EFFECT OF OIL AND MINERAL ADJUVANTS ON EFFICACY AND PHYSICOCHEMICAL PROPERTIES OF FORAMSULFURON AND IODOSULFURON SPRAY MIXTURE

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The effect of adjuvant on physico-chemical properties and efficacy of foramsulfuron + iodosulfuron mixture was evaluated. Foramsulfuron + iodosulfuron at recommended rate (45 + 1.5 g ha\(^{-1}\)) and at reduced rate (22.5 + 0.75 g ha\(^{-1}\)) was applied with petroleum oil (PO), two methylated rapeseed oils (MSO 1 and 2) and with urea-ammonium nitrate (UAN), ammonium nitrate (AMN), and ammonium sulfate (AMS) fertilizers. Foramsulfuron + iodosulfuron at recommended rate with oil adjuvants reduced biomass of rapeseed plants by 81 (MSO 2) and 84% (MSO 1 and PO). Efficacy of foramsulfuron + iodosulfuron applied at reduced rate was 2 to 9% lower. Addition of MSO 1, MSO 2 or PO to the herbicide applied at reduced rate did not change dynamic surface tension (DST) of the spray solution compared to recommended rate. Methylated rapeseed oil (MSO 2) decreased DST more than MSO 1 and PO. Dynamic surface tension of foramsulfuron + iodosulfuron spray mixture with MSO 2 and UAN, AMN or AMS was generally lower than with MSO 1 or PO. The applied adjuvants influenced spray deposit area, but differences were no more than 6 – 12%. The addition of nitrogen fertilizers such as urea (U), ammonium sulfate (AMS) or ammonium nitrate (AMN) maximized nicosulfuron efficacy when applied with petroleum (PO) or pH-buffered methylated seed oil (MSO 2) adjuvants.

Keywords: Adjuvants, contact angle, pH of spray mixture, sulfonylurea herbicide, surface tension

INTRODUCTION

Weeds can reduce yield of maize even up to 80% (Bijanzadeh and Ghadiri, 2006; Idziak and Woznica, 2010) and greatly decrease grain quality (Umeris et al., 2009). Weed control is an important management practice for maize production (Skrzypczak et al., 1995; Goršić et al., 2008) and a proper selection of herbicides influence on treatment efficacy (Idziak and Woznica, 2010). Foramsulfuron and iodosulfuron-methyl-sodium, similarly as the other sulfonylurea herbicides, exert their herbicidal activity by inhibiting acetolactate synthase (ALS), a key enzyme in the biosynthesis of branched-chain amino acids (Ashton and Monaco, 1991). Sulfonylurea herbicides are known for being highly selective and having low use rates. To reduce the costs and risks of poor weed control, the frequency of applications or herbicides rates should be reduced or optimized (Kucharski et al., 2008). Foramsulfuron + iodosulfuron mixes are formulated with the safener isoxadifen-ethyl and are typically applied at 30 – 45 g + 1 – 1.5 g ha\(^{-1}\) (Maister 310 WG at 100 – 150 g ha\(^{-1}\)) (Anonymous, 2010). Foramsulfuron is mainly absorbed through leaves (Woznica, 2008) and iodosulfuron both – through leaves and roots (NRA, 2001).

Physico-chemical properties of a spray mixture can have significant effect on the characteristics of the spray, for instance spray volume, droplet size, and droplet surface tension (Hewitt, 2008) and affect herbicide retention (Matysiak, 1995). Furthermore, herbicide formulation influenced spray droplet dispersal patterns on the leaf, leaf traits including surface topography, roughness, and crystalline or amorphous epicuticular waxes that influence herbicidal retention (Boize et al., 1976; de Ruiter et al., 1990; Hess and Falk, 1990; Wirth et al., 1991; Antonious and Snyder, 1993). Adjuvants added to herbicide spray mixtures enhance spray droplet retention on leaf surface and penetration of active ingredient through the cuticle (Young and Hart, 1998). According to Green and Green (1991) the spray droplet dynamic surface tension is thought to be the most important characteristic related to spray droplet retention by difficult-to-wet plants. However, Green and Green (1993) and Stock et al. (1993) indicated that dynamic surface tension is not nearly as important as the ethoxylate chain length of surfactants what indicate that these adjuvants also function in ways other than facilitating spray retention. The reduction in surface tension caused by adjuvants decreased contact angle and thus the adhesion spreading factor and surface coverage factor of droplets increase (Basu et al., 2002). Adjuvants may decrease the surface tension of the spray droplets, which results in more uniform spreading over the leaf surface (Anderson, 1996).

In the present study, the influence of mineral adjuvants applied in a mixture with methylated seed oils and petroleum oil on physical properties of spray (pH, surface tension,
contact angle and spray deposit area) and on weed control efficacy of foramsulfuron and iodosulfuron-methyl-sodium mixture was determined.

MATERIALS AND METHODS

Rapeseed (Brassica napus ssp. oleifera) seeds were planted in the greenhouse in 1.5L, 15 cm diameter, plastic pots containing a mixture of soil and peat (at 1:1 ratio). Plants were thinned to 8 uniform seedlings per pot 2 weeks after emergence. Soil moisture was maintained at 65-75% of soil water capacity, by regular replenishment water losses to appropriate weight of pots. Additionally soil moisture was systematic measured by ML3 – ThetaProbe Soil Moisture Sensor. The greenhouse temperature was maintained at 25±5°C during the day and at 20°C during the night and relative humidity varied from 50 to 80%. Natural sunlight was supplemented with lamps for an intensity of 600 μE m \(^{-2}\) s \(^{-1}\).

Foramsulfuron + iodosulfuron at recommended rate (45.0 + 1.5 g ha \(^{-1}\)) and reduced rate (22.5 + 0.75 g ha \(^{-1}\)) and adjuvants at rates corresponding to recommended for field conditions were applied at three to four leaf-stage of rapeseed plants using a laboratory nozzle sprayer calibrated to deliver 220 L ha \(^{-1}\) through a TeeJet AIXR 11004 nozzle at an operating pressure of 0.2 MPa. The commercial formulation of foramsulfuron + iodosulfuron (Maister 310 WG) was applied with oil and mineral adjuvants: PO – petroleum oil (Atpolan 80 EC) @ 1.5 L ha \(^{-1}\), MSO 1 – methylated rapeseed oil (Actirob 842 EC) @ 1.5 L ha \(^{-1}\), and MSO 2 – methylated rape seed oil with a build-in system buffering pH of the spray mixture (Atpolan BIO 80 EC) @ 1.5 L ha \(^{-1}\). Oil adjuvants were used alone and in combination with mineral fertilizers: 28% N urea-ammonium nitrate (UAN) @ 8 L ha \(^{-1}\), ammonium nitrate (AMN), and ammonium sulfate (AMS) both @ 4 kg ha \(^{-1}\). The herbicide with adjuvants were applied with medium hard water – 14.6°dH (German degree of hardness) that contained 104.4 mg Ca\(^{2+}\) and 14.7 mg Mg\(^{2+}\) L \(^{-1}\). Trial, repeated two times, was designed as a randomized complete block with four replications. Percentage herbicidal efficacy based on fresh weights of rapeseed plants reduction was determined.

The surface tension (DST), measured after 0.1 s, mean contact angle (CA) and spray deposit area (SDA) were estimated by the KSV Optical tensiometer Theta Lite equipped with a camera taking over 60 photos per second (frame interval 16 ms). The pH of spray liquids were measured using Elmetron pH conductometer CPC-505 equipped with EPS-1 electrode. Physico-chemical measurements were performed at a constant room temperature of 20±1°C and relative humidity of 55%. All data were submitted to an analysis of variance with ARM 8 (Agricultural Research Manager, Gylling Data Management, Inc.) and the Student-Newman-Kells test was used to verify the significant differences among treatment means at the 0.05 level.

RESULTS AND DISCUSSION

The results presented in Table 1 indicate that foramsulfuron + iodosulfuron applied at recommended rate of 45 + 1.5 ha \(^{-1}\), respectively with MSO 1 and PO adjuvants reduced rapeseed biomass by 84% and with MSO 2 by 81%. By reducing rate of herbicides to 22.5 + 0.75 g ha \(^{-1}\) and addition of MSO 1, PO and MSO 2 rapeseed control decreased only

<table>
<thead>
<tr>
<th>Adjuvant</th>
<th>Adjuvant rate</th>
<th>foramsulfuron + iodosulfuron (% control)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>45 + 1.5</td>
</tr>
<tr>
<td>MSO 1</td>
<td>1.5 L</td>
<td>84</td>
</tr>
<tr>
<td>MSO 1 + UAN</td>
<td>1.5 L + 8 L</td>
<td>-</td>
</tr>
<tr>
<td>MSO 1 + AMN</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
</tr>
<tr>
<td>MSO 1 + AMS</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
</tr>
<tr>
<td>MSO 2</td>
<td>1.5 L</td>
<td>81</td>
</tr>
<tr>
<td>MSO 2 + UAN</td>
<td>1.5 L + 8 L</td>
<td>-</td>
</tr>
<tr>
<td>MSO 2 + AMN</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
</tr>
<tr>
<td>MSO 2 + AMS</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
</tr>
<tr>
<td>PO</td>
<td>1.5 L</td>
<td>84</td>
</tr>
<tr>
<td>PO + UAN</td>
<td>1.5 L + 8 L</td>
<td>-</td>
</tr>
<tr>
<td>PO + AMN</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
</tr>
<tr>
<td>PO + AMS</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
</tr>
</tbody>
</table>

LSD 0.05 6.6

MSO 1 – methylated seed oil of rapeseed oil fatty acids; MSO 2 – methylated seed oil of rapeseed oil fatty acids with a build-in system buffering pH of the spray mixture and surface active agents; PO – petroleum oil; UAN – 28% N urea ammonium nitrate; AMN – ammonium nitrate; AMS – ammonium sulfate.
Effect of copper on broad bean

The addition of UAN to the oil adjuvants, except MSO 1, improved rapeseed control with the reduced rate of foramsulfuron + iodosulfuron. Also AMN and AMS in a mixture with MSO 2 and PO adjuvants increased herbicide efficacy, however the control level was not biologically acceptable. Addition of AMN to the reduced rate of foramsulfuron + iodosulfuron applied with MSO 1 did not improve effectiveness at all. Thus, the results indicate that the addition of mineral fertilizer may be beneficial only if appropriate oil adjuvant is used. Sulfonylurea herbicides are applied at low rates, and they have excellent crop selectivity (Beyer et al., 1988). Adjuvants, for instance, mineral oils and plant origin oils, mainly MSO are effective in improving the activity of several sulfonylurea herbicides (Nalewaja et al., 1995; Jordan, 1996). The further increase of herbicide absorption and finally effectiveness can be improved by the addition of UAN (Miller et al., 1999; Bunting et al., 2004a), AMN or AMS (Bunting et al., 2004b). Most post emergence herbicide labels recommend addition of AMS or UAN along with oil adjuvants (Zollinger and Nalewaja, 2010).

The addition of UAN, AMN or AMS to the reduced rate of foramsulfuron + iodosulfuron applied with MSO 2 and PO significantly increased herbicide efficacy probably by overcoming the antagonism caused by antagonistic cations present in the spray water. Activity of herbicides due to the presence of calcium, magnesium, iron and sodium salts in spray carrier water may decrease (Fagerness and Penner, 1998; Penner, 2000). Salt antagonisms can be overcome with addition of ammonium salts that effectively restore herbicide activity (Thelen et al., 1995; Bernards et al., 2005).

Results of the study indicate that the addition of MSO 1 to foramsulfuron + iodosulfuron applied at reduced rate did not reduce dynamic surface tension (DST) of spray mixture comparing to herbicide applied at recommended rate. Dynamic surface tension of foramsulfuron + iodosulfuron spray mixture at the reduced rate applied with MSO 1 and UAN and also with AMN or AMS ranged from 33.6 to 37.3 mN m⁻¹ (Table 2). In case of spray mixture containing foramsulfuron + iodosulfuron at reduced rate and MSO 2 oil adjuvant changes of DST during measurement were not observed. The incorporation of PO to foramsulfuron + iodosulfuron applied at recommended and reduced rates did not lead to reduction of DST. In case of MSO 2 a lower DST was observed than with MSO 1 and PO. Addition of MSO 2 with mineral adjuvants reduced DST of spray mixture to 32 – 33 mN m⁻¹, and PO 35 – 36 mN m⁻¹, except PO plus AMS. Table 2 indicate that DST of foramsulfuron + iodosulfuron with MSO 2 and UAN, AMN or AMS was generally lower than with MSO 1 and ranged from 30 to 33.2 mN m⁻¹. These changes were not statistically proven and therefore, can only be considered as trends. Physico-chemical properties of spray liquid, beside weather conditions, and spray application technique affected spray droplet drift (Schampheleire et al., 2009), retention and herbicide efficacy. Chemical nature of adjuvants plays an important role in droplet contact angle, wettability, and spread area formation (Zabkiewicz et al., 1988; Sundaram, 1990).

Surface tension is the interactions between molecules at a surface and the force it takes to disturb those interactions.

Table 2. Influence of oil adjuvants on physical properties of spray mixture containing foramsulfuron + iodosulfuron

<table>
<thead>
<tr>
<th>Adjuvant</th>
<th>Adjuvant rate</th>
<th>DST¹ (mN m⁻¹)</th>
<th>SDA² (mm²)</th>
<th>CA³ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>foramsulfuron + iodosulfuron (g ha⁻¹)</td>
<td>45 + 1.5</td>
<td>22.5 + 0.75</td>
<td>45 + 1.5</td>
</tr>
<tr>
<td>MSO 1</td>
<td>1.5 L</td>
<td>36.9</td>
<td>37.3</td>
<td>8.7</td>
</tr>
<tr>
<td>MSO 1 + UAN</td>
<td>1.5 L + 8 L</td>
<td>-</td>
<td>35.1</td>
<td>-</td>
</tr>
<tr>
<td>MSO 1 + AMN</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
<td>33.6</td>
<td>-</td>
</tr>
<tr>
<td>MSO 1 + AMS</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
<td>36.8</td>
<td>-</td>
</tr>
<tr>
<td>MSO 2</td>
<td>1.5 L</td>
<td>32.1</td>
<td>32.5</td>
<td>8.8</td>
</tr>
<tr>
<td>MSO 2 + UAN</td>
<td>1.5 L + 8 L</td>
<td>-</td>
<td>33.2</td>
<td>-</td>
</tr>
<tr>
<td>MSO 2 + AMN</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
<td>32.0</td>
<td>-</td>
</tr>
<tr>
<td>MSO 2 + AMS</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
<td>32.1</td>
<td>-</td>
</tr>
<tr>
<td>PO</td>
<td>1.5 L</td>
<td>35.0</td>
<td>35.2</td>
<td>8.9</td>
</tr>
<tr>
<td>PO + UAN</td>
<td>1.5 L + 8 L</td>
<td>-</td>
<td>36.3</td>
<td>-</td>
</tr>
<tr>
<td>PO + AMN</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
<td>34.9</td>
<td>-</td>
</tr>
<tr>
<td>PO + AMS</td>
<td>1.5 L + 4 kg</td>
<td>-</td>
<td>32.1</td>
<td>-</td>
</tr>
<tr>
<td>LSD 0.05</td>
<td></td>
<td>4.08</td>
<td>0.36</td>
<td>1.68</td>
</tr>
</tbody>
</table>

¹ dynamic surface tension at 0.1 s; ² spray deposit area; ³ contact angle at 14 s
MSO 1 – methylated seed oil of rapeseed oil fatty acids; MSO 2 – methylated seed oil of rapeseed oil fatty acids with a build-in system buffering pH of the spray mixture and surface active agents; PO – petroleum oil; UAN – 28% N urea ammonium nitrate; AMN – ammonium nitrate; AMS – ammonium sulfate.
Dynamic surface tension is changing dynamically and describes the speed at which molecules move to an air-liquid surface and it is useful for comparing kinetics of adsorption to a hydrophobic surface (Stock and Briggs, 2000; Whiddon, 2010). Formulation of new substance-air interface proceeds rapidly (~1–20 ms) and measurements of these changes are necessary to quantify the ability of the surfactants in a tank mix to lower the ST. Dynamic surface tension may have an important effect upon droplet formation. Due to Hewitt (2008) many studies showed that the DST of most agricultural tank mixtures at a surface lifetime age of 20 ms fall within a range of 32–73 mN m⁻¹.

None of oil or mineral adjuvants tested increased or decreased pH of spray liquid more than by 1.0 (Fig. 1). Higher pH, above 7, may increase the solubility of sulfonylurea herbicides and usually their activity. Foramsulfuron solubility in water increases as pH increases – from 0.04 g L⁻¹ at pH 5 to 94.6 g L⁻¹ at pH 8 (APVMA, 2011). Iodosulfuron solubility in water varies between 0.02 to 65 g L⁻¹ at pH 4 and 9, respectively (Anonymous, 2000). Green and Cahill (2003) indicated that the addition of adjuvants that increase pH of spray liquid usually increases the biological activity of sulfonylurea herbicides. Also adjuvants with a build-in system buffering pH of the liquid spray, called basic bland adjuvants, increase the pH of spray solution to solubilize sulfonylurea herbicides (Green and Hale, 2005).

As shown with spray deposit area differences caused by various tested adjuvants were found but they were not more than 6% (foramsulfuron + iodosulfuron + MSO 1 + mineral adjuvants), 9% (foramsulfuron + iodosulfuron + MSO 2 + mineral adjuvants) and 12% (foramsulfuron + iodosulfuron + MSO 2 + mineral adjuvants). Considering mixtures of foramsulfuron + iodosulfuron + PO, the inclusion of either AMN or AMS significantly reduced SDA. In case of mixture with MSO 1 only addition of AMS led to significant reduction of SDA. There was no correlation between spray deposit droplet area and the herbicide mixture efficacy. According to Woznica and Skrzypczak (1998) activator adjuvants should first of all increase the retention and create good conditions for the absorption of the active ingredient by weed cuticle. The increase in spray retention increases the amount of active ingredient, which can penetrate into the plant (Manthey et al., 1998). Praczky (1998) showed a positive correlation between retention and the herbicide efficacy, but Nicholls et al. (1995) did not observe such correlation.

Data in Table 2 indicated that the contact angle (CA) of foramsulfuron + iodosulfuron applied at recommended and reduced rates depended on adjuvant type used. The lower CA was observed when MSO 2 was added and the highest with MSO 1 and PO. The addition of UAN, AMN or AMS to foramsulfuron + iodosulfuron applied with MSO 1 increased CA only slightly – from 55.7° to 56.1°, compared to 54° with foramsulfuron + iodosulfuron applied only with MSO 1. Generally addition of mineral adjuvants to the mixture of foramsulfuron + iodosulfuron with oil adjuvants did not influenced CA. Assuming a hydrophobic surface, the smaller CA the better wetting of the surface occurs (Whiddon, 2010). A high CA means that the droplet is prone to dislodge and run off from the leaf. Therefore, addition of built-in or tank-mix surfactants, reduces surface tension (DST) and CA, increasing the spread of spray droplets on the leaf surface (Cobb and Reade, 2011), penetration of active ingredient into plant cells and herbicide efficacy. However, reduction in CA and DST not always increases weed mortality (Singh and Singh, 2006).

This research demonstrates the importance of adjuvant selection when using with foramsulfuron + iodosulfuron for weed control and changes of physico-chemical properties of spray mixture. Properly selected adjuvant can reduced herbicide rate while maintaining good efficiency of the treatment. Oil adjuvants tested decreased, and mineral adjuvants did not change DST and CA of foramsulfuron + iodosulfuron spray mixture. The reduction of DST and CA by adjuvants can not absolutely explain the enhanced foramsulfuron + iodosulfuron efficacy. Also other mechanisms, like a specific effect of ammonium ion on faster and more complete herbicide absorption (Gronwald et al., 1993; Woznica, 2005), as well as overcoming of antagonistic salts the spray liquid by adjuvants could be involved (Nalewaja and Matysiak, 1993). To maximize biological activity of herbicide its physico-chemical

**Figure 1. Influence of oil and mineral adjuvants on pH of spray mixture containing foramsulfuron + iodosulfuron at full rate (F) and reduced rate (R).**

MSO 1 – methylated seed oil of rapeseed oil fatty acids; MSO 2 – methylated seed oil of rapeseed oil fatty acids with a build-in system buffering pH of the spray mixture and surface active agents; PO – petroleum oil; UAN – 28% N urea ammonium nitrate; AMN – ammonium nitrate; AMS – ammonium sulfate.

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properties and adjuvant selection should be matched to infested weed species, their size and environmental conditions at application time (Vanlieshout and Loux, 2000). In our experiments the addition of nitrogen fertilizers such as urea (U), ammonium sulfate (AMS) or ammonium nitrate (AMN) maximized nicosulfuron efficacy when applied with petroleum (PO) or pH-buffered methylated seed oil (MSO 2) adjuvants.

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Abdel Latef and Abu Alhmad


