Influence of surfactants on efficacy of different herbicides in control of *Cyperus rotundus* and *Oxalis latifolia*

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Pollution of the environment is now a major concern. Newer techniques have to be developed to reduce the chemical dose as well as volume of spray in agricultural crop production systems in order to reduce the chemical load. Addition of surfactants to herbicide spray solution reduces the surface tension of the solution and thus enhances spread and contact area of the spray drop on the leaf. Two surfactants (laffmul DA and ethoxylated castor oil (EO 40) – both non-ionic crop oil concentrates having 67.7 and 76.4 mN/m surface tension respectively) were added to different herbicide spray solutions and assessed for surface tension and altered herbicide efficacy through biomass reduction of *Cyperus rotundus* and *Oxalis latifolia*. After 45 days of herbicide spray, fresh weight was recorded as the sprouting ability of underground propagules depending on the entry and translocation of the herbicide. Negative relation between surface tension and spread of droplet on the foliage of *C. rotundus* and *O. latifolia* was observed. In spite of low surface tension of all herbicides with laffmul DA, enhanced efficacy was observed only in glufosinate ammonium and glyphosate herbicide. Whereas, though castor oil has high surface tension, it enhanced the efficacy in imazapyr and oxyfluorfen. Addition of surfactants did not increase the efficacy of 2,4-D and imazethapyr. Importance of surfactants on spread of droplets on the leaf surface and penetration of herbicide through the cuticle is discussed.

SURFACTANTS along with herbicides in spray solution enhance herbicide efficacy by: (i) altering the surface properties of the droplet, viz. wetting, spreading, retention, coverage; (ii) affecting the availability of herbicide molecule, viz. prevention of crystallization, volatilization, ionization, salt and other complex formation; (iii) changing the diffusion co-efficient of the herbicide molecule (K_{ow}) and its mobility[1,2]. Schonherr[3] showed that ethylene oxide (EO) content altered volatilization, water solubility and stable micelle formation. The EO content of surfactant matched the K_{ow} (partition between cuticle and water) of the herbicide and increases the penetration of the herbicide through co-penetration along with adjuvant. Umamahesh[4] showed the importance of surfactants and their EO in increasing cuticular penetration of ^{14}C-glyphosate and enhanced efficacy.

Addition of surfactants to spray solutions reduced greatly the surface tension and maximized the spread of droplets on the leaf. A strong negative relationship between surface tension and droplet spread on the foliage of *Cyperus rotundus* and *Oxalis latifolia* was observed in a previous study[5]. This communication is intended to study whether reduced surface tension can be used universally for increasing the efficacy of all herbicide solutions.

Five surfactants, viz. codacide, nonyl phenol with EO 10, laffmul DA, laffmul 3434 and castor oil EO 40 were added to water at different concentrations (%), viz. 0.01, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4 and 0.5 v/v. The critical micelle concentration (CMC) was assessed according to Buick *et al.*[6]. Further, the influence of surfactant and its concentration on surface tension of water was determined. About 2.5 times the CMC (0.2%) was used to assess the efficacy in control of weed growth, as suggested by Tan and Crabtree[7]. Surfactants laffmul DA and castor oil EO 40 (66.03 and 75.64 mN/m surface tension respectively, at 0.2%) were selected to assess the equilibrium surface tension (after 1 h of ageing) of different herbicides, viz. glyphosate (433 g ai/ha), imazapyr (83 g ai/ha), imazethapyr (33 g ai/ha), glufosinate ammonium (333 g ai/ha), oxyfluorfen (40 g ai/ha) and 2,4-D Na salt (666 g ai/ha) prepared in water and to assess the efficacy with or without surfactants. Only 40% of the recommended doses for all the herbicides were used, since the effect of surfactants on herbicide efficacy was more pronounced at low concentrations of the herbicide.

An aluminum ring was suspended from a specific-gravity measuring digital analytical balance attachment (AND electronic balance FX41). The balance was placed on a stool with an opening at the centre such that the ring was freely suspended below the stool. With the help of a hydraulic jack (placed below the stool such that the solution surface touches the ring) the solution in the beaker was lowered, which caused the pull at the surface. Maximum weight needed to separate the ring from the surface of the solution was recorded. Surface tension (ST) of the solution was computed and expressed in milli Newton/metre (mN/m) as follows.

$$\mathrm{ST} = W \times 980.7/2 \times \pi \times D, \qquad (1)$$

where W denotes maximum weight (g) needed to separate the ring from the surface of the solution, 980.7 is the factor to convert gravitational force to mN/m and D represents diameter of the ring. Surface tension was measured thrice for each solution.

Carbonized rubber-battery pots of size 30 cm × 10 cm × 10 cm were filled with a mixture of soil, Kandic Paleustalf and well-decomposed organic matter in a ratio 4 : 1. *C.*

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Table 1. Influence of various concentrations of surfactant on surface tension (mN/m) of water

Concentration (% v/v)	Codacide	Nonyl phenol EO 10	Laffmul DA	Laffmul 3434	Castor oil EO 40
0.01	68.5	75.4	67.8	69.7	76.8
0.05	68.1	74.9	67.7	69.6	76.4
0.1	67.8	74.8	67.8	69.2	76.0
0.15	67.7	74.4	66.6	68.7	76.0
0.2	67.6	72.9	66.0	68.6	75.6
0.25	67.3	72.4	65.4	68.4	75.4
0.3	67.2	71.3	63.4	68.1	74.9
0.35	67.1	71.1	63.2	67.7	74.7
0.4	66.4	70.8	62.7	67.2	73.9
0.5	65.6	70.3	62.1	66.7	71.5

Surface tension of water 73 mN/m.
CD (P = 0.05) for surfactant, 0.28; Concentration, 0.19 and Surfactant × concentration, 0.629.

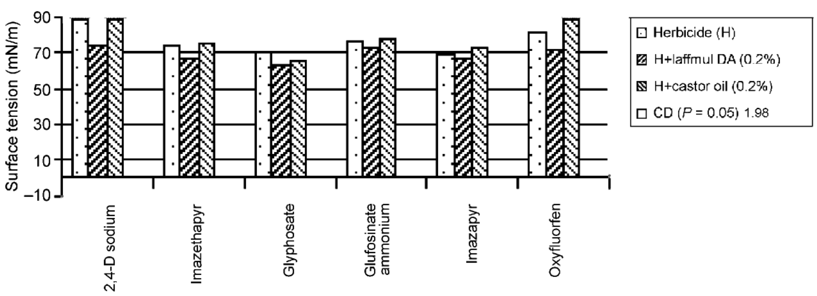

Figure 1. Effect of surfactant on surface tension (mN/m) of different herbicides.

rotundus and *O. latifolia* were raised by planting a single tuber and bulb respectively. Pots were irrigated daily throughout the experimental period. Glyphosate (433 g ai/ha), imazapyr (83 g ai/ha), imazethapyr (33 g ai/ha), glufosinate ammonium (333 g ai/ha), oxyfluorfen (40 g ai/ha) and 2,4-D Na salt (666 g ai/ha) were sprayed on foliage of 30-day-old *C. rotundus* and *O. latifolia* to find the efficacy with or without surfactants (each at 0.2%). The sprouting ability in terms of fresh weight (g/plant) was recorded 45 days after spraying. Fifteen days after spraying, the mortality of the foliage was observed in treated pots. Regeneration and fresh growth of plants are influenced by the amount of entry and translocation of foliar-applied herbicide. Each treatment was replicated thrice and analysed in CRD.

Addition of adjuvant laffmul DA significantly reduced the surface tension of water at all concentrations of surfactant compared to addition of castor oil (Table 1). Castor oil EO 40 at 0.2% had significantly higher surface tension compared to water alone. Thus these two surfactants were selected.

Surface tension of the herbicide solution with laffmul DA was significantly low compared to that without surfactant (Figure 1). Addition of castor oil EO 40 had differential influence on the surface tension of herbicide solutions. Addition of castor oil increased the surface tension as in the case of imazapyr, oxyfluorfen, glufosinate ammonium or significantly reduced surface tension as in glyphosate. Castor oil had no significant effect on the surface tension of herbicide solution prepared from 2,4-D Na salt and imazethapyr. Thus castor oil EO 40 behaves differently in altering surface tension of the solution depending upon the type of herbicide compared to laffmul DA.

Extent of fresh weight (g/plant) reduction due to herbicides reflected the herbicide efficacy. More the efficacy of the herbicide, the plants had least fresh weight and vice versa. Amongst herbicides, only glufosinate ammonium and 2,4-D Na salt showed significant enhancement in efficacy for laffmul DA (0.2%). Castor oil EO 40 did not alter the efficacy of these herbicides, as all these plants had fresh weight on par with the herbicide alone, except glufosinate ammonium (Figure 2 *a*). Further, though surface tension increased significantly with glufosinate ammonium and castor oil EO 40, there was enhanced efficacy compared to glufosinate ammonium alone. This suggests that glufosinate ammonium and 2,4-D Na salt need laffmul DA as surfactant to enhance their efficacy and not other herbicides.

Addition of both the surfactants reduced the efficacy of glufosinate ammonium and 2,4-D Na salts (Figure 2 *b*). For glyphosate, though both the surfactants significantly enhanced the efficacy, marked increase in efficacy was observed with laffmul DA. For imazapyr, though both the

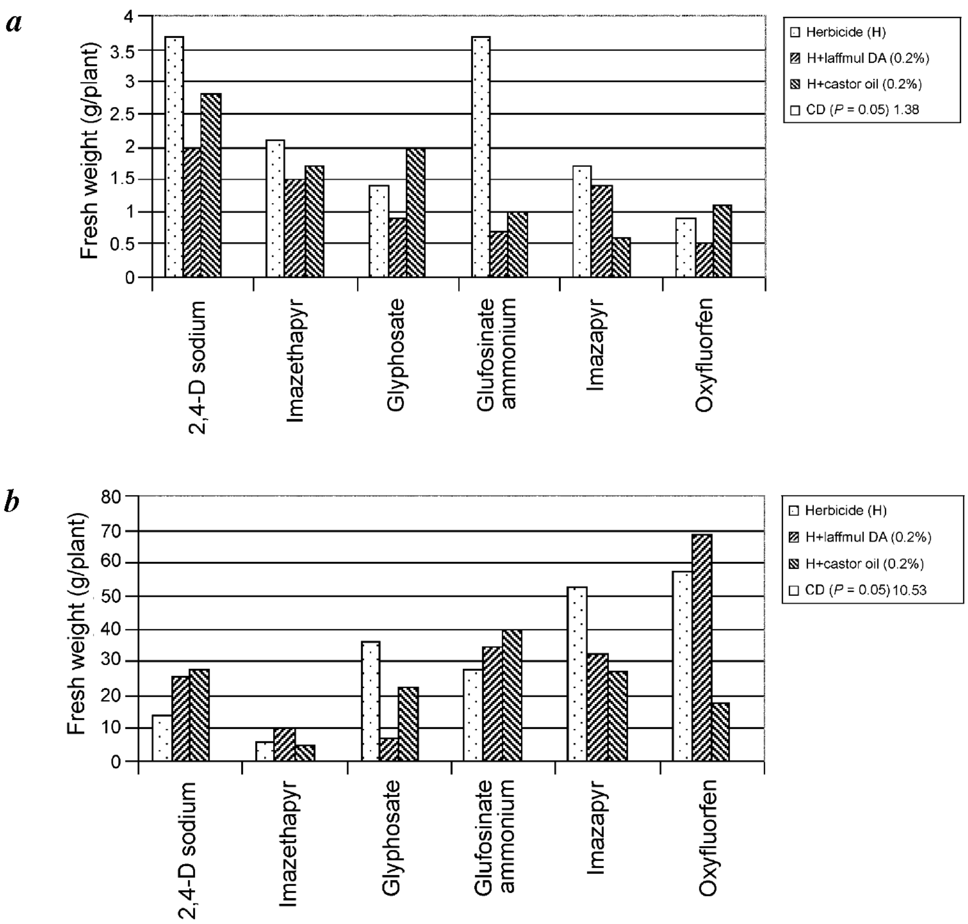

Figure 2. Influence of surfactants along with different herbicides on fresh weight of *Oxalis latifolia* (***a***) and *Cyperus rotundus* (***b***).

surfactants enhanced the efficacy, differences amongst surfactants were not significant. In the case of imazethapyr, both surfactants did not enhance the efficacy, whereas for oxyfluorfen, addition of castor oil EO 40 showed significant enhancement of herbicide efficacy. These data suggest that the efficacy of these herbicides with surfactant varied amongst weed species. Addition of laffmul DA to glyphosate and castor oil EO 40 to imazapyr respectively, caused maximum efficacy in controlling both weed species.

The herbicide efficacy is a reflection of both the amount of herbicide that penetrates into the cuticle and is translocated to the underground propagules. Surfactants influence the spread and pattern of entry of herbicides into the cuticle. Further, for example, studies on the spread of chemical molecule in a droplet deposited on the leaf is also influenced by the chemical. Auto-radiogram of ^{14}Cprochloraz partition into cuticle was found to be concentrated on an entire area of droplet contact on both the smooth and glaucous surfaces of the foliage. ^{14}C 2,4-D was found to be concentrated on the entire area of the droplet only in the smooth surface, but on the glaucous surface it is concentrated only in the narrow edges of the droplet periphery[8]. The deposited droplet dries out fast within 15 to 45 min depending on environmental conditions, herbicide–surfactant–cuticle characteristics, extent of spread, partition of herbicide molecule between droplet and cuticle, etc. Within this duration, the molecule has to be loaded into the cuticle for maximizing the potency of the herbicide.

There was no relationship between surface tension of herbicides and their respective efficacy with or without surfactants in both weed species. Similarly, there was no relationship between surface tension and spreading coefficient; e.g. methylated and non-methylated soybean oil though both have similar surface tension, the former has 55 times more spread than the latter[9]. Thus apart from spreading of the drop, diffusion of the herbicide molecule into the cuticle plays an important role in deciding the efficacy of foliar-applied herbicides.

Significant negative relationship between molar volumes of molecule and diffusion coefficient across cuticle was noticed. Further, more the double bonds in a compound more will be the diffusion coefficient[10]. In other words, diffusion is a passive process with greater diffusion for higher molecular weight molecules for a given

Table 2. Physico-chemical properties of herbicides

Herbicide	Mol wt	Dose in g ai/ha	Dose in mM	Log K_{ow}	Water solubility (g/l)	p*K*a
2,4-D sodium	243	666	7	2.6 (pH 1)	18 (20°C)	2.73
Glyphosate	169.1	433	6	< –3.4 (20°C)	11.6 (25°C)	0.8, 3.0, 6.0 and 11
Glufosinate ammonium	198.2	333	4	< 0.1 (pH 7, 22°C)	1370 (22°C)	2, 2.9 and 9.8
Imazapyr	261.3	83	0.7	0.11 (22°C)	9.74 (15°C)	1.9, 3.6 and 11
Imazethapyr	289.3	33	0.3	1.04 (pH 5), 1.49 (pH 7) and 1.2 (pH 9) it 25°C	1.4 (25°C)	2.1, 3.9
Oxyfluorfen	361.7	40	0.3	4.47	0.0001 (25°C)	–

Molar concentration was calculated by taking 400 l of water spray/ha.

molar volume. A negative correlation coefficient (r = –0.732) was observed between recommended dose (mM) and molecular weight of the herbicide. Thus, the dose of different herbicides is varied, but herbicide efficacy is not related to molecular weight of the active ingredients. This indicates that diffusion of herbicides not only depends on molecular weight but also on other physico-chemical properties (Table 2). Bukovac *et al.*[11] showed the importance of physico-chemical properties (logK_{ow} and pK_a) in cuticle penetration. Based on the model proposed by Bromilow *et al.*[12], the physico-chemical properties of herbicide also determine the herbicide mobility in plant. If K_{ow} is more than 4.0, the herbicide molecule is lipophilic and non-mobile in plants (oxyfluorfen). Owing to high fat soluble in nature, oxyfluorfen loads into the cuticle and its penetration was influenced by the presence of castor oil, especially into *C. rotundus* cuticle. Spread of the drop on *C. rotundus* seems to be more than that in *O. latifolia*, due to low contact angle formed between the drop and the leaf surface for a given surface tension solution in *C. rotundus* than in *O. latifolia*[5]. A similar effect was observed with imazapyr and castor oil in enhancing the efficacy.

Both oxyfluorfen and imazapyr are rapidly degraded by sunlight, especially UV light. Addition of castor oil may protect the photo-degradation of herbicides, which resulted in increased concentration for diffusion into the cuticle. For 2,4-D and imazethapyr, none of the surfactants helped in enhancing the efficacy. Probably the herbicide molecule has necessary physico-chemical properties that facilitated penetration into the cuticle and phloem mobility. Glyphosate and glufosinate ammonium are highly water soluble in nature and addition of laffmul DA facilitated increased spread and contact area on the cuticle. This led to enhanced efficacy. Using radioactive surfactants, it has been shown that the surfactant co-penetrates across the cuticle along with the herbicide and does not move out of the fed spot unlike the herbicide[13]. This suggests that surfactants play an important role in accelerating the penetration of the herbicide across the cuticle apart from reducing the surface tension alone. Thus it is imperative to identify a surfactant which will enhance penetration of the herbicide more rapidly into the cuticle and thereby increase the efficacy of the herbicide.

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ACKNOWLEDGEMENT. Financial assistance from the Indian Council of Agricultural Research, New Delhi is acknowledged.

Received 7 October 2003; revised accepted 18 December 2003