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Effect of Simulated Radiation on Sethoxydim Performance Used with and without Vegetable Oils

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Abstract

The photodecomposition of post emergence herbicides on leaf surface can be affected via adding vegetable oils to spray tank. Nine vegetable oils were compared to assess the photodecomposition of sethoxydim on wild oat leaf surface under simulated light conditions. The experiment was conducted as completely randomized factorial design with three replications at the College of Agriculture, Ferdowsi University of Mashhad, Iran, in 2013. Each herbicidal solution (with and without vegetable oil) was exposed to simulated light at 0, 5, 10, 20, 30, 60, 120 and 240 MAS (min after spray), for 30 min. The performance of sethoxydim in the presence of turnip, olive, soybean, corn, sunflower, canola, sesame, castor and cotton seed oils, compared to non-vegetable oil solution, increased up to 4.02-, 3.44-, 3.22-, 3.08-, 2.86-, 2.09-, 1.96-, 1.77- and 1.25- fold. All vegetable oils significantly improved the resistance of sethoxydim to light treatment. The effect of vegetable oils on the resistance to photodecomposition of sethoxydim was significant different at less than 60 MAS, while no significant differences were noted among vegetable oils when light treatment occurred at 120 and 240 MAS. Data from the light treatments have confirmed that when vegetable oils were added to sethoxydim, light adverse effect was lower, which is presumably due to disturbance of the cuticule and the rapid absorption of sethoxydim by wild oat leaves. Vegetable oils fatty acids composition effect the resistance to photodecomposition of sethoxydim, as with increasing the unsaturated fatty acid values, the resistance to photodecomposition was improved.

Keywords: cuticule, fatty acid, photodecomposition, simulated light, wild oat

Abbreviations: ED-effective dose; MAS-min after spraying; RP-relative potency

Introduction

Decomposition processes of herbicide include abiotic oxidation and reduction, hydrolysis, biodegradation and photolysis (Schnoor, 1991). One of the most significant decomposition pathways after spraying is photodecomposition. Herbicide photodecomposition is a chemical reaction in which an herbicide compound is broken down by photons and it is not limited to visible light. Any photon with sufficient energy can affect the chemical bonds of a solutions' compound. It may occur in surface waters, in soil, in the atmosphere and on the leaf surface. Ultraviolet radiation (UV) reaching the earth's surface is the most important factor that can affect herbicide photodecomposition (Katagi, 2004). This can be biologically harmful, but on the other hand, decomposition of environmental pollutants, including herbicides, has a positive effect. Various factors can affect herbicide photodecomposition, including the sunlight intensity (dependent on the season and weather conditions), characteristics of the application site (such as latitude, altitude etc.), the application method, the characteristics of the herbicide, formulation and adjuvants added to their formulations or applied as tank mix to herbicide spray solution (Fred, 1997).

Many studies dealt with photodecomposition of sethoxydim (Shoaf and Carlson, 1986; Sevila moran *et al.* 2010), alloxydim (Sevilamoran *et al.*, 2008), clethodim (Falb *et al.*, 1990), atrazine (Sun *et al.*, 2011), imazamox (Quivet *et al.*, 2006), bentazon, clopyralid and triclopyr (Eyheraguibel *et al.*, 2009), HW-02 (Lu *et al.*, 2010), tribenuron-methyl (Bhattacharjeel and Dureja, 2002), acifluorfen (Vulliet, 2001), MCPA (Zertal *et al.*, 2005), EPTC (Abu-Qare and Duncan, 2002), norflurazon (Massad *et al.*, 2004), sulcotrione (Wiszniowski *et al.*, 2009), fluometuron (Halladja *et al.*, 2007), all conducted in water solution. However, herbicide reactivity on leaves' surface at different light is seldom evaluated. Moreover, the effect of adjuvants is rarely considered.

Commercial formulations of some herbicides, such as sulcotrione, include different neutral materials, including adjuvants, due to which photodecomposition occurs faster than in the case of pure active ingredient (Wiszniowski *et al*., 2009). Adjuvants are important tools used to improve physical aspects of herbicide application and/or to enhance their biological efficacy, therefore are present in majority of herbicide formulations (Rashed-Mohassel *et al*., 2009; 2010; 2011). Along with the adjuvants, penetration agents, by increasing the rate of herbicide entrance and absorption into leafs, can influence photodecomposition (Devendra *et al*, 2004). Vegetable derived oils are one of the main groups of penetration agents (Ramsey *et al*., 2005). Harrison and Wax (1985) reported that vegetable oil can enhance photodecomposition of 2,4-D bentazon and holoxyfop herbicides when released. Therefore, the use of vegetable oils can reduce photodecomposition on leaf surface (increase herbicide penetration into leaf) and enhance photodecomposition in the environment. As little information about the effect of adjuvants on herbicide photostability on leaf surface exists, this study aimed to evaluate the effect of applying vegetable oils on sethoxydim and analyze its performance under simulated light on wild oat (*Avena ludoviciana* L.).

Material and methods

Plant growth

About 500 g wild oat caryopsis fruit were collected from the fields near the Greenhouse of College of Agriculture, Ferdowsi University of Mashhad, Iran, and preserved in a refrigerator (at 4±1 °C). To break seed dormancy, the caryopsis fruit were dehulled and seeds placed in 11 cm diameter Petri dishes over the surface of a single layer of Whatman no. 1 filter paper. Ten ml of KNO_3 solution (2 g L^{-1}) were added to each Petri dish, two times. Petri dishes were placed in a refrigerator at 4-5 °C in the dark for two days and then transferred to an incubator with 20/10 °C temperature in 45/65% relative humidity, for a 16/8 h day/night for germination. As soon as the rootlets emerged from the seeds, they were sown in 2 L plastic pots that were filled with a mixture of sand, silty loam soil (19.8% sand, 20.1% clay, 58% silt, 4.1% organic matter and a pH of 6.7) and peat (1:1:1; v/v/v) at a 0.5 cm depth. The pots were irrigated every three days with tap water. The seedlings were thinned to five per pot at the two leaf stage and 40 mL of a water-soluble N:P:K (20:20:20) fertilizer, at a concentration of 3 g of fertilizer per liter of tap water, were supplied to each pot. The greenhouse temperature varied from 24±3 °C during the day and 16±2 °C at night.

Extraction of the vegetable oils

Oils of soybean, cottonseed, canola, sesame, castor, corn, sunflower and turnip were extracted from grains via mechanical extraction method (Kemper, 2005), while olive oil was extracted from fruits with Decanter centrifugation (horizontal centrifuge rotating 3.000 rpm) method (Rubio, 2008).

Fatty acid content detection

To determine the fatty acid of the oils, fifteen drops of each vegetable oil were added to 7 ml N-hexane, plus 2 ml of potassium hydroxide in methanol (11.2% m/v). Four replications of these compounds were shacked for 1 min and heated to 55 °C for 5 min, when the solution separated in two-phases. The upper phase were desiccated with sodium lauryl sulfate and filtered for analyzing with gas chromatography (Mehmood *et al.*, 2008).

The fatty acid content was determined using specialized gas chromatography equipped with a flame ionization detector and a CP-Sil 88 Wcot fused silica column (100 m × 0.25 mm i.d. × 0.2 μm film thickness). The carrier gas was ultra-high purity helium (1:100 split mode) and a flame-ionization detector. The GC oven temperature was maintained at 140 °C for five min, then ramped to 240 °C at 4 °C/min and kept at 240 °C for 15 min. Flow rate of helium was 20 ml/min. The injector and detector temperatures were 250 and 280 °C, respectively. The volume of injected sample was 1 μl. Fatty acids were identified by matching their retention times with those of their relative standards. The reference standards of fatty acid methyl esters in methylene chloride (ampule containing 10 mg/ml) was purchased (grain fatty acid methyl ester mix 99–100%).

Dose-response study

The experiment was arranged in a randomized complete factorial design with four replications and carried out in a greenhouse at the Faculty of Agriculture, Ferdowsi University of Mashhad, Iran, in 2013. Wild oat plants were sprayed with herbicide at the four-leaf stage. Sethoxydim treatment consisted of seven doses against wild oat (0, 23.4, 46.8, 93.7, 187.5, 281.2 and 375 g ai ha^{-1}). A non-ionic emulsifier and 100% alkylarylpolyglycol were added to each vegetable oil at 10% (v/v). This compound (90% vegetable oil + 10% emulsifier) was added to the sethoxydim solution at 0.5% (v/v) in tank mix, for all treatments- with or without simulated light. Simulated light was applied at 5, 10, 20, 30, 60, 120 and 240 min after spraying (MAS), for a 30 min period, by using a light simulator that was supplied with a xenon arc lamp (1500 W) equipped with two ventilator fans; no light treatment was used as control. Treatments were applied using an overhead trolley sprayer equipped by 8002 flat fan nozzle tip, delivering 238 L ha-1 at 200 kPa. Four weeks after spraying, above-ground biomass of all the plants in each pot were harvested and weighed (fresh weigh), then oven dried at 75 °C for 48 h and reweighed (dry weigh). This experiment was repeated twice and gave similar results. Hence, the results of one of the two will be reported.

Statistical analyses

Since fresh weight and dry weight data showed similar trend, only ED_{50} dose based on dry weight data was included. Weight data of all the treatments were subjected to non-linear regression analyses by using a logistic dose-response model (Ritz *et al*., 2006):

$$U = C + \frac{D - C}{1 + \exp[b(\log(z) - \log(ED_{50}))]}$$

where, U is the plant response to the herbicide treatment, z is the dose, D and C are the upper and lower limits of the curve respectively. ED_{50} denotes the required dose of herbicide to give 50% wild oat control and b is proportional to the slope of the curve around the ED_{50}.

The logistic response-dose model was fitted to the experimental data by the R software and then based on available information the relative potency (RP) value was used to describe horizontal displacement between the dose-response curves:

$$RP = ED_{50 sethoxy\dim} / ED_{50x}$$

where, ED_{50x} is the ED_{50} of sethoxydim alone or in combination with (i) vegetable oils and (ii) vegetable oils plus simulated light.

If the RP-value was equal to 1, the addition of vegetable oils and the application of light treatment would not have any effect on herbicidal responses. While if the RP-value was bigger or smaller than 1, herbicide usage with treatments would be more or less potent than herbicide alone (Ritz *et al*., 2006).

Results and discussion

Vegetable oils effect on sethoxydim performance

The results from this research showed that when sethoxydim was combined with each vegetable oil, wild oat control was remarkably increased. The ED_{50} values of sethoxydim were significantly decreased (Tab. 1) and the RP-value was considerably increased when each vegetable oil were added to sethoxydim (Tab. 2). These results indicate an increase in the performance of sethoxydim. The performance of sethoxydim in the presence of turnip, olive, soybean, corn, sunflower, canola, sesame, castor and cottonseed oils, compared to non-vegetable oil treatment, increased up to 4.02-, 3.44-, 3.22-, 3.08-, 2.86-, 2.09-, 1.96-, 1.77- and 1.25- fold respectively (Tab. 2). Therefore, turnip and cottonseed oil had the highest and the lowest efficiency when they were added to sethoxydim solution. Increasing the foliar activity of sethoxydim, quizalofop, fluazifop, fenoxaprop and haloxyfop in grassy weeds and bentazone, acifluorfen, lactofen, fomesafen and imazaquin in broadleaf weeds as a result of vegetable oils has been reported by Nalewaja (1994). This action may be due to increasing retention, penetration on cuticular wax and dissolve process in cuticule (Hazen, 2000; Ramsey *et al*., 2005).

Effect of light on sethoxydim with vegetable oils on leaf surface

Simulated light increased remarkably the ED_{50} values of sethoxydim (Tab. 1) and the RP-value was considerably decreased when simulated light happened immediately after spraying sethoxydim (Tab. 1). When simulated light treatment was applied at 5, 10, 20, 30, 60, 120 and 240 MAS, the ED_{50} values of sethoxydim increased from 111.76 (without oil) to 995.23, 927.24, 804.94, 632.27, 214.38, 111.88 and 112.25 g ai ha^{-1}, respectively. Namely, for obtaining the same performance with no light treatment we must apply sethoxydim solution by 8.91-, 8.29-, 7.20-, 5.66-, 1.92-, 1.01-, 1.00- fold, respectively. Increasing the interval time between sethoxydim spray and light treatment led to a decrease photodecomposition from the surface of leaves, due to increased penetration of sethoxydim on leaves' cuticule, and eventually a decrease of the adverse effect of light in sethoxydim performance, as when light happen at 120 and 240 MAS adverse effect of light is very low (Tab. 1). In general, increasing herbicide penetration on cuticular wax and dissolving cuticule are the main reasons for enhancement of resistance to light in the presence of vegetable oils (Hazen, 2000; Ramsey *et al*., 2005; Devendra *et al*, 2004).

Tab. 1. ED_{50} dose (g ai ha^{-1}) of sethoxydim (alone and in a mixture with vegetable oils), affected by different light treatments

	No Light	Light at 5 MAS	Light at 10 MAS	Light at 20 MAS	Light at 30 MAS	Light at 60 MAS	Light at 120 MAS	Light at 240 MAS
No vegetable oil	111.76 (7.04)	995.23 (48.36)	927.24 (45.73)	804.94 (23.92)	632.27 (22.71)	214.38 (11.39)	112.88 (6.04)	112.25 (5.31)
Turnip	27.83 (2.76)	711.57 (35.24)	674.46 (27.46)	321.43 (17.12)	227.25 (10.31)	71.14 (3.12)	28.11 (1.56)	27.85 (1.24)
Olive	32.46 (2.91)	721.75 (36.89)	688.36 (29.87)	334.74 (18.16)	235.67 (11.31)	75.47 (3.61)	32.51 (1.61)	31.96 (1.37)
Soybean	34.76 (3.04)	732.76 (37.68)	696.43 (30.68)	359.84 (18.94)	241.34 (11.96)	82.32 (3.24)	36.87 (1.54)	35.11 (1.96)
Corn	36.27 (3.29)	743.57 (38.56)	704.76 (31.17)	377.57 (19.21)	249.71 (12.73)	85.87 (4.27)	38.86 (2.24)	37.49 (2.11)
Sunflower	38.96 (3.74)	747.74 (38.63)	710.13 (34.67)	387.67 (20.04)	284.41 (13.07)	87.69 (5.09)	41.22 (2.54)	40.81 (2.25)
Canola	53.42 (3.86)	790.24 (39.22)	732.39 (37.46)	414.68 (21.14)	345.37 (14.39)	110.31 (6.35)	53.74 (3.02)	53.08 (2.95)
Sesame	57.15 (3.97)	794.64 (39.54)	751.18 (38.13)	443.97 (22.07)	357.81 (16.64)	114.54 (6.76)	57.89 (3.18)	56.01 (3.74)
Castor	63.27 (4.37)	801.28 (41.92)	772.72 (39.24)	478.37 (24.78)	381.24 (18.21)	127.25 (7.26)	62.74 (3.96)	62.03 (3.24)
Cottonseed	89.43 (5.33)	823.97 (44.62)	786.57 (40.89)	501.57 (25.41)	431.34 (21.48)	162.24 (8.84)	93.91 (4.44)	90.96 (4.38)

Standard errors are in parentheses (P = 0.05). MAS- minutes after spraying

Tab. 2. Relative potency of sethoxydim (alone and in a mixture with vegetable oils) affected by light treatments

	No Light	Light at 5 MAS	Light at 10 MAS	Light at 20 MAS	Light at 30 MAS	Light at 60 MAS	Light at 120 MAS	Light at 240 MAS
No vegetable oil	1	1	1	1	1	1	1	1
Turnip	4.02 (0.36)	1.40 (0.07)	1.38 (0.05)	2.50 (0.13)	2.78 (0.12)	3.01 (0.13)	4.01 (0.21)	4.03 (0.17)
Olive	3.44 (0.28)	1.38 (0.08)	1.35 (0.06)	2.40 (0.12)	2.68 (0.12)	2.84 (0.13)	3.47 (0.16)	3.51 (0.14)
Soybean	3.22 (0.26)	1.36 (0.07)	1.33 (0.07)	2.24 (0.11)	2.50 (0.13)	2.60 (0.10)	3.06 (0.12)	3.20 (0.17)
Corn	3.08 (0.26)	1.34 (0.07)	1.32 (0.06)	2.13 (0.10)	2.41 (0.10)	2.50 (0.11)	2.90 (0.16)	2.99 (0.16)
Sunflower	2.86 (0.25)	1.33 (0.06)	1.31 (0.05)	2.08 (0.10)	2.13 (0.07)	2.44 (0.13)	2.74 (0.16)	2.75 (0.14)
Canola	2.09 (0.14)	1.26 (0.06)	1.27 (0.06)	1.94 (0.09)	1.76 (0.08)	1.94 (0.11)	2.10 (0.11)	2.11 (0.11)
Sesame	1.96 (0.13)	1.25 (0.06)	1.23 (0.06)	1.81 (0.08)	1.69 (0.08)	1.87 (0.10)	1.95 (0.10)	2.00 (0.13)
Castor	1.77 (0.11)	1.24 (0.05)	1.20 (0.05)	1.68 (0.08)	1.58 (0.07)	1.68 (0.09)	1.80 (0.11)	1.81 (0.09)
Cottonseed	1.25 (0.07)	1.21 (0.04)	1.18 (0.05)	1.60 (0.07)	1.40 (0.06)	1.32 (0.06)	1.20 (0.06)	1.23 (0.06)

Standard errors are in parentheses (P = 0.05)
MAS- minutes after spraying

Effect of vegetable oil composition on the photodecompositon sethoxydim on leaf surface

Vegetable oils' compositions are summarized in Tab. 3. Fatty acids of vegetable oils may affect the solubilizing, softening or disrupting of the cuticular waxes (Hazen, 2000). Therefore, fatty acids composition may affect the herbicide photodecomposition on leaf surface. The type of saturate or unsaturate fatty acids constitutive of vegetable oil affect the sethoxydim performance (Tab. 3). Similar results have been reported by Izadi-Darbandi *et al*. (2013). The results from this study revealed that fatty acids from vegetable oils had effect on sethoxydim photodecomposition on leaf surface, as with increasing unsaturated fatty acid values, the photodecomposition decreased and therefore the performance of sethoxydim on wild oat increased (Fig.1). A positive relationship exist between relative potency and unsaturated fatty acid values, as with increasing unsaturated fatty acid values, relative potency increased in various light treatment. To test the significance of the correlation coefficients (Snedecor and Cochran, 1989) correlation coefficients were used. This test showed significant differences between correlation coefficients. A negative relationship exist between linoleic fatty acid values and relative potency, as with increasing linoleic fatty acid values, relative potency decreased in various light treatment (Tabs. 2 and 3).

Tab. 3. Fatty acid composition of vegetable oils

Source	Saturates					Mono- Unsaturates					Poly-Unsaturates		Unsat/Sat ratio
	16:0	18:0	20:0	22:0	24:0	16:1	18:1	20:1	22:1	24:1	18:2	18:3	
Turnip	3.85	1.13	0.75	1.01	0.56	0.27	15.38	9.34	43.99	2.19	8.96	10.65	12.4
Soybean	5.63	3.26	0.83	0.49	0.14	0.14	54.11	1.68	0.67	-	25.75	7.3	8.66
Cottonseed	20.87	3.19	0.37	-	-	0.55	20.1	-	-	-	53.78	0.21	2.94
Sunflower	6.54	3.92	0.32	1.13	0.50	0.26	51.68	0.32	-	-	35.23	-	6.99
Olive	7.1	2.05	0.24	-	-	0.5	69.84	0.14	-	-	19.85	-	9.64
Castor	9.54	10.52	0.92	-	-	-	34.05	2.73	-	-	37.94	4.29	3.76
Sesame	9.90	5.95	0.82	0.22	0.07	0.20	40.55	0.29	-	-	41.19	0.54	4.83
Corn	4.92	2.95	0.91	0.52	0.22	0.25	60.54	2.15	-	0.26	18.41	8.04	8.66
Canola	12.32	2.49	0.75	0.20	0.37	0.14	30.89	0.29	-	-	50.70	0.86	4.84

Percentages may not add to 100% due to rounding and other constituents not listed

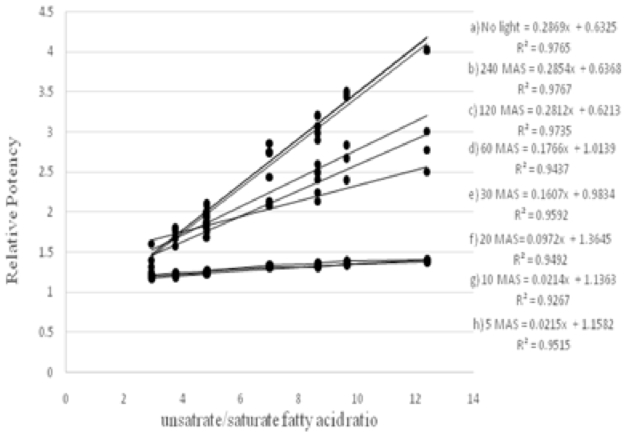

Fig. 1. Relationship between relative potency of sethoxydim (alone and in a mixture with vegetable oils), in light treatments and unsatrate/saturate fatty acid ratio

Conclusion

Based on the results of this study, the following conclusions can be made: (*i*) by using vegetable oils the performance of sethoxydim has been highly improved comparing with control (no vegetable oil); (*ii*) vegetable oils can be ranked based on relative potency value to turnip > olive > soybean > corn > sunflower > canola > sesame > castor > cottonseed; (*iii*) based on their ability to enhance the efficacy of sethoxydim under the simulated light condition, the rank is turnip > olive > soybean > corn > sunflower > canola > sesame > castor > cottonseed; (iv) when light treatment was applied at 120 and 240 MAS, it did not decrease sethoxydim performance.

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