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Mobility of Sulfosulfuron and Its Metabolite Aminopyrimidine in Soil under Laboratory Conditions.

Chandran Loganayagi, and Atmakuru Ramesh*.

Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai, Chennai 601301 Tamil Nadu, India.

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*For Correspondence

Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai, Chennai 601301 Tamil Nadu, India.

Telephone: +91 44

27174246/66;

Fax: +91 44 27174455

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ABSTRACT

Leaching potential of sulfosulfuron and one of its metabolite aminopyrimidine in two different soils were studied under laboratory condition. The soils used were sandy clay with lower organic carbon content (1.25%) and clay loam having higher organic carbon content (5.5%). Sulfosulfuron and aminopyrimidine were sprayed on the surface of the soil column. The applied dosages are sulfosulfuron @ 25 g.a.i/ha, 50 g/ha, 100 g.a.i/ha and aminopyrimidine @ 5 g.a.i/ha, 10 g.a.i/ha, 20 g.a.i/ha. Collected the leachates from the columns every day after applying 60 mm of rainfall for a period of fifteen days. There after soil columns were cut in to cross sectional and analyzed for the residues of sulfosulfuron and aminopyrimidine at five cm difference in depth. A high performance liquid chromatography with Fluorescence detector was used for the quantification of residues. Limit of quantification for sulfosulfuron and aminopyrimidine was established as 0.001µg/ml. The recovery study conducted for Sulfosulfuron and aminopyrimidine at two different concentrations (LOQ and 10 × LOQ) showed mean recovery of 94.6%, 96.9% in water, 92.3%, 94.1% in Sandy clay soil and 89.2%, 90.0% in clay loam soil. Analysis of leachates collected from sandy clay soil columns showed the residues of sulfosulfuron 0.01 - 2.8 µg/ml and aminopyrimidine 0.005 to 0.76 µg/ml. Leachates collected from clay loam soil columns showed the residues of sulfosulfuron 0.001 to 0.10 µg/ml and aminopyrimidine 0.001 to 0.032 µg/ml. Sandy clay soil samples showed the residues of sulfosulfuron 0.01 to 0.09 µg/g and aminopyrimidine 0.001-0.012 µg/g and clay loam soil samples showed the residues of sulfosulfuron 0.002-0.50 µg/g and aminopyrimidine 0.006 to 0.04 µg/g. Leachates of soil columns applied with sulfosulfuron showed the residues of metabolites such as aminopyrimidine, desmethyl sulfosulfuron, substituted guanidine, rearranged amine and sulfonamide. Metabolites were confirmed by Electrospray tandem mass spectrometry (LC-MS/MS-ESI) analysis.

INTRODUCTION

Sulfosulfuron {1-(4,6-Dimethoxy-pyrimidin-2-yl)-3-(2-Ethylsulfonylimidazo[1,2-a]pyridin-3-yl)sulfonylurea} a sulfonylurea herbicide is generally used in controlling broad leaf weeds and other grassy weeds. The movement of herbicides through soil is an important process that determines their fate in both soil and aquatic environment. Protecting groundwater from pesticide contamination is a high priority. Leaching of herbicides occurs when water moves down through soil [13]. The risk of contamination varies from soil to soil and is mainly depends on the soil's organic carbon content and structure [6]. It is generally accepted that adsorption of pesticides by soils is more closely related to the soil organic matter content than any other single property. The displacement of pesticides from soil to water strongly depends on the extent to which they are retained in soils, which in turn depends on the adsorption and desorption properties of the soil [9]. The use of soil column is an easy method to understand the movement of herbicide by following the amount of herbicide released in the leachate volume [5]. Leaching study conducted for atrazine with two different soils showed the lower leaching in orchard soil than conventionally tilled

soil due to a greater organic matter^[16]. Several investigators proved that nature of herbicidal activity related to the organic carbon content of soils. Soil type plays an important role in leaching of chemicals through the soils^[1]. The movement of herbicides through soil depends on several factors such as general characters of soil, interaction between soil and herbicide, climatic conditions which mainly influence the leaching in soil^[3]. Leaching is primarily dependent on the existence and the extent of preferential flow which has been found to occur in both sandy and clayey soils^[19]. Near Infra red spectra can be used as a rapid and simple method to study the pesticide sorption and leaching from soils^[2].

In general herbicides are more likely to leach down when they are both weakly adsorbed and persistent in the soil. The extent of adsorption increases as percentage of organic matter and clay composition increases. Acidic pesticides, such as the sulfonylurea, are adsorbed in moderate amounts on organic matter and in relatively low amounts on clay minerals^[4]. Sulfosulfuron adsorption increases with decreasing soil pH^[18]. Adsorption reduces the amount of chemical available to plants and slows leaching. Sulfonylurea herbicides are degraded more slowly in alkaline, cold, dry and low-organic matter soils^[8]. Mobility of sulfonylureas increases with increasing pH and decreasing soil organic matter^[10]. Sulfonylurea herbicides are degraded more slowly in alkaline, cold, dry and low-organic matter soils^[12]. The greater the adsorption of a herbicide to a particular soil, the less the losses from leaching and volatilization. The mobility of the sulfonylurea herbicides decreases as organic matter content increases^[17]. Organic amendment may be an effective management practice for controlling pesticide leaching^[20]. Wondimagegnehu Mersie and Chester L. Foy Conducted Laboratory and greenhouse studies to determine adsorption and movement of chlorsulfuron in four soils^[11]. A study on the photo degradation of sulfonylurea in water can contribute to an understanding of their environmental fate, their behaviour both in soil solution and in surface water owing to their high leaching potential^[7]. The Purpose of this study is to investigate the leaching potential of sulfosulfuron a sulfonylurea herbicide and its metabolite aminopyrimidine in soil column using soil samples of varied organic carbon content under laboratory condition.

MATERIALS AND METHODS

Materials

Sandy clay and clay loam soil samples

Sulfosulfuron 75% WG a commercial formulation purchased from local market and Aminopyrimidine from Aldrich chemicals.

Soil Column Preparation

Soil samples collected from the field was dried and sieved through 2 mm sieve. Physicochemical properties such as pH, Electrical conductivity, organic carbon content, water holding capacity and soil texture were determined. Leaching study for sulfosulfuron and aminopyrimidine in two different soils under laboratory condition was studied using the soil column of 35cm length x 6.9cm id. The column was sealed at the bottom and created ≈ 0.3 cm i.d., hole at the bottom, for the collection of leachates. Added pebbles at the bottom of the column (2 cm level) and packed the soil to 30 cm height. The column was then saturated with 0.01 M CaCl₂ solution and kept undisturbed overnight to drain.

Herbicide Application

Two different experiments were conducted by applying sulfosulfuron @ 25 g.a.i/ha, 50 g.a.i/ha, 100 g.a.i/ha and aminopyrimidine @5 g.a.i/ha, 10 g.a.i/ha, 20 g.a.i/ha on the surface of the soil column of clay loam and sandy clay soil. After the application of the herbicide the columns were covered with 1.0 cm sand previously washed with acid followed by water and solvent to prevent the disturbance on the surface of the column at the time of leaching. The column was closed with aluminum foil to avoid evaporation and volatile losses.

Leachate Collection

Every day 60 mm rain was applied using micro spray applicator on the surface of the column. Leachate was collected through a funnel below the column. The residues were quantified using HPLC with Fluorescence detector. The concentration of sulfosulfuron and its breakdown product aminopyrimidine were measured for 15 days. After completion of the study period the soil columns were equally sectioned as 0-5 cm, 6-10 cm, 11-15 cm, 16-20 cm, 21-25 cm, 25-30 cm, 30-33 cm and analyzed

Extraction of Water Sample

Filtered the column leachates and acidified using 5% phosphoric acid. The acidified leachate was then partitioned with dichloromethane and then reconstituted in acetonitrile for column cleanup using the florisil in between the two layer of anhydrous sodium sulphate. The collected eluate was constituted to smaller volume in

acetonitrile and quantified the residues of sulfosulfuron and its metabolites by an HPLC-RF method. The metabolites identified were confirmed by Electrospray tandem mass spectrometry (LC-MS/MS – ESI) analysis [14].

Extraction of Soil Sample

The soil sample collected from the column was extracted using acetonitrile/ water (50:50) the volume was reduced to 10 ml in a rotary evaporator at 40°C. Then acidified with 2% phosphoric acid, partitioned with methylene chloride and concentrated to near dryness. The residue was re-dissolved in 2 ml of methylene chloride and diluted with 8 ml of isooctane. The entire sample was then transferred into the column and the residues were eluted with 40 ml of 2% methanol in methylene chloride. Evaporated the solvent under vacuum and reconstituted the residues using acetonitrile for HPLC analysis [15].

Instrumentation

A high performance liquid chromatograph equipped with a fluorescence detector, at the excitation wavelength 260 nm and emission wavelength 405 nm was used for the quantification of residues of sulfosulfuron and aminopyrimidine. The column used for separation was Lichrospher RP C18, 4.6 mm i.d. x 250 mm length and the mobile phase 550 ml of acetonitrile and 450 ml of water having pH 3.0 (adjusted with 5 % phosphoric acid solution) used for separation at a flow rate of 1 ml/min.

Electrospray Tandem Mass Spectrometry

A high capacity ion trap (HCT plus) LC-MS/MS (n) system manufactured by Bruker Daltonik GmbH was used in the study. Drying gas as well as nebulising gas was nitrogen generated from pressurized air in a Nitrox UHPLCMS nitrogen generator. The nebuliser gas flow was set to approximately 80 l/h and the desolvation gas flow to 800–900 l/h. For operation in MS/MS mode, collision gas was argon with a pressure of 4×10^{-4} mbar. A capillary voltage of -3 and 3.5 kV was used in negative and positive ionization mode, respectively. The interface temperature was set to 350°C and the source temperature to 120°C. Dwell times of 0.1 s/scan was selected and the scan range 50–600 m/z. Agilent 1200 HPLC with Xterra MS C18 (2.5 μ m, 2.1 cm i.d. x 50 mm length) column, gradient elution of flow rate 0.20 ml/min at the temperature 20°C with the solvents H₂O in B and ACN in A was used. The injection volume was 10 μ l.

Limit of Detection and Limit of Quantification

Method validation was performed with different known concentrations of sulfosulfuron and aminopyrimidine in acetonitrile by diluting the stock solution of reference analytical standards. Recovery study was conducted for water and soil before the initiation of leaching experiment. The recovery study conducted by spiking two different known concentrations of Sulfosulfuron and aminopyrimidine at 0.001 to 0.01 μ g/ml showed mean recovery of 94.6%, 96.9% in water, 92.3%, 94.1% in Sandy clay soil and 89.2%, 90.0% in clay loam soil. From the analytical determinations the limit of detection based on signal-to-noise ratio is 3:1 was established as 0.001 μ g/ml and limit of quantification 0.001 μ g/ml was established based on recovery and S/N ratio 10:1.

RESULTS AND DISCUSSION

Leaching behavior of sulfosulfuron and aminopyrimidine in different soils having different physicochemical properties are presented in the Table 1. The physicochemical properties of the two soils clearly showed the lower carbon content (1.25%) in sandy clay soil sample and higher organic carbon content in clay loam soil (5.5%). The clay loam soil column leachates analysed for 11 days at the tested dosages 25, 50 and 100 g.a./ha showed the residues of sulfosulfuron 0.001 to 0.1 μ g/ml, and aminopyrimidine 0.001-0.032 μ g/ml. Further analysis of leachates collected on 12th day onwards showed the residues below detectable level at the lower dosage. In sandy clay soil leachates analyzed for 13 days showed the residues of sulfosulfuron 0.01 to 2.83 μ g/ml and aminopyrimidine 0.005-0.76 μ g/ml. Leachates collected on 14th and 15th day showed the residues below the detectable level at the lower dosage. Summarized results are presented in Table 2 and Table 3.

Samples of higher dosages were further analyzed and found traces of different metabolites. Out of five metabolites identified, aminopyrimidine was found to be in higher concentration. The metabolites identified are aminopyrimidine (MW-155) Desmethylsulfosulfuron (MW-455), Substituted Guanidine (MW-374), Rearranged amine (MW-363), and sulfonamide (MW-289). Details were presented in Figure 1 and Figure 2. Analysis of soil samples from the clay loam soil column showed the presence of residues of sulfosulfuron in the range 0.002 to 0.5 μ g/g and aminopyrimidine 0.007 to 0.04 μ g/g, sandy clay soil columns showed the residues of sulfosulfuron in the range 0.01 to 0.09 μ g/g and aminopyrimidine 0.001 to 0.012 μ g/g.

Higher concentration of sulfosulfuron and aminopyrimidine remained in the soil columns and lower amount in the leachates of clay loam soil can be attributed due to their higher organic carbon content. In the case of sandy

clay soil, higher concentration of sulfosulfuron and aminopyrimidine were found in the leachate than in soil. Summarized graphical results (Figure 3 to Figure 6) clearly reveals that 75% of the herbicide was found in soil after 15 days study in clay loam soil whereas higher percentage of residues were found in leachate in sandy clay soil.

Figure 1: Extracted ion chromatogram of soil extract

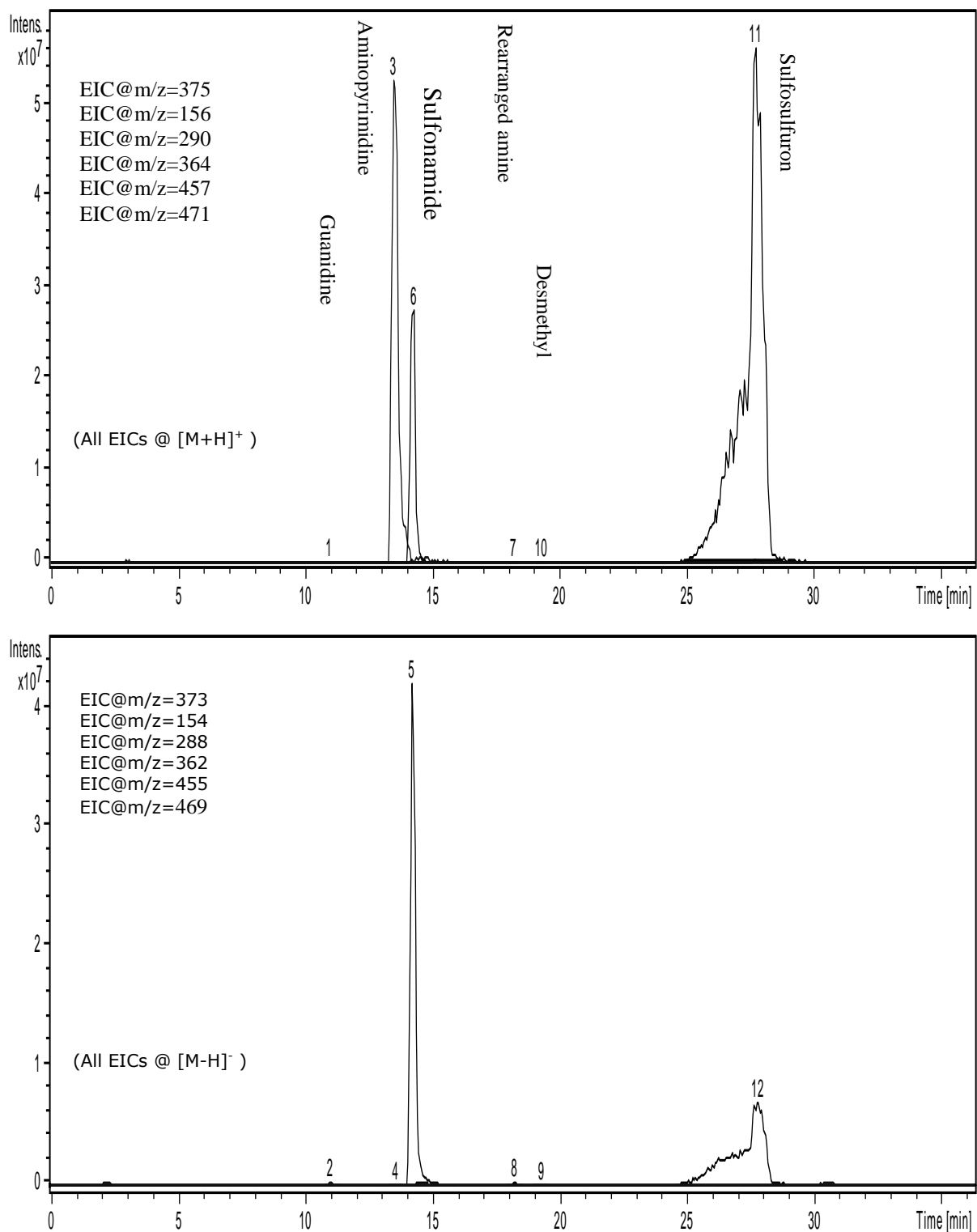


Figure 2: Confirmation of residues by Electrospray Tandem mass spectrometry

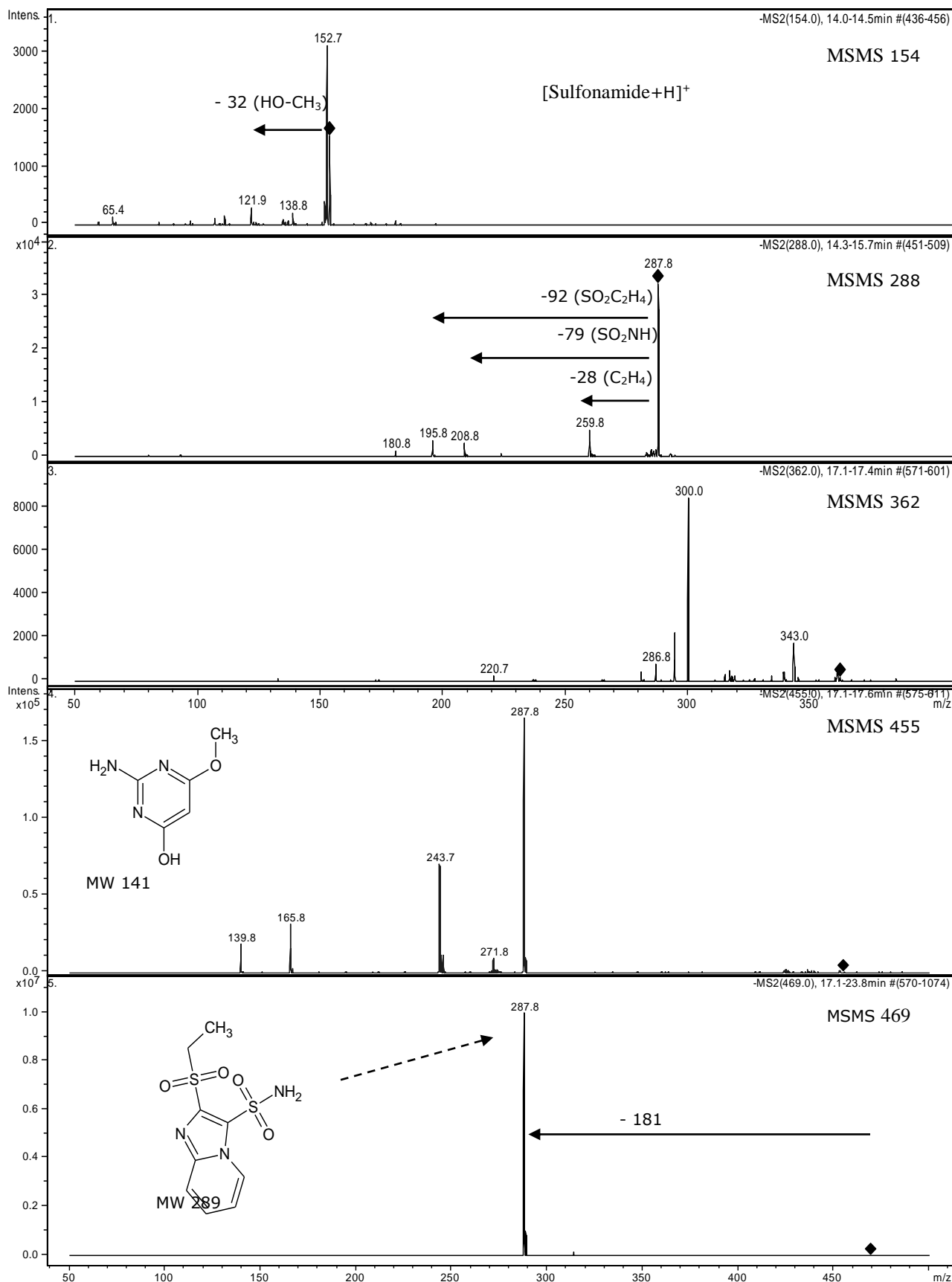


Figure 3: Sulfosulfuron residues in clay loam soil at different depth

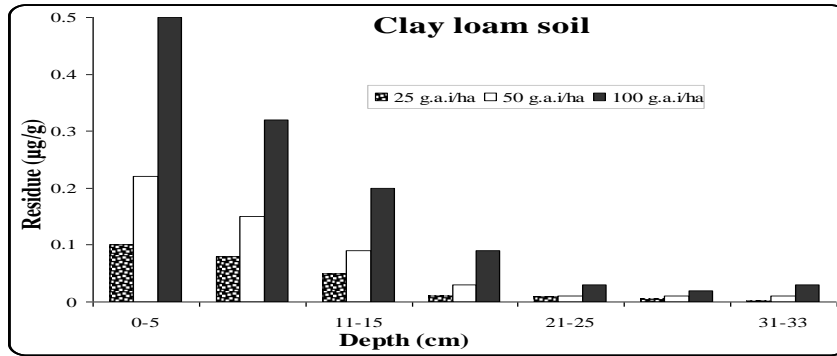


Figure 4: Sulfosulfuron residues in Sandy clay soil at different depth

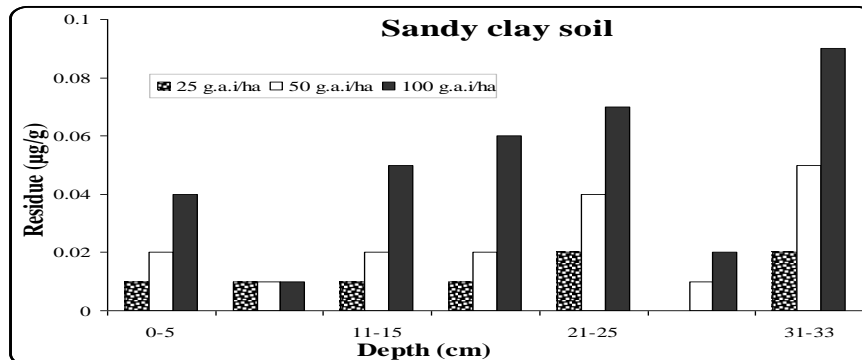


Figure 5: Aminopyrimidine residues in clay loam soil at different depth

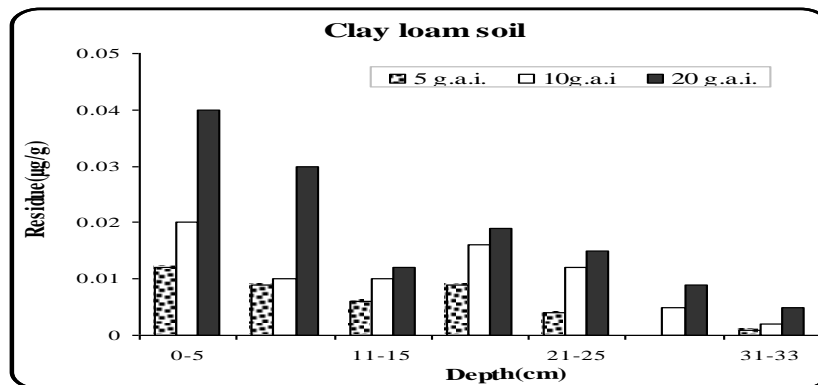


Figure 6: Aminopyrimidine residues in sandy clay soil at different depth

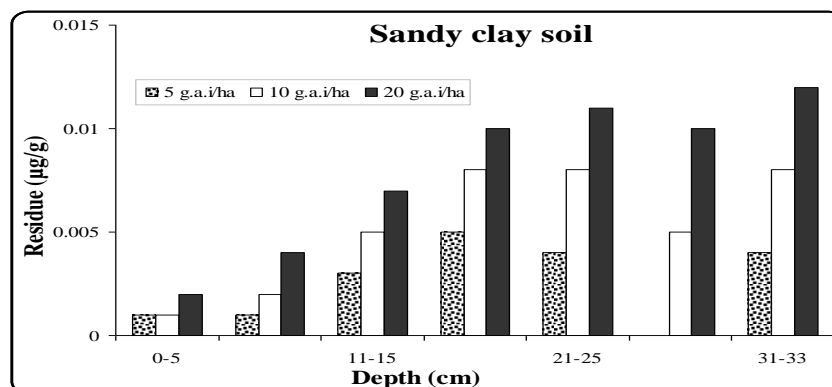


Table 1: Soil physico-chemical properties

Soil texture	Clay loam	Sandy clay
Clay (%)	30.8	32
Silt (%)	45.6	26
Sand (%)	23.6	42
pH	6.2	7.08
Organic carbon content (%)	5.5	1.25
CEC(meq/100g)	34.57	35.05
Sol. Salts (milli mhos/cm)	0.24	0.26
Water holding capacity (ml/100g)	28	29
Nitrogen (mg/kg)	2772	2659
Phosphorous (mg/kg)	40	32
Potassium (mg/kg)	120	150
Magnesium (mg/kg)	709	698
Calcium (mg/kg)	3428	3450
Sodium (mg/kg)	14	12
Bulk Density (g/cc)	1.11	1.10

Table 2: Concentration of sulfosulfuron in leachate in µg/ml

Occasion in days	clay loam			sandy clay		
	25 g.a.i/ha	50 g.a.i/ha	100 g.a.i/ha	25 g.a.i/ha	50 g.a.i/ha	100 g.a.i/ha
1	0.01	0.02	0.05	0.11	0.19	0.37
2	0.05	0.08	0.10	0.71	1.36	2.83
3	0.02	0.02	0.08	0.32	0.61	1.31
4	0.05	0.01	0.05	0.09	0.19	0.34
5	0.02	0.01	0.04	0.08	0.16	0.33
6	0.03	0.02	0.03	0.07	0.13	0.28
7	0.02	0.01	0.02	0.06	0.10	0.21
8	0.01	0.004	0.02	0.05	0.09	0.2
9	0.004	0.003	0.01	0.04	0.10	0.16
10	0.001	0.005	0.01	0.03	0.08	0.12
11	0.001	0.002	0.008	0.01	0.06	0.09
12	BDL	BDL	0.005	0.01	0.03	0.08
13	BDL	BDL	0.002	0.01	0.02	0.03
14	BDL	BDL	0.001	BDL	0.01	0.03
15	BDL	BDL	0.001	BDL	0.01	0.02

Table 3: Concentration of aminopyrimidine in leachate in µg/ml

Occasion in days	clay loam			sandy clay		
	5 g.a.i/ha	10 g.a.i/ha	20 g.a.i/ha	5 g.a.i/ha	10 g.a.i/ha	20 g.a.i/ha
1	0.002	0.004	0.009	0.01	0.15	0.26
2	0.005	0.014	0.032	0.20	0.39	0.76
3	0.001	0.002	0.005	0.12	0.30	0.55
4	0.004	0.008	0.012	0.09	0.32	0.59
5	0.005	0.009	0.016	0.08	0.19	0.60
6	0.006	0.013	0.022	0.05	0.14	0.26
7	0.003	0.006	0.012	0.02	0.12	0.30
8	0.003	0.007	0.017	0.01	0.10	0.40
9	0.009	0.017	0.03	0.03	0.05	0.22
10	0.003	0.008	0.013	0.02	0.02	0.30
11	0.003	0.007	0.012	0.01	0.01	0.20
12	0.004	0.002	0.009	0.01	0.009	0.09
13	0.001	0.003	0.006	0.005	0.01	0.05
14	BDL	0.002	0.005	BDL	0.009	0.03
15	BDL	0.001	0.002	BDL	0.007	0.01

CONCLUSION

The leaching study conducted in soils of varied organic carbon content with three dosages viz., 25 g.a.i/ha, 50 g.a.i/ha, and 100 g.a.i/ha. for sulfosulfuron and 5 g.a.i/ha, 10 g.a.i/ha, and 20 g.a.i/ha for aminopyrimidine showed that higher concentration were found in leachates after 90 cm rain fall reveals the mobility is greater in the

soil of lower organic carbon content but higher percentage of residues were retained in the soil of higher organic carbon content. Higher mobility of sulfosulfuron and aminopyrimidine might be due to its lower adsorption capacity and higher solubility. Even after continuous leaching procedure, small amount of sulfosulfuron and aminopyrimidine were retained in soils. This low amount retained by soil clearly reveals the high stability of the herbicide in soil.

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