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Leaching behaviour of halosulfuron-methyl in sandy loam soil

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Abstract
Halosulfuron-methyl is a new frequently used sulfonylurea herbicide however there is lack of published information on its leaching potential in soil. The mobility of halosulfuron-methyl at two application rates 50 and 100 µg in sandy loam soil was studied under laboratory conditions. Residues of halosulfuron-methyl in soil and leachate were estimated by HPLC-QDA. Under continuous as well as discontinuous flow conditions with stimulated rainfall of 300 mm, the movement of halosulfuron-methyl was observed throughout the column. Percent retention of halosulfuron-methyl was found to be maximum from 25-30 cm under continuous flow condition and maximum retention of halosulfuron-methyl was from 15-25 cm under discontinuous flow condition. Results obtained by the study revealed that halosulfuron-methyl was highly mobile in soil column. A comparable retention of halosulfuron-methyl residues at both doses was observed. Leachate fraction also contains halosulfuron-methyl residues.

Keywords: Halosulfuron-methyl, Leaching, Sandy loam, QuEChERS, HPLC-QDA

Introduction

Sulfonylureas are being used largely in cereal crops in India (Sondhia, 2006) due to low application rates and high degree of weed selectivity. Halosulfuron-methyl, 3-chloro-5-(4, 6-dimethoxypyrimidin-2-ylcarbomylsulfamoyl)-1-methylpyrazole-4-carboxylate is a systemic pyrazol sulfonylurea group herbicide. It is widely used as post-emergence herbicide for the control of broad leaf and cyperaceous weeds in graminaceous crops particularly in rice and sugarcane. It acts on weeds by inhibition of production of acetolactate synthase enzyme, which is responsible for biosynthesis of branched-chain amino acids such as isoleucine, leucine and valine. Herbicide leaching through soil is particularly important in a number of environmental and agronomic problems (Costa *et al*., 1994) [1]. Leaching is considered as the main cause of ground-water contamination by herbicides (Flury, 1996) [4] which are largely determined by physical and chemical properties of herbicides. Several factors such as adsorption of the pesticide by the soil particles, water solubility of the pesticide, volume of leachate, pH and soil texture can influence the leaching of the pesticide through the soil (Kidd and James, 1991; Halimah *et al*., 2004) [8, 5]. Leaching of the pesticide is a major concern worldwide. Increasing use of herbicides with high potential mobility may cause serious environmental problems through off site movement, which must be controlled to minimize harmful effects on non-targeted organism. Sulfonylureas are considered relatively mobile compounds and their mobility increases with increasing pH and decreasing soil organic matter (Mersie *et al*., 1986; Shea, 1986; Hay, 1990) [9, 12, 7]. Despite of the extensive use of sulfonylurea herbicides, very little is known about their leaching behaviour in Indian soil. Since groundwater is the main source of drinking and irrigation water thus to assess the risk of ground water contamination by halosulfuron-methyl, present study was undertaken, to predict its rate of leaching under continuous and dis-continuous flow conditions.

Materials and Methods

Soil

Soil samples were collected from Research Farm, CCS HAU, Hisar, which had no previous history of halosulfuron-methyl application. The physico-chemical properties of the soil were as depicted in Table 1.

Table 1: Physico-chemical characteristics of soil

Soil property	Content
Texture	Sand 65.5%, silt 22.5% and clay 12%
pH	7.6
Electric conductivity (dS/m)	2.0
Organic Carbon	0.67%

Preparation of Standard Solution

Standard solutions of halosulfuron-methyl of concentration ranging from 0.001 to 1µg/ml required for plotting a calibration curve were prepared in acetonitrile from stock solution of 100 µg/ml of halosulfuron-methyl by serial dilution using acetonitrile. All standard solutions were stored at 4 ^{0}C.

Leaching Experiment

The leaching experiment was conducted under laboratory conditions at Agrochemicals Residues Testing Laboratory in CCS HAU, Hisar during February to April in 2017. Commercial formulation of halosulfuron-methyl (Sempra 75 WG) was used for leaching experiment. Plexi glass columns (60×3 cm i.d.) fitted with perforated glass sieve covered with filter paper (Whatmann No. 1) at bottom was used for leaching study. Each column was filled with soil up to 40 cm height to a uniform bulk density of 1.50 g/cm^3 ± 0.1. Weighed amount of soils, i.e, 53 g soil (calculated by following the equation 1) was poured in the column each time with the help of funnel (1 cm i.d.) tapped gently from a fixed height and pressed uniformly by a wooden roller. This process was repeated until each column was uniformly filled to a height of 40 cm. The soil in each column was covered with a filter paper, which was tapped by glass wool swab. Soil column so filled was installed vertically on wooden stand with their bottom resting on the fixed perforated sieve to facilitate collection of effluents during leaching. Leaching studies were carried out in triplicates. Soil (5 g) was fortified with 50 µg (single dose) and 100 µg (double dose) solution of halosulfuron-methyl and this fortified soil was added at the top of the column. Cotton swabs pre-washed with acetone and dried were placed in between the column soil and fortified soil and the top of the column to avoid disturbance of soil. One column packed with soil was kept as control to which no herbicide was added. Soil column was leached with 50 mm of distilled water at a time. Each time 50 mm lot of leaching water (35 ml) was added with the help of pipette, with the care that no spattering of soil took place. The leaching with the next 50 mm lot of distilled water was done after 24 hour of disappearance of standing water in the column for continuous flow condition and after one week for discontinuous flow conditions. Leaching was repeated until each leaching cycle of 300 mm depth was completed. During leaching, the columns were covered with perforated polythene bags to minimize the loss of leaching water due to evaporation. During leaching 2-3 drops of toluene solution was added to each column to check microbial growth in it.

Eqn 1: Calculation of soil and water used in column

Amount of soil = $\pi r^2 h \times BD$

r = radius of the column

h = height of the column (here for 5 cm each)

BD = bulk density of soil (1.50 mg/cm^3 of sandy loam soil)

Amount of water = $\pi r^2 h$

Chemical Analysis

After completion of leaching, intact soil cores were taken out of the plexi glass column. The cores were sliced into pieces of height of 5 cm each. These pieces were air dried, ground and sieved through a 2 mm sieve before extraction of halosulfuron-methyl. The herbicide from each soil section was extracted following the modified QuEChERS method developed by Feng *et al*. (2014) [3] with slight modifications. 20 gm of soil was taken in 50 ml centrifuge tube and 25 ml AcN acidified with 2 ml formic acid (5%) was added to it. The contents were shaked on rotaspin for 30 min. Then 3 gm NaCl was aaded to it. Mixture was vortexed for 1 min and is followed by centrifugation at 2500 rpm for 3 min. Supernatant was taken and evaporated for dryness. Residues were reconstituted in 2 ml AcN, 50 mg PSA was added to it and vortexed for 1 min followed by centrifugation at 5000 rpm for 10 min. Extract was filtered through 0.45 µm Millipore system before injection into the HPLC system. Water eluting from the columns was collected in flask and stored at 4 ^{0}C. These water samples (leachate) were liquid-liquid extracted with dichloromethane. Leachate samples were taken in 250 ml separatory funnel and added 2 gm of sodium chloride. The solution was partitioned thrice (50, 30 and 20 ml) with dichloromethane. The organic layers were collected and passed through 2-3 cm pad of anhydrous sodium sulfate for dehydration and evaporated in a rotatry vaccum evaporator for complete dryness. The process was repeated thrice by adding 5 ml AcN to ensure complete removal of dichloromethane. The residues were re-dissolved in AcN to make final volume to 2 ml for HPLC analysis.

Instruments

Halosulfuron-methyl was analysed using Waters e 2695 (e-alliance) high performance liquid chromatographic system equipped with Quadrupole Dalton Mass (QDA) detector having mass range 100-650 (m/z), cone voltage 15 V and sampling frequency is 5 Hz. HPLC operating parametrs were: column: Sunfire RPC-18 having internal dimension 250×4.6 mm, mobile phase: acetonitrile:water (7:3) in gradient mode at a flow rate of 1 ml/min. The approximate retention time for halosulfuron-methyl was 0.963 min.

Result and Discussion

In the present investigation, recovery experiments were carried out to establish the reliability and validity of the analytical method and to determine the efficiency of the extraction and clean up procedure for the soil and water. The soil and water control samples were spiked at 0.005, 0.01 and 0.1 µg/g respectively and processed by following the methodology as described above. Mean recoveries of halosulfuron-methyl in soil was found to be ranged from 88.7 to 94.5% and in water ranged from 84.1 to 93.0% (Table 2).

The average recovery values from all the fortified samples were in excess of 85%. Therefore the results have been presented as such without applying any correction factor. The limit of detection (LOD) and limit of quantification was found to be 0.001 and 0.005 µg/g. The overall result of leaching potential of halosulfuron–methyl under continuous flow condition is presented in Table 3. Percent retention of halosulfuron-methyl drawn with soil depth (Figure 1 & 2) revealed that halosulfuron-methyl residues were detected up to 40 cm depth under continuous and discontinuous flow conditions. Maximum residues (32.3 µg in single dose and 30.8 in double dose application) were retained at depth of 25-30 cm. Amount of residues retained in leachate were comparable in both doses. Recovered amount of halosulfuron-methyl residues at various soil depths were analysed statistically. Significant differences in the recovered amount of halosulfuron-methyl at various depths were observed at both application rates. Irrespective of soil depth, residue levels were significantly lower following single dose applications compared to double dose application. Under discontinuous flow conditions, concentration of residues retained in 35-40 cm soil depth were 2.2 and 1.3 µg while it was 0.2 and 0.6 µg for leachate at single and double dose, respectively (Table 4). The rate of leaching was found to be invariably higher and faster under continuous and discontinuous flow conditions. Comparable amount of halosulfuron-methyl residues from leachate fraction at both doses i.e. 1.7 and 1.6 µg under continuous flow condition and 0.2 and 0.6 µg under discontinuous flow condition shown that the movement of halosulfuron-methyl was unaffected by dose application. Greater mobility of halosulfuron-methyl can be explained on the basis that coarse textured sandy loam soil resulted in weaker binding of halosulfuron-methyl residues and hence higher leaching potential. Sulfonylureas are all weakly acidic with dissociation constants (pKa) ranging from 3.3 to 5.2. Consequently, these herbicides should be predominantly neutral at pH values below the herbicides pKa and anionic when the pH is above the pKa (Senseman, 2007). Experimental soil taken for leaching experiment in the present study have pH value 7.6 which is greater than pKa value of halosulfuron-methyl, hence molecules predominately exist in anionic form. Negatively charged species react very weakly with soil matrices and organic matter and thus move freely through soil. Rajasekharam and Ramesh (2013) [10] concluded that adsorption of halosulfuron-methyl negatively correlate with soil pH and positively correlate with organic matter and clay content. The results in the present finding corroborate with the findings of Hall *et al*. (1999) [6] who concluded that sulfonylurea herbicides are more susceptible for leaching in calcareous soils. Present results are also in agreement with the findings of Sondhia (2009) [14] who studied the leaching behaviour of metsulfuron applied at 4 and 8 g a.i./ha in sandy loam and clay loam under laboratory conditions and result indicated high mobility of metsulfuron (up to 82 cm in columns) in sandy loam as compared to clay loam soil. Tandon *et al*. (2016) [16] also reported high mobility of metsulfuron-methyl under saturated moisture conditions. Srivastava *et al*. (2006) [15] also found faster leaching of sulfosulfuron in sandy loam soil.

Table 2: Percent recoveries of halosulfuron-methyl using modified QuEChERS in soil and water

Fortification level (µg/g)	Soil	Water
	[a]Recovery % ±SD	Recovery % ±SD
0.005	88.7 ± 2.3	84.1 ± 3.3
0.01	88.0 ± 1.2	90.3 ± 4.2
0.1	94.5 ± 3.0	93.0 ± 1.5

[a] Average of three replicates

Table 3: Leaching behaviour of halosulfuron-methyl in sandy loam soil under continuous flow conditions

Soil depth (cm)	Residues* (µg)				
	Single dose (50 µg) ± SD	Percent Retention	Double dose (100 µg) ± SD	Percent Retention	Mean
0-5	0.08 ± 0.02	0.2	1.1 ± 0.56	1.4	0.6
5-10	0.6 ± 0.36	1.7	2.7 ± 1.33	3.4	1.7
10-15	2.2 ± 1.45	6.2	8.5 ± 3.78	10.9	5.3
15-20	3.6 ± 2.40	10.2	12.2 ± 4.75	15.6	7.9
20-25	10.5 ± 2.66	29.8	17.8 ± 2.74	22.8	14.2
25-30	11.4 ± 3.41	32.3	24.1 ± 5.78	30.8	17.7
30-35	5.8 ± 2.17	16.5	8.3 ± 2.33	10.6	7.1
35-40	0.4 ± 0.21	1.1	2.2 ± 1.50	2.8	1.3
Leachate	0.6 ± 0.3	1.7	1.3 ± 0.6	1.6	
Mean	4.3		9.6		

CD at 5% level of significance
Dose = 1.595
Soil depth = 3.190
Dose × Soil depth = 4.511

Table 4: Leaching behaviour of halosulfuron-methyl in sandy loam soil under discontinuous flow conditions

Soil depth (cm)	Residues* (µg)				
	Single dose (50 µg) ± SD	% Retention	Double dose (100 µg) ± SD	% Retention	Mean
0-5	0.6 ± 0.45	1.9	0.9 ± 0.30	1.3	0.8
5-10	2.0 ± 1.27	6.3	3.4 ± 0.67	4.9	2.7
10-15	4.4 ± 1.36	13.9	15.2 ± 3.74	21.9	9.8
15-20	7.3 ± 2.87	23.1	19.0 ± 2.29	27.3	13.1
20-25	8.5 ± 2.05	26.9	18.8 ± 2.36	27.1	13.7
25-30	5.8 ± 1.10	18.3	7.5 ± 1.60	10.8	6.6
30-35	2.1 ± 0.61	6.6	3.2 ± 0.70	4.6	2.6
35-40	0.7 ± 0.27	2.2	0.9 ± 0.35	1.3	0.8
Leachate	0.2 ± 0.4	0.6	0.6 ± 0.8	0.9	
Mean	3.9		8.6		

*Average of three replicates
CD at 5% level of significance
Dose = 0.977
Soil depth = 1.955
Dose × Soil depth = 2.765

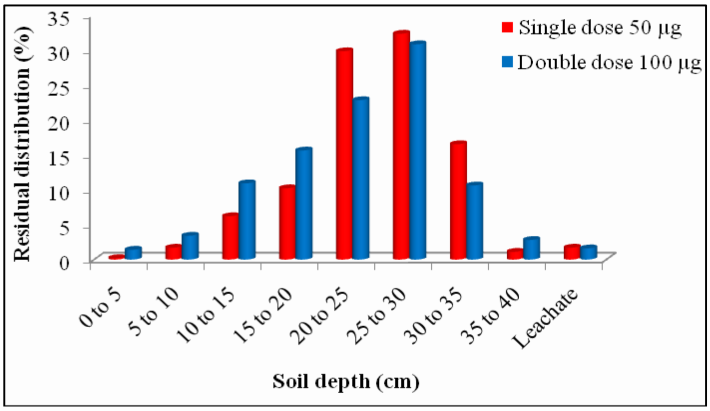

Fig 1: Percent retention of halosulfuron-methyl under continuous flow conditions

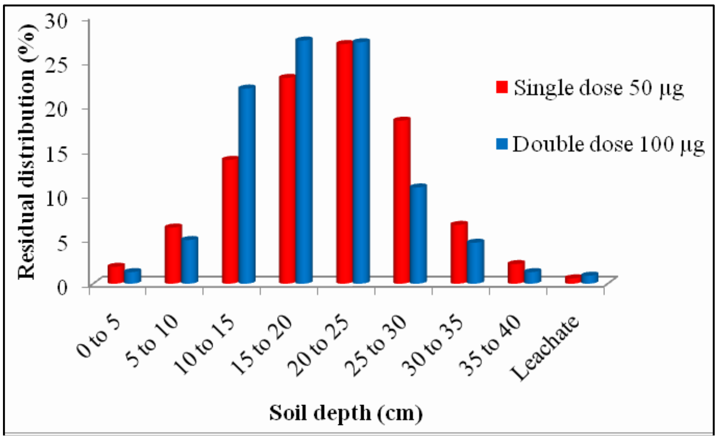

Fig 2: Percent retention of halosulfuron-methyl under discontinuous flow conditions

Conflicts of Interest: "The authors declares that there is no conflict of interest regarding the publication of this paper."

Conclusion

Result indicated that, halosulfuron–methyl has a potential to leach down that is significant in term of groundwater contamination. Halosulfuron-methyl was detected to all depths and accumulated highest in the middle of the column. Rate of leaching was found to be unaffected by dose application. Slightly more leaching was observed under continuous flow condition than under discontinuous flow conditions

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