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Effects of Cationic Surfactants on Leaching of Bromacil and Norflurazon

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Groundwater contamination resulting from leaching of pesticides is a common and growing problem in major agricultural regions of the world (Hallberg 1988). Both natural and synthetic adjuvants have been tested to reduce the leaching (Fleming *et al.* 1992; Jain and Singh 1992). A few examples are corn starch, activated charcoal, polymers, and surfactants.

Certain cationic surfactants were found to reduce or nearly eliminate the leaching of substituted urea herbicides in soils (Bayer 1967; Bayer and Foy 1982). The reduction of leaching by cationic surfactants was attributed to an increase in adsorption of the herbicide onto the soil (Smith and Bayer 1967). Gaynor and Volk (1976) also observed the greater soil adsorption of picloram from solutions containing cationic surfactants than that containing no surfactant or nonionic surfactants. Nonionic surfactants did not affect the adsorption (Smith and Bayer 1967) and had no effect on or increased the leaching (Helling, 1971; Huggenberger *et al.* 1973; Koren 1972; Smith and Bayer 1967).

Sandy soil and high precipitation in Florida make herbicide leaching a major environmental concern in agriculture. Among many herbicides, bromacil and norflurazon are commonly used for citrus in Florida (Reddy and Singh 1993; Singh *et al.* 1985). The objective of this experiment was to examine the effects of three types of cationic surfactants on leaching of bromacil and norflurazon in sandy soil.

MATERIALS AND METHODS

Leaching of bromacil [5-bromo-6-methyl-3-(l-methylpropyl)-2,4(l*H*,3*H*) pyrimidinedione] and norflurazon [4-chloro-5-(methylamino)-2-(3-trifluoromethyl)phenyl)-3(2*H*)-pyridazinone] were studied by using acrylic columns with a height of 8 cm and an inner diameter of 7 cm. The bottom of the column was constructed by using a thin nylon mesh above the perforated acrylic plate. This allowed free water movement while maintaining soil column integrity. The column was packed by adding a small amount of soil to the column while it was shaken on a vortex shaker. The soil was Candler fine sand that had 1.2% organic matter, 96% sand, and a pH of 6.3. Before packing, the soil was screened through a No. 10

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sieve. The columns were packed to attain a bulk density of 1.5 g/cm^3 based on the dry weight and packed volume of the soil in the columns. The packed columns were placed in a plastic tub containing deionized water so they can be saturated with the water from the bottom by capillary force and then allowed to drain for 18 hr.

The tested cationic surfactants included ethoxylated amine, quaternary ammonium chloride, and substituted imidazoline. The ethoxylated amine surfactants (Exxon Chemical Co., Milton, WI 53563) were E-14-2 [bis-(2-hydroxyethyl) isodecyloxypropylamine], E-14-5 [poly (5) oxyethylene isodecyloxypropylamine], E-18-2 [bis-(2-hydroxyethyl) octadecylamine], and E-18-5 [poly (5) oxyethylene octadecylamine]. The quaternary ammonium surfactants (Witco Corp., Dublin, OH 43017) included Adogen 444 (cetyl trimethyl ammonium chloride), Adogen 461 (coco trimethyl ammonium chloride), Adogen 462 (dicoco dimethyl ammonium chloride), and Adogen 471 (tallow trimethyl ammonium chloride). The substituted imidazoline surfactants (Mona Industries, Inc., Paterson, NJ 07544) had Monazoline CY (substituted imidazoline of caprylic acid), Monazoline C (substituted imidazoline of coconut fatty acid), Monazoline O (substituted imidazoline of oleic acid), and Monazoline T (substituted imidazoline of tall oil).

Bromacil (Hyvar X 80WP) was mixed with each of the tested cationic surfactants in equal amounts, i.e. 1 g active ingredient of the herbicide was mixed with 1 g active ingredient of the surfactant. Bromacil alone was the control. For the experiment on ethoxylated amine surfactants, pH of all the mixtures was adjusted to 7.0. ^{14}C-labeled bromacil was added to non-radioactive bromacil-surfactant mixture. The same procedures were employed for norflurazon (Solicam 80DF) except that only the quaternary ammonium chloride and substituted imidazoline surfactants were tested for norflurazon. The ^{14}C-labeled herbicides were [Carbonyl-2-^{14}C] bromacil (specific activity = 263 kBq/µmole, purity = 98%) and [4,5-^{14}C] norflurazon (specific activity = 1.52 MBq/µmole, purity = 99.8%).

One mL of the mixture (7x10^4 dpm) was applied uniformly to the soil surface of each column as small drops by using a pasteur pipet. This was equivalent to 5 kg ai/ha of bromacil or norflurazon. Two pieces of filter paper were placed on the soil surface and deionized water was applied by a peristaltic pump at a rate of 94 mL/hr (equivalent to 2.4 cm/hr rainfall). The leachate was collected at each pore volume (PV = 125 mL = 3.2 cm rainfall) up to four pore volumes. Two mL of leachate from each pore volume was mixed with 18 mL scintillation cocktail (ScintiVerse II, Fisher Scientific Co., Pittsburgh, PA 15219) in a vial. Radioactivity was quantified by a liquid scintillation counter (LS 6000, Beckman Instruments Co., Fullerton, CA 92634).

Leaching of bromacil or norflurazon was monitored by calculating the level of radioactivity present in the leachate at each pore volume. Data were expressed as a cumulative percent of the total dpm applied to the column that had been leached at each pore volume. Analysis of variance was performed at each pore volume. Means of the surfactant treatments were separated by Tukey's Honestly Significant Difference Test; Orthogonal Contrast Test was used to separate group means.

RESULTS AND DISCUSSION

Leaching of norflurazon increased as the amount of applied water increased (Table 1). For control, the leaching percentage of norflurazon increased from 5 to 48 as the amount of water increased from 3.2 cm to 13.0 cm. Monazoline C significantly decreased the leaching of norflurazon comparing with the control when the amount of water application was 13.0 cm. None of the other tested cationic surfactants had any effect on leaching of Norflurazon in comparison with the control (Table 1).

The leaching extent of norflurazon after mixed with Adogen 471 was significantly higher than that mixed with any Monazoline surfactant at water application level of 13.0 cm. Conversely, norflurazon leached significantly less after mixed with Monazoline C than mixed with Adogen surfactants at water application levels of 9.7 and 13.0 cm except Adogen 461. When the impact of the two groups of cationic surfactants on norflurazon leaching was compared by Orthogonal Contrast Test, Monazoline surfactants were found to lead a less extent of leaching than Adogen surfactants did at the water application level of 6.5 cm or above (Table 1).

The reduced leaching of herbicides by cationic surfactants has been suggested to be 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 will lead a great increase in mineral surface sorptivity for non-charged herbicides and consequently decrease the mobility or leaching of the herbicides.

Similar to norflurazon, the amount of water applied to the soil column also had impact on leaching of bromacil (Tables 2). For the control, it needed only 3.2 cm water to leach out 45% of bromacil added in the soil columns (Table 2), while 13.0 cm water was needed for 48% leaching of norflurazon (Table 1). Bromacil was more mobile than norflurazon in the soil columns.

None of the tested Adogen and Monazoline surfactants had any effect on bromacil leaching (Table 2). The two groups of surfactants were also not different in affecting the leaching of bromacil. Similarly, all the tested ethoxylated amine surfactants had no effect on the leaching of bromacil (Table 3).

Foy (1992) reported that cationic surfactants caused variable effects on herbicide movement, depending on the herbicide, surfactant, dosage or

Table 1. Effects of cationic surfactants, Adogen and Monazoline, on leaching of norflurazon

	Amount of water applied to the soil column (cm)			
Surfactant	3.2	6.5	9.7	13.0
Adogen 444	3 ± 0.4[a] a[b]	21 ± 2.2 ab	38 ± 1.9 ab	49 ± 1.2 ab
Adogen 461	3 ± 0.7 a	18 ± 1.7 ab	34 ± 3.1 abc	46 ± 4.5 abc
Adogen 462	2 ± 0.1 a	24 ± 2.2 ab	42 ± 3.9 ab	56 ± 4.0 ab
Adogen 471	6 ± 1.7 a	28 ± 4.1 ab	47 ± 3.5 a	60 ± 3.1 a
Monazoline CY	3 ± 0.3 a	16 ± 1.3 ab	31 ± 1.1 abc	42 ± 2.4 bc
Monazoline C	2 ± 0.1 a	11 ± 1.9 b	21 ± 3.6 c	31 ± 4.4 c
Monazoline O	3 ± 0.5 a	16 ± 2.2 ab	29 ± 2.3 bc	40 ± 2.1 bc
Monazoline T	4 ± 0.7 a	18 ± 1.9 ab	31 ± 1.6 bc	41 ± 1.8 bc
Control	5 ± 1.6 a	20 ± 3.5 ab	36 ± 5.2 abc	48 ± 4.6 ab
Adogen (average)	3 ± 0.6 a	23 ± 1.5 a	40 ± 1.9 a	53 ± 2.1 a
Monazoline (average)	3 ± 0.3 a	15 ± 1.1 b	28 ± 1.5 b	39 ± 1.7 b

[a] Percent of leached radioactivity = (dpm of ^{14}C-labeled bromacil in leachate)/(dpm of ^{14}C-labeled bromacil originally applied); average of four replications for each treatment and 16 replications for a group mean ± standard error.
[b] Means of treatments in the column were separated by Tukey's Honestly Significant Difference Test; group means in the column were separated by Orthogonal Contrast Test.

Table 2. Effects of cationic surfactants, Adogen and Monazoline, on leaching of bromacil

Surfactant	Amount of water applied to the soil column (cm) 3.2	6.5	9.7	13.0
Adogen 444	43 ± 7.1[a] a[b]	89 ± 3.3 a	98 ± 0.9 a	100 ± 0.6 a
Adogen 461	42 ± 6.5 a	88 ± 2.2 a	97 ± 1.1 a	99 ± 1.1 a
Adogen 462	45 ± 1.0 a	91 ± 5.2 a	100 ± 2.7 a	100 ± 2.1 a
Adogen 471	50 ± 4.5 a	89 ± 1.2 a	97 ± 1.2 a	99 ± 1.3 a
Monazoline CY	55 ± 8.0 a	92 ± 3.2 a	100 ± 2.6 a	100 ± 2.6 a
Monazoline C	41 ± 3.0 a	91 ± 3.8 a	100 ± 1.2 a	100 ± 0.4 a
Monazoline O	49 ± 3.9 a	92 ± 2.5 a	98 ± 2.3 a	100 ± 2.3 a
Monazoline T	42 ± 1.7 a	89 ± 3.2 a	99 ± 0.8 a	100 ± 0.7 a
Control	45 ± 2.4 a	90 ± 3.3 a	99 ± 1.7 a	100 ± 1.5 a
Adogen (average)	45 ± 2.5 a	89 ± 1.5 a	98 ± 0.8 a	100 ± 0.8 a
Monazoline (average)	47 ± 2.6 a	91 ± 1.5 a	99 ± 0.9 a	100 ± 0.9 a

[a]Percent of leached radioactivity = (dpm of ^{14}C-labeled bromacil in leachate)/(dpm of ^{14}C-labeled bromacil originally applied); average of four replications for each treatment and 16 replications for a group mean ± standard error.
[b]Means of treatments in the column were separated by Tukey's Honestly Significant Difference Test; group means in the column were separated by Orthogonal Contrast Test.

Table 3. Effect of ethoxylated amine surfactants on leaching of bromacil

	Amount of water applied to the soil column (cm)			
Surfactant	3.2	6.5	9.7	13.0
Ethoxylated amine E-14-2	39 $\pm$ 7.0[a] a[b]	85 $\pm$ 3.2 a	96 $\pm$ 1.5 a	98 $\pm$ 1.2 a
Ethoxylated amine E-14-5	44 $\pm$ 8.7 a	91 $\pm$ 1.6 a	99 $\pm$ 0.8 a	100 $\pm$ 1.2 a
Ethoxylated amine E-18-2	47 $\pm$ 4.3 a	91 $\pm$ 2.0 a	99 $\pm$ 2.6 a	100 $\pm$ 2.8 a
Ethoxylated amine E-18-5	47 $\pm$ 4.4 a	91 $\pm$ 2.8 a	99 $\pm$ 1.8 a	100 $\pm$ 2.2 a
Control	33 $\pm$ 5.7 a	89 $\pm$ 1.9 a	98 $\pm$ 1.8 a	100 $\pm$ 2.3 a

[a]Percent of leached radioactivity = (dpm of ^{14}C-labeled bromacil in leachate)/(dpm of ^{14}C-labeled bromacil originally applied); average of four replications for each treatment and 16 replications for a group mean $\pm$ standard error.
[b]Means of treatments in the column were separated by Tukey's Honestly Significant Difference Test; group means in the column were separated by Orthogonal Contrast Test.

concentration, soil type, and preleaching conditions. Variable effects of cationic surfactants on the leaching of norflurazon and bromacil in this study confirms the findings by Foy. Apparently, interactions between herbicides, cationic surfactants, soils, and environments are very complex and cannot be simply explained by the possible binder role of cationic surfactants suggested by several researchers as mentioned before in this section (Bouchard *et al.* 1989; Smith and Bayer 1967).

Certain cationic surfactants were able to decrease the leaching of norflurazon but the effect was dependent on the amount of applied water. Imidazoline surfactants had significantly greater potential than quaternary ammonium surfactants in reducing norflurazon leaching. None of the tested cationic surfactants had any effect on bromacil leaching. The leaching of both norflurazon and bromacil increased as the amount of applied water increased.

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