same conditions as for the efficacy experiments except that the isoproturon dosage was 1500 g·ha⁻¹. The sprays contained 0.01% fluorescein as in Richardson's experiments (1984). After the spray had dried on the foliage, the plants were cut off at ground level and shaken for 30 s in 50 ml 5 mM NaOH. Readings were made in a Jobin and Yvon 3-D spectrofluorimeter at 490/510 nm. Plants were then placed at 80°C for 24 h and the dry matter weighed. For ryegrass, experiments comprised 6 repetitions with 25 plants each and for wheat, 3 repetitions with 10 plants each.

Isoproturon penetration

Ring ¹⁴C labelled isoproturon (150 MBq·mmol⁻¹) was dissolved in ethanol. An aliquot containing the desired radioactivity was deposited at the bottom of a conical tube and the ethanol evaporated to dryness. The isoproturon suspension was then added at a concentration corresponding to a 1500 g·ha⁻¹ isoproturon, at either a 75 or 500 l·ha⁻¹ treatment. Gentle shaking for 2 h interspersed with two 10 s sonication spells redissolved radiolabelled isoproturon. Radioactivity of the preparation was 16.7 Bq·μl⁻¹ and cold herbicide was 99.2% (500 l·ha⁻¹) or 99.9% (75 l·ha⁻¹) of total herbicide. Adjuvant concentrations in the applied suspension corresponded to those defined and were calculated on a ha basis. It follows that adjuvant concen-

treatments were 6.7 times higher in conditions corresponding to 75 l·ha⁻¹ treatments than in 500 l·ha⁻¹ treatments.

Four 0.5 µl droplets of the above suspension were deposited on the upper third of the second leaf and the plants placed in a growth cabinet at 17/9°C (day/night), 14 h photoperiod and 65/95% relative humidity. Penetration was studied on wheat adaxial surface and on the abaxial surface of ryegrass (isoproturon suspension droplets did not adhere to the adaxial surface). Absorption was determined 1 and 3 d after deposit (in a preliminary experiment, it was checked that all deposited radioactivity was washed off at time 0). Each measurement was carried out on 5 plants from the same pot and the experiment was conducted with 3 replicates. Absorption was evaluated by washing the treated area of each leaf with 1 ml acetone followed by 1 ml chloroform. Washes were combined and evaporated to dryness. Ethanol was added to dissolve isoproturon which was counted in Dynagel (JT Baker Chemicals, The Netherlands) by scintillation counting. Leaves were dried (24 h, 80°C) and combusted in an oxidizer for radioactivity assessment. Recovery figures varied from 76 to 97%.

Statistics

Data were subjected to analysis of variance and means were compared using the Newman and Keuls test at the 5% level (Cochran and Cox, 1968). In the figures, data marked with the same letters do not differ significantly.

RESULTS

Herbicide efficacy

The mixture of adjuvants did not significantly improve isoproturon efficacy on ryegrass at application volumes of 75 and 150 l·ha⁻¹. At 300 and 500 l·ha⁻¹ the efficacy increase was significant: 67 and 64%, respectively (fig 1). No volume effect was detected when plants were treated with the isoproturon suspension, whereas in the presence of the mixture of adjuvants, isoproturon was more effective at application volumes of 300 and 500 l·ha⁻¹ than 75 and 150 l·ha⁻¹.

Retention

Ryegrass retained more than 500 µl spray per g dry weight at application vol 500 l·ha⁻¹ (fig 2). Retention was roughly proportional to the applied volume and was not significantly affected by the mixture of adjuvants.

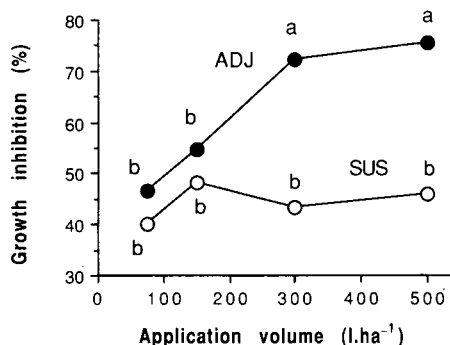


Fig 1. Effect of isoproturon on ryegrass growth as influenced by the mixture of adjuvants and the application volume. Growth was defined as dry matter increase between treatment and harvest. Growth inhibition is expressed as % control growth (1.470 ± 0.182 g dry matter). SUS: treatment with the isoproturon suspension; ADJ: treatment with the suspension combined with the mixture. Data marked with the same letters do not differ significantly.

In contrast, wheat was poorly wettable and retained 3 (at 75 l·ha⁻¹) to 4.8 (at 300 l·ha⁻¹) times less spray than ryegrass (fig 2). The mixture of adjuvants increased retention by 33 to 45%, without interaction with volume.

Penetration

Isoproturon penetration through ryegrass abaxial surface was low: after 3 days it amounted to 2.1% of the applied radiolabelled isoproturon at 75 l·ha⁻¹ and 2.3% at 500 l·ha⁻¹ (fig 3A). The mixture of adjuvants increased penetration to 10.2% and 8.6% at 75 and 500 l·ha⁻¹ respectively. There was no volume effect.

Without adjuvants isoproturon penetration into wheat was low: 2.7% at 75 l·ha⁻¹ and 3.9% at 500 l·ha⁻¹ after 3 d (fig 3B). The mixture of adjuvants dramatically increased penetration to 27.8% and 28.6% respectively.

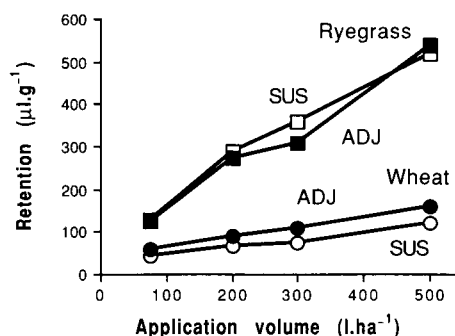


Fig 2. Effect of the mixture of adjuvants on spray retention by ryegrass (A) and wheat (B). SUS, ADJ (fig 1).

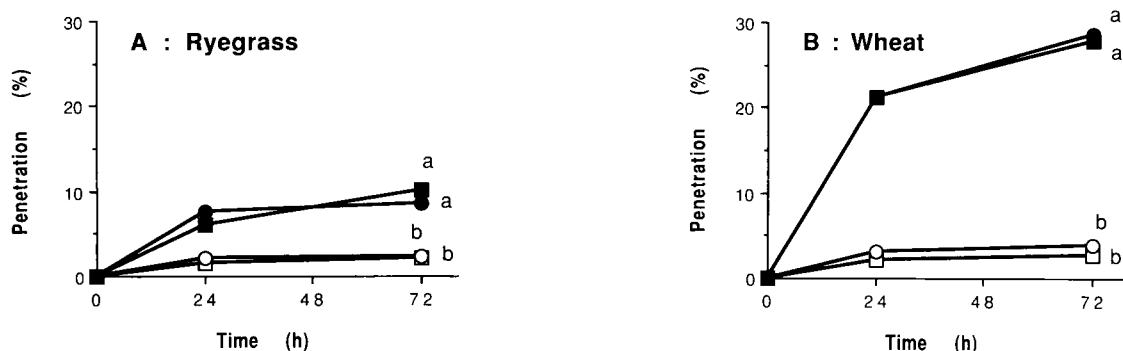


Fig 3. Isoproturon penetration through abaxial surface of ryegrass (A) and adaxial surface of wheat (B) as influenced by the mixture of adjuvants and application volume. □, isoproturon suspension at 75 l·ha⁻¹; ○, isoproturon suspension at 500 l·ha⁻¹; ■, isoproturon suspension combined with the mixture of adjuvants at 75 l·ha⁻¹; ●, isoproturon suspension combined with the mixture of adjuvants at 500 l·ha⁻¹. Data marked with the same letters do not differ significantly.

When added individually to isoproturon suspension, adjuvants exhibited different effects on isoproturon penetration (fig 4). Végélux oil, Citowett and isophorone had no significant action, the emulsifier slightly increased penetration, whereas liquid nitrogenous fertilizer more than doubled it.

DISCUSSION

Isoproturon efficacy

The mixture of adjuvants increases isoproturon efficacy at high application volumes (fig 1). This is in agreement with outdoor results by Bouchet and Beaufreton (1988) who observed that the same mixture of adjuvants increased efficacy of isoproturon against ryegrass (*Lolium multiflorum* Lam), wild-oat (*Avena sativa* L) and blackgrass (*Alopecurus myosuroides* Huds).

In the presence of the mixture of adjuvants, isoproturon efficacy is higher at 300 and 500

l·ha⁻¹ than at 75 and 150 l·ha⁻¹ (fig 1). A lower efficacy at low application volumes is often observed with contact herbicides (Taylor, 1981). However, isoproturon action is not generally qualified as contact, since its application favours slow entry of the herbicide *via* the roots: in these conditions, no contact action would be expected from a photosynthetic inhibitor (Fedtke, 1982). In contrast, the mixture of adjuvants allows a quick and massive isoproturon entry into the leaves (fig 3), which might lead to rapid "contact" action.

Retention

Isoproturon spray retention on wheat is noticeably lower than on ryegrass. The difference is in agreement with isoproturon selectivity since the ratio varies from 3 (75 l·ha⁻¹) to 4.8 (300 l·ha⁻¹) (fig 2).

The mixture of adjuvants does not affect retention by ryegrass. This is in line with observations by Blackman *et al* (1958) and De Ruiter and Uffing (1988) who found that on wettable plants the increase in retention by surfactants was either nil or limited.

In contrast, the mixture of adjuvants increased retention in wheat (fig 2). As expected (De Ruiter and Uffing, 1988), the wetting agent Citowett was found to be responsible for this: added alone to the isoproturon suspension it brought about the same increase in retention as the complete mixture (data not shown).

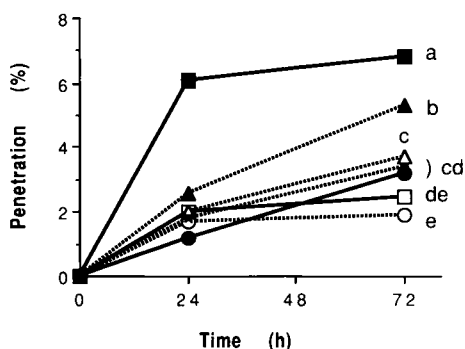


Fig 4. Isoproturon penetration through ryegrass abaxial surface as influenced by adjuvants; □, isoproturon suspension; ▲, liquid nitrogenous fertilizer; Δ, emulsifier; ●, oil; ○, isophorone; X, Citowett; ■, mixture of adjuvants. Data marked with the same letters do not differ significantly.

Penetration

When applied by way of a microsyringe, isoproturon suspension droplets do not adhere to the adaxial surface of ryegrass leaves, which are far

less wettable than the abaxial surface (Field and Bishop, 1988 for *Lolium perenne* L; Schott *et al*, 1990 for *Lolium multiflorum*). This feature is all the more important as ryegrass first and second leaves are twisted and expose their abaxial surface upwards; in other words towards the spray. The portions of abaxial ryegrass surface so exposed retain about 2/3 of formulated diclofop-methyl spray (Schott *et al*, 1990). Hence, it is the main collecting surface on this plant and justifies studying herbicide penetration through it. On the contrary, due to the erect morphology of wheat, the main spray-collecting surface on this plant is the adaxial surface and hence we made penetration studies on this.

Isoproturon penetration into wheat and ryegrass leaves is low when it is applied as a suspension: the figures are, in all cases, lower than 4% of the deposited radioactivity. In this preparation, although post-emergence applied, isoproturon is not formulated as a foliar herbicide since it is not in a dissolved state and hence cannot be expected to display high foliar penetration rates. Indeed, Blair's experiments (1978) have shown that isoproturon action occurs mainly by penetration *via* the roots.

The mixture of adjuvants drastically increases isoproturon penetration (fig 3) and in our opinion it explains the improvement in herbicidal efficiency upon their addition. Penetration rates are independent of application volumes. In this case, active ingredient as well as adjuvant concentrations in the suspension do not influence passage through the cuticle.

All adjuvants present in the mixture do not participate equally in the increase in penetration. The oil (Végélux), the solvent (isophorone) and the surfactant (Citowett) have no detectable effect. The emulsifier only has a limited one.

Being a solvent, isophorone could be expected to solubilize isoproturon and thus promote its penetration. However, we found that isoproturon solubility in isophorone is only $(30 \pm 2) \text{ g}\cdot\text{l}^{-1}$ at 20 °C (data not shown). Since 500 ml isophorone was applied per ha it would solubilize 15 g isoproturon, that means only 1% of herbicide dosage ($1\,500 \text{ g}\cdot\text{ha}^{-1}$). This poor solubility might explain isophorone inactivity.

Végélux's lack of effect is puzzling since numerous reports show that oils promote herbicide entry into plants (Grafstrom and Nalewaja, 1988; Gillepsie *et al*, 1988; McCall, 1988; Wanamarta *et al*, 1989; Gauvrit and Dufour, 1990; Schott *et al*, 1990). One explanation could be that oil can increase penetration only if the active ingredient

is dissolved, which is not the case in the suspensions. In this case, isoproturon molecules are aggregated in particles, a physical form that does not allow high penetration rates (Stevens *et al*, 1988).

Surfactants can promote herbicide entry into plants (Sharma *et al*, 1978; Harper and Appleby, 1984; O'Donovan *et al*, 1985) and both the emulsifier and Citowett could thus be expected to do so. We did not observe such action in the present experiments. One cannot exclude the fact that action of surfactants on penetration depends on herbicide physico-chemical properties, the type of surfactant and plant species.

Liquid nitrogenous fertilizer noticeably increases penetration, although to a lower extent than the complete mixture. This is in line with observations that it improves activity of some herbicides (Horn *et al*, 1986; Chow, 1988) but not all (Sander *et al*, 1987). Its action could result from its hygroscopicity (Norden, 1988) which prevents the deposit from drying completely. Visual observations confirm that in the presence of the mixture of adjuvants, deposits never take the appearance of a white precipitate as in the case of isoproturon suspension alone. The liquid or visquous state of the deposit could favour penetration (Stevens *et al*, 1988). In such conditions the active ingredient might be less prone to precipitation, and diffusion inside the deposit maintained (Price, 1982). However, Babiker and Duncan (1975) showed that humectants such as glycerol and sorbitol reduce aminotriazole penetration into bracken (*Pteridium aquilinum* L).

Combining the effects on retention and penetration it follows that at $75 \text{ l}\cdot\text{ha}^{-1}$ the mixture of adjuvants increases 4.7 times the amount of isoproturon that enters into ryegrass, whereas the corresponding figure in wheat is 13.6. At $500 \text{ l}\cdot\text{ha}^{-1}$ these figures are 3.9 and 9.8, respectively. Hence, the mixture of adjuvants increases herbicide entry into plants more in wheat than in ryegrass, which is adverse to selectivity. However, wheat readily degrades isoproturon (Müller *et al*, 1977) and this very likely explains why the use of such a mixture of adjuvants does not generally bring about phytotoxicity in wheat (Bouchet and Beaufreton, 1988).

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