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Leaching and Sorption of Norflurazon in Soils as Affected by Cationic Surfactants

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Herbicides are very effective weed control tools, but their use has caused environmental concerns including herbicide leaching into groundwater. Groundwater contamination from pesticide leaching is a growing problem in major agricultural regions of the world (Hallberg 1988). Leaching of pesticide metabolites and formulation impurities also raises concerns (Barrett et al. 1993). Herbicide leaching not only causes groundwater contamination but also reduces activity on weeds by decreasing available herbicide in top soil where weed roots and seeds are (Graph et al. 1985).

Many synthetic adjuvants such as polymers and surfactants have been tested to reduce herbicide leaching (Fleming et al. 1992, Jain and Singh 1992). Certain cationic surfactants were found to reduce or nearly eliminate the leaching of substituted urea herbicides in soils (Bayer and Foy 1982). Reduction of herbicide leaching by cationic surfactants was believed to be attributed to an increase in adsorption of the herbicide onto the soil (Gaynor and Volk 1976). Cationic surfactants can replace metals on the mineral surface exchange complex due to ionic attraction of surfactant by soil particles. The mineral surface of the soil is transformed from hydrophilic to hydrophobic by the presence of the hydrocarbon moiety of the sorbed surfactant cations (Bouchard et al. 1989). The result can be a great increase in mineral surface sorptivity for neutral organic compounds and a decrease in herbicide mobility (Gaynor and Volk 1976).

In studying the effect of cationic surfactants on herbicide leaching, substituted imidazoline (Earl 1990) were more effective than quaternary ammonium chloride (Reck 1990) in reducing norflurazon leaching (Tan and Singh 1995). Substituted imidazoline of coconut fatty acid (Monazoline C) had shown potential for reducing norflurazon leaching. The objectives of this study were (1) to examine the relationship between surfactant chemical structures and their leaching- inhibition activity, (2) to investigate the influence of the amount of Monazoline C and water applied on norflurazon leaching, and (3) to study the impact of Monazoline C on norflurazon sorption in the soil.

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MATERIALS AND METHODS

Leaching of norflurazon as affected by the type of cationic surfactants, the amount of water applied, and the surfactant : herbicide ratio was studied by using polyvinyl chloride (PVC) columns. The columns were 130 cm long and 10 cm in diameter and were split longitudinally into two equal halves. At every 15 cm from bottom, a ridge of silicone was placed on the inside wall of each half to prevent 'edge flow' of water along the soil-wall interface. The two halves were joined by waterproof tape to form a column. A PVC end-cap with a small drain hole was fitted to the bottom of the column. The column was packed with soil collected from 0-20 cm depth in the field. The soil was Candler fine sand (Typic Quartzipsamment) and had 1.2% organic matter and a pH of 6.3. After packing, the column was kept in an upright position on a wooden frame, saturated with tap water from the top, and allowed to drain for 18 hr.

The type of cationic surfactants, the amount of water applied, and the Surfactant : herbicide ratio were used as treatment factors to characterize norflurazon leaching as affected by some of the combinations of these three factors. The impact of each factor on the leaching was examined when the other factors were set at a fixed level. Three cationic surfactants were compared for their effect on leaching of norflurazon (Solicam 80DF, Sandoz Agro Inc, Des Plaines, IL) at the surfactant : herbicide ratio of 0.25:1 and the water application of 25.4 cm. The surfactants were coco trimethyl ammonium chloride (Adogen 461, Witco Corp, Dublin, OH), substituted imidazoline of coconut fatty acid (Monazoline C, Mona Industries Inc, Paterson, NJ), and substituted imidazoline of oleic acid (Monazoline O, Mona Industries Inc.). Effect of water quantity (12.7, 25.4, and 38.1 cm) on norflurazon leaching reduction by Monazoline C was investigated at the Monazoline C:norflurazon ratio of 0.25:1. Norflurazon leaching as affected by various ratios of Monazoline C:norflurazon (0, 0.1, 0.25, 0.5, 0.75, and 1) was examined at the water quantity 25.4 cm.

Norflurazon (7.85 mg) was placed in a 20-mL glass vial containing 20 mL deionized water. Each of the three cationic surfactants (1.96 mg) was added in the separate glass vials to make different surfactant-norflurazon solutions with the surfactant: herbicide ratio of 0.25:1. Monazoline C weighed 0.78, 1.96, 3.93, 5.89, and 7.85 mg was added in the separate vials containing norflurazon and water to make Monazoline C-norflurazon solutions with Monazoline C-norflurazon ratios of 0.1, 0.25, 0.5, 0.75, and 1, respectively. For all treatments, two mL solution was applied uniformly on the soil surface of a soil column as small drops using a 1.5 mL pasteur pipette. The norflurazon application rate was equivalent to 10 kg ai ha 1. The column was leached by applying deionized water at 2.54 cm hr^{-1} over filter paper placed on the soil surface. Duration of water application was 5, 10, and 15 hr for 12.7, 25.4, and 38.1 cm water treatments, respectively. The filter paper was used to ensure uniform distribution of water on the soil surface. After leaching, the column was allowed to drain for 18 hr and split longitudinally into two halves. Each half was planted with yellow foxtail, which is very sensitive to norflurazon, in four rows paralleling to the length of the column.

Norflurazon leaching in the column was evaluated by measuring the soil depth within which yellow foxtail was killed by leached norflurazon. The leaching distance of norflurazon was indicated by soil depth with dead yellow foxtail. Since each column had four rows of yellow foxtail brass, their average control depth was used for analysis of variance. Completely randomized designs were employed with six replications for all leaching experiments. Means of treatments were separated by Tukey's Honestly Significant Difference Test at 5% significant level (Steel and Torrie 1960). The relationship between norflurazon leaching and the ratio of Monazoline C:norflurazon was established by regression.

Sorption of norflurazon on soils as affected by the ratio of Monazoline C: norflurazon was studied using the ^{14}C-labeled norflurazon and batch-equilibrium technique (Alva and Singh 1990). A 2.5 g sample of air-dried soil was placed in an eight-mL glass vial. Three mL ^{14}C-norflurazon solution, containing 13.3 μg norflurazon and having the specific activity of 492 Bq mL^{-1}, was added to each vial. Samples were equilibrated by shaking on an orbit shaker for 24 hr and then centrifuged for 20 min. One mL of supernatant was pipetted into a vial containing 10 mL scintillation cocktail (ScintiVerse II, Fisher Scientific Co, Pittsburgh, PA). Radioactivity was quantified by a liquid scintillation counter (LS 6000, Beckman Instruments Co, Fullerton, CA). Sorption was expressed as the amount of norflurazon sorbed by one gram soil, and sorption percent was calculated based on the equation: Sorption percent = (amount of norflurazon sorbed by soil) / (Total amounts of norflurazon applied) X 100. A completely randomized design was used for sorption study with three replications. Data were subjected to analysis of variance, and means of treatments were separated by Tukey's Honestly Significant Difference Test at 5% significant level.

RESULTS AND DISCUSSION

Monazoline C significantly reduced norflurazon leaching at the Monazoline C:norflurazon mix ratio 0.25:1 and the water application 25.4 cm (Table 1). While at the same mix ratio, Adogen 461 and Monazoline O did not affect norflurazon leaching although both surfactants contain one similar moiety in their molecules to Monazoline C. Both Monazoline C and Adogen 461 have a cocoyl moiety, while both Monazoline C and Monazoline O contain an imidazoline component. It appears that the molecular moiety of the cationic surfactant was not as important as the entire molecular structure (the combination of the moieties) in affecting norflurazon leaching.

The quantity of water applied significantly influenced the effect of Monazoline C on norflurazon leaching (Fig. 1). Monazoline C decreased norflurazon leaching at all levels of water applications except the treatment without water. As the water quantity increased, differences between the leaching distance of norflurazon with and without Monazoline C were also widened. Increasing water quantity amplified the effect of Monazoline C on the leaching of norflurazon.

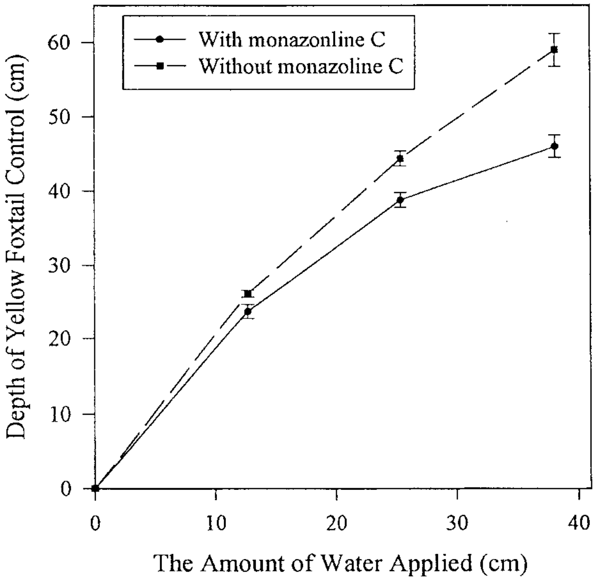

Figure 1. Effects of monazoline C and the amount of water applied on the leaching depth of norflurazon as indicated by the depth of yellow foxtail control at the Monazoline C:norflurazon ratio of 0.25:1

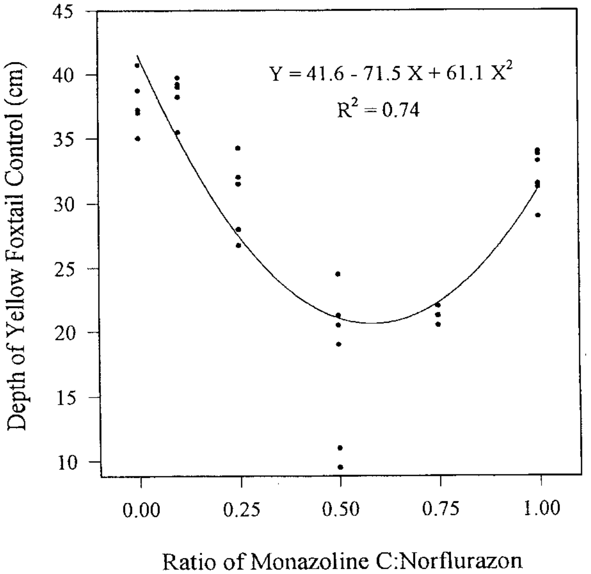

Figure 2. Relationship between the monazoline C:norflurazon ratio and the depth of norflurazon leaching as indicated by the depth of yellow foxtail control at the water application 25.4 cm

Table 1. Effect of different cationic surfactants on the leaching distance of norflurazon in soil columns.*

Cationic surfactant		Leaching distance †of norflurazon (cm)
Trade name	Chemical name	
Adogen 461	coco trimethyl ammonium chloride	39.8 ± 0.08 a‡§
Monazoline C	substituted imidazoline of coconut fatty acid	31.1 ± 1.28 b
Monazoline O	substituted imidazoline of oleic acid	38.1 ± 0.44 a
Check	without surfactant	37.6 ± 0.79 a

*At the surfactant:norflurazon ratio 0.25:1 and the water application 25.4 cm.
†Leaching distance: soil depth within which yellow foxtail was controlled by leached norflurazon.
‡Average of six replications t standard error.
§In this table and the proceeding table means followed by the same letter are not different (Tukey's Honestly Significant Difference Test, $\alpha = 0.05$).

Table 2. Sorption of norflurazon on the soil as affected by the monazoline C:norflurazon mix ratio.

Monazoline C:norflurazon ratio	Norflurazon sorption by the soil	
	μg norflurazon g^{-1} soil	sorption %†
0	2.5 ± 0.00 a‡§	47.4 ± 0.45
0.25	2.5 ± 0.03 a	46.5 ± 0.21
0.50	2.4 ± 0.03 a	44.8 ± 0.28
0.75	2.5 ± 0.03 a	46.6 ± 0.72
1.00	2.4 ± 0.07 a	44.5 ± 1.12

†Sorption % = (The amount of norflurazon sorbed by soil)/(Total amounts of norflurazon applied) X 100.
‡Average of three replications ± standard error.

Norflurazon leaching was closely related to the Monazoline C:norflurazon ratio (Fig. 2). As the ratio increased from zero to 0.5, the leaching distance of norflurazon decreased on average from 38 to 17 cm. The leaching distance increased from 17 to 32 cm when the ratio increased from 0.5 to one. The best fit regression equation to describe the relationship between the norflurazon leaching and the Monazoline C:norflurazon ratio was Leaching Distance = 41.6 - 71.5 (Ratio) + 61.1 $(\text{Ratio})^2$ with

$R^2 = 0.74$. The P-values for the regression coefficients were smaller than 0.01. This regression shows that Monazoline C:norflurazon ratio near 0.5 was the optimum combination for the maximum leaching reduction of norflurazon.

Reduction of herbicide leaching by cationic surfactants has been attributed to the ionic attraction of positively-charged cationic surfactants by soil particles (Bouchard et al. 1989, Smith and Bayer 1967). The soil surface is then transformed from hydrophilic to hydrophobic by the presence of the hydrocarbon moiety of the sorbed surfactant cations. This process is believed to be able to increase mineral surface sorptivity for non-charged herbicides and consequently decrease the mobility or leaching of the herbicides.

To examine if this hypothesis explains the leaching reduction of norflurazon by Monazoline C, norflurazon sorption on the soil as affected by Monazoline C was investigated with various Monazoline C:norflurazon ratios. With a range of Monazoline C:norflurazon ratios from 0.25 to one, none of the surfactant treatments affect norflurazon sorption in the soil (Table 2). Monazoline C reduced norflurazon leaching without affecting norflurazon sorption in the soil. The leaching reduction of norflurazon by Monazoline C was apparently not attributed to the change in soil sorption of norflurazon.

In conclusion, specific moieties of cationic surfactant molecules were not important in affecting norflurazon leaching. Monazoline C decreased norflurazon leaching, and the effect was amplified by the increased water application. The effect was also dependent on the ratio of Monazoline C:norflurazon. The maximum leaching reduction was achieved at the Monazoline C:norflurazon ratio of 0.5:1. Norflurazon sorption in the soil was unaffected by Monazoline C regardless of the amount of Monazoline C. It appears that Monazoline C reduced the leaching of norflurazon in the soil through other mechanisms than increasing soil sorption of norflurazon. The best regression equation to describe the relationship between the norflurazon leaching and the Monazoline C:norflurazon ratio was Leaching Distance = 41.6 - 71.5 (Ratio) + 61.1 $(\text{Ratio})^2$ with a range of Monazoline C:norflurazon ratios from zero to one. This study showed that Monazoline C can be used as a spray adjuvant to reduce norflurazon leaching.

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