



Leaching behaviour of metsulfuron–methyl

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A major concern about weed management in the agricultural scenario is persistence, mobility, and bioavailability of pesticide residues in the environment (Sachan *et al.* 2007). Long persistence and high mobility of a herbicides increase the risk of contamination of surface water and ground water. Metsulfuron-methyl [2-(4-methoxy-6-methyl-1, 3,5-triazin-2-yl-carbamoylsulfamoyl) methyl benzoate] is selective pre-emergence and post-emergence sulfonylurea herbicide, used primarily to control various broad-leaf and grassy weeds. It was already established that sulfonylurea group of herbicides are very effective against various broad-leaf weeds and grasses. Metsulfuron-methyl is a systemic compound with foliar and soil activity and it works rapidly after it is taken up by the plants. It is very effective on weeds that include bulbs or tubers and is extensively used in agriculture in India. Work on metsulfuron fate and leaching has been done by some workers (Pons and Barriuso 1997 and James *et al.* 2004). Despite its extensive use, very little is known about its percolation potential in Indian soil (Sondhia 2009, Singh *et al.* 2014). Thus, our objective was to evaluate the downward movement/leaching potential of metsulfuron-methyl with representative clay loam soil of Pantnagar, Uttarakhand, India.

Soil samples of different depth, *i.e.* 0-15, 15-30, 30-45, and 45-60 cm from N.E Borlaug Crop Research Center, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand, India were collected, air dried and passed through a 2 mm sieve. Soil was clay loam (clay 32.0%, silt 44.0% and sand 24.0%) with 1.30% organic carbon, 7.34 pH and 0.174ms EC. Technical and commercial grade of metsulfuron-methyl (Convo 20 WP) obtained from M/s Atul Ltd, Valsad, India was used in leaching experiments.

Leaching experiment was conducted in 2009 at room temperature and arranged in completely randomized design with three replicates. The leaching

studies were performed in columns made from vertically polyvinyl chloride columns (10 cm internal diameter and 60 cm long). The columns were cut longitudinally into two halves and rejoined by using packing tape. The average volume of the column was recorded. One end of PVC column was covered with muslin cloth and a funnel was attached to the bottom of each column for collection of leachates into 1000 ml flasks. Individual columns were packed with 6.5 kg clay loam soil (1.75 kg for 45-60 cm, 1.70 kg for 30-45 cm, 1.55 kg for 15-30 cm and 1.50 kg for 0-15 cm depth respectively). Columns were filled with soil according to the different depth taken. Columns were saturated overnight by flowing water from above and also keeping them dipped in water contained in a bucket. Excess water was drained out by 1 day drainage cycle and columns were covered with aluminum foil to prevent evaporation. For monitoring vertical movement and leaching loss of metsulfuron-methyl, 10 ml of the herbicide was applied to surface of column with pipette at recommended dose *i.e.* 4 g/ha.

The addition of water was done for seven days at the rate of 200 ml for 12 h per day (equivalent to 1730 mm annual rainfall) so that infiltration rate of soil does not exceed. A set of soil columns receiving same amount of water only served as control. Water eluting from the column was collected daily in flask and processed for analysis of herbicide. After seven days, when addition of water was completed, the soil columns were allowed to dry for 24 hours. Columns were cut into two halves and the soil was cut into 5 cm segment each and processed for residue analysis. Detection and quantification of metsulfuron-methyl was done by HPLC.

A 20 gm representative air dried soil sample was extracted with 50 ml of dichloromethane: methanol (1:3 v/v) shaken over an orbital shaker for one hour and filtered. The procedure was repeated twice with 25 ml of solvent mixture. All filtrates were pooled and concentrated to 1 ml under vacuum at 45±1 °C. The extract was loaded on a pre-washed solid phase C-18

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solid phase extraction (SPE) cartridge and eluted by using methanol. Elute obtained was dried under vacuum and the residue was filtered through 0.22µ millipore PTFE filter and dissolved into HPLC grade acetonitrile for further analysis.

Water sample (50 ml) of leachate was liquid – liquid partitioned with methylene chloride (100 ml and twice with 50 ml), the organic layer was pooled and was dried over anhydrous sodium sulphate and volume was reduced to dryness in a rotary vacuum evaporator (40±1°C). The residue was filtered through 0.22µ Millipore PTFE filter and dissolved in 5 ml mobile phase.

The Beckman model 322 Gradient HPLC systems equipped with 100 A pump 420 gradient microprocessor controller, 7725i rheodyne injector, 160 selectable wavelength UV detector, 5 µl loop and HP 3395 series integrator recorder. The operating parameters were Column: Supelco's ODS-II column 5µm (250 x 4.6 mm i.d.), mobile phase: Acetonitrile: Methanol: Water: (6:3:1v/v), mode: isocratic, flow rate: 1ml/min, chart speed: 1 cm/min, aufs: 0.02 and UV detection at 229 nm.

The per cent recovery values of metsulfuron-methyl in water and soil is given (Table 1). The amount of residues of metsulfuron-methyl in different fractions of leachates which were collected from 1 to 7 days are presented (Table 2). The data showed that, no residue of metsulfuron-methyl was detected in the first fraction of leachate of 1st and 2nd

Table 1. Per cent recovery of metsulfuron-methyl from water and soil

Metsulfuron-methyl (ppm)	Water	Soil
0.5	89.05± 0.01	87.30± 0.02
1.0	92.51± 0.01	89.42± 0.02
2.0	94.44± 0.03	90.39± 0.01

Table 2. Concentration of metsulfuron-methyl in the leachates

Day	Metsulfuron-methyl (µg/ml)
1	ND
2	ND
3	0.17± 0.03
4	0.36 ± 0.05
5	0.54 ± 0.07
6	0.47 ± 0.07
7	0.32± 0.08

Values are mean of three replicates

day. Residue starts appearing in 3rd to 7th day leachate fraction. The concentration of the herbicide in the leachate, increased from 3rd to 5th day. It was highest

on 5th day, but decreased thereafter. The content of metsulfuron-methyl in 5th day fraction of leachate was 0.54 µg/ml.

The per cent recovery values of applied metsulfuron-methyl in leachate and soil columns were out of 13 µg a.i metsulfuron-methyl added to soil column, 8.86 µg (68.75 %) was recovered from the soil, 2.06 µg (15.84%) from water and 2.08 µg (16.00 %) was lost during processing of the soil/water samples.

The distribution of herbicide residue in soil cores at different depths after passing 1.40 liters of water has been presented (Table 3). Surface applied metsulfuron-methyl got distributed throughout the

Table 3. Concentration of metsulfuron-methyl in different sections of soil columns.

Soil depth (cm)	Metsulfuron-methyl (mg/kg)
0-5	0.58 ± 0.01
5-10	0.67 ± 0.07
10-15	0.75± 0.10
15-20	0.79 ± 0.07
20-25	0.89± 0.08
25-30	0.92 ± 0.07
30-35	1.08 ± 0.02
35-40	1.00± 0.02
40-45	0.84 ± 0.08
45-50	0.74 ± 0.01
50-55	0.66 ± 0.08
55-60	0.38 ± 0.04

Values are mean of three replicates

whole length of column but the distributed concentration varied at different soil depths. The residue concentration was more at the middle of column mainly at the depth of 30 to 35 cm, then it started to decrease from 40 to 60 cm indicating high mobility of metsulfuron-methyl in soil column.

As metsulfuron-methyl has low affinity to organic carbon and therefore more susceptible to leaching, this might have added further on movement of metsulfuron-methyl under saturated moisture conditions. In this study, soil columns received continuous 200 ml water per day (equivalent to 1730 mm annual rainfall) that may be the reason that metsulfuron-methyl could be detected at all depths and accumulated highest in the middle of the column and detected in the leachates.

The reason for this pattern is also related to soil pH and organic carbon content. Metsulfuron-methyl is adsorbed poorly in acidic soils (pH 5.6-6.5) and soil column experiments with freshly treated acid soils (pH 5.6-6.7) showed that 85 to 100% of the applied radio labeled compound leached through the columns

(Anonymous 1987). In soils with a higher pH, the mobility of metsulfuron-methyl is expected to increase because of increased solubility, increased ionization of the chemical and decreased adsorption and organic matter which lowers the pesticide degradation by adsorption processes (Pal *et al.* 2005). Walker *et al.* (1989) reported adsorption of metsulfuron-methyl herbicide and found negative correlation of the herbicide with soil pH, while positive correlation with soil organic matter content and microbial biomass.

Metsulfuron-methyl degradation mainly resulted in the formation of the amino-triazine. In the acidic soil, degradation was characterised by rapid hydrolysis giving two specific unidentified metabolites. Low recovery of metsulfuron-methyl could be due to the result of chemical hydrolysis, mineralization of metsulfuron-methyl, formation of different metabolites as well as formation of bound residues (Pons and Barriuso 1997). Results of the controlled laboratory studies cannot be reliably extrapolated to field conditions and field studies will be a more realistic approach.

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SUMMARY

Leaching potential of metsulfuron-methyl herbicide was evaluated under laboratory conditions in Mollisol soil of Pantnagar, Uttarakhand with simulated rainfall. Metsulfuron-methyl was applied at recommended dose (4 g/ha) on 60 cm long soil

columns. After seven days of experiment, maximum concentration was observed in 30-35 cm column depth and some amount of herbicide leached out and was detected in leachates. Study indicated high mobility of metsulfuron-methyl under saturated moisture conditions which may pose significant ground water contamination.

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