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Column leachability test for understanding the persistence of four commonly used pesticides for cotton crop in Vidarbha, Maharshtra, India

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ABSTRACT
Leaching, which can be defined as the movement of any liquid vertically into the deeper soil layers. It is an important phenomenon as it is one of the important influencing factors for groundwater contamination. The objective of present study is to evaluate the potential leaching and persistence of four pesticides viz. confidor, profex super, ulala and missile for agricultural soils in Vidharbha region of Maharashtra. Soil samples collected from the field location were tested on LCMS for pesticide residues. Leaching study was carried out using disturbed soil columns of 30 cm length and 10 cm diameter. Persistence studies were carried out for 60 days duration under laboratory conditions. Leach ate was collected from 4 soil columns artificially contaminated with fixed intensity of pesticides and are tested for nitrogen and chloride content to understand persistence of pesticides in soil.

Keywords: *chemical pesticides, leaching, soil columns, pesticide residues, persistence*

I. INTRODUCTION
Evaluation of the leaching potential of every type of soil in respective regions has taken up more importance in the last decade with the increase in the use of agrochemicals mainly chemical pesticides and fertilizers. These factors can affect the quality of ground and surface water through percolation and surface runoff as they are meant to get easily dissolved in water and thus can affect the natural life cycle in the vicinity.

Pests species getting resistant to the pesticide composition and need of increased cultivation outputs has resulted in the competition amongst pesticide manufacturers for creating more effective pesticides. As a result the concentrations of these pesticides have gone so far that they are affecting the environment and are creating saviour health concerns for human beings.

Several leaching methods have been developed and implemented into environmental regulations in many countries. These include batch tests, column tests, lysimeter tests, and sequential leaching tests. These methods aim to determine the concentrations of chemicals expected in water that has come in contact with contaminated soil or other solid materials for a certain period of time.

Column tests resemble field conditions more closely and are suitable to assess the long-term release of chemical constituents from soil into water bodies. The column test's advantage over a batch test is that it allows for the observation of high initial concentrations of percolates at low L/S ratios (equilibrium concentrations) and the time-dependent release of chemicals, which is required for the prediction of leaching behavior under field conditions.

A. Pesticides, their persistence in soil and effects
Pesticide is any component of organic or inorganic origin that is used in order to curb the growth of any limiting factor affecting the growth of a particular crop thereby facilitating better growth. It covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, plant growth regulators and others. These pesticides may fall on

soil at the time of application or get dissolved in water droplets from the sprayed crops and gets leached into the soil.

Pesticides are widely applied to control pests and produce good quality food at reasonable prices and costs. Their use is constantly increasing and also the probability of causing any unwanted side effects in the natural environment. These undesirable effects must be identified and as far as possible eliminated, but some risks are inevitable because pesticides can provoke an impact in nature through spray drift, leaching and runoff into water, or effects on living organisms exposed. Upon application, the concentration of pesticides in the environment varies due to several processes as scattering, volatilization, chemical and biological degradation and leaching, and the extension in which happens every process depends on the physicochemical properties of each compound, the properties of water and soil, the climatic conditions of the area and the method of application.

B. column leaching study

A soil column is defined as a discrete block of soil located either outdoor or in a laboratory, which allows control and measurement of the infiltration and which incorporates equipment for the total recovery of the effluent. This is usually achieved by encasing the soil column in a rigid and impermeable shell material, both for structural reasons and to prevent fluid loss.

Columns made of suitably inert material (glass, stainless steel, aluminum, PVC, etc) are packed with soil and afterwards saturated and equilibrated with an "artificial rain" solution and allowed to drain. Then the surface of each column is treated with the test substance and/or aged residues of the test substance. Artificial rain s then supplied to these columns and leach ate is collected. After the leaching process the soil is removed from the column and is sectioned into appropriate number of segments depending upon the information required from the study. Each soil segment and the leach ate are then analyzed for the test substance and, if appropriate, for transformation products and other chemical of interest.

C. Abbreviations and Acronyms

LCMS- Liquid Chromatography mass spectrophotometry
PVC - Polyvinyl Chloride
BDL - Below Detection Limit

II. MATERIALS AND METHODS

This study consists of soil sample collection, initial testing of the samples collected, column construction and experimentation on soil columns.

A. Sample collection

Fig.1- location of Pandhri village , Maharastra , India
Source-Google map

Samples are collected from a village (Pandhri) located 10 kms away from Yavatmal district which is quite famous in Maharashtra these days for agricultural problems. Samples were pretested on LCMS for pesticide residues which gave negligible values and BDL values on liquid chromatograph.

Samples are collected at different depths of 0.5 m, 1 m and 1.5 m to check for the potential leaching.

B. Characteristics of pesticides

The selected pesticides are the ones which are commonly used in the region for cotton cultivation. Most of the chemical pesticides used for pest control on cotton crops are organ chlorine pesticides and are the compounds of nitrogen, hydrogen and chlorine.

Soil contaminants due to excessive use of chemical fertilizers are nitratre, phosphate, cadmium, lead, chromium, nickel. Table shows regularly used pesticides on the farm from which soil samples are collected and for whom the samples are tested for residual values.

Table no.1-list of pesticides used in the farm from which samples are collected and their molecular formulas

Sr. No.	Pesticide	Base chemicals	Molecular formula
1	Confidor	Imidacloprid	C9H10ClN5O2
2	Pride	Acetamipirid	C10H11ClN4
3	Monocrotophos	-	C7H14NO5P
4	Profenofos	-	C11H15BrCl O3P5
5	Polo	Diafenthiuron	C23H32N2O5
6	Emamectin, Benoate	-	C56H81NO15
7	Tracer	Spinosad	C41H65NO10
8	Lano	Pyriproxyfen	C20H19NO3
9	Fem	Flubendiamide	C23H22F71N 2O4S
10	Ulala	Flonicamid	C9H6F3N3O
11	Profex Super	Profenofos, cypermethrin	C11H15BrClO3 C22H19Cl2NO3
12	Missile	Imamectin, benzoate	C56H81NO15

C. Column construction and filling

Following the OECD guidelines for testing of chemicals, 4 columns are made using PVC material 40 cm in length and 10 cm diameter in which soil is filled upto 30 cm height so as to make soil columns of 30 cm height and 10 cm diameter.

Fig.2-Column made of PVC pipe

The soil to be filled in these columns is first tested for pH, organic carbon, and chloride and nitrogen contents before filling in the columns. Other related properties of soil like moisture content, plasticity, elasticity, etc. are determined in the laboratory with conventional methods. The soil is first passed through is sieve 4.75 mm before filling in the columns for maintaining the homogeneity of soil column and reducing the errors like formation of preferential flow paths and fingering.

Following parameters of soil are tested prior to column filling

1. Sieve analysis on the soil samples indicates well graded soil.
2. Average water content was found to be 18.89 %.
3. Liquid limit was found to be 54.32 %.
4. Plastic limit is 33.79 %.
5. Shrinkage limit is 18.995 %

Each of these columns are spiked with separate pesticide that we have chosen for the study (viz.- Confidor, Missile, Ulala, Profex super).The column arrangement is made, soil is filled in the columns such as to make a soil column of height 30 cm and the columns are then filled with water so as to make them completely saturated. It takes at least 24 hours for a soil column to get completely saturated with water; we kept each column for a period 72 hours.

Columns are given no.1 to 4 and are marked with pesticide names Confidor, Missile, Ulala, Profex super to avoid confusion. Each column is then spiked with 5 mg of pesticide mixed in 20 ml of distilled water.

D. Leachate collection method

A stand like arrangement (column leachate collector stand) fixed with a filter paper fitted in a funnel is made from another PVC pipe in order to support the column and to make the collection of the leached elute easier. Fig.2 shows the arrangement. Soil columns made were already fitted with 1mm steel

mesh at the bottom to support the soil in the PVC column and to allow only leachate to pass through.

The column leachate collector stand is also fixed with a 0.5 mm steel mesh and a nylon membrane in a way so as the nylon membrane gets supported in between these 2 meshes. This arrangement supports the soil in the soil column even in saturated conditions and allows only the liquid leachate to pass through preventing even the smaller particles of soil.

The elute thus gets passed through these 3 membranes and falls on the filter paper in the funnel and is collected drop by drop in the glass beakers. Fig. 2 and 3 explains the above paragraph.

Fig.2 – Column leachate collector stand

Fig.3 -Inside view of the stand

III. METHODOLOGY

Column and stand thus made are connected and made water proof to prevent losses. Columns are then made saturated with water, spiked with respective pesticides and left for 24 hours. Distilled water is then passed through the columns at the rate of 225 ml per day and the leachate is collected on some predefined days according to the half lives of the respective pesticides.

Approximately 220 ml of elute is collected from each column on decided days and are tested for pH, chlorides and kjeldahl nitrogen in laboratory by titration.

The soil used for column feeling was initially tested for organic carbon, pH, nitrogen and chloride and will be tested once the column leaching is done for the said half lives.

IV. RESULTS AND DISCUSSION

Soil samples collected from the field were tested on LCMS but all the results were below detection limits as shown in table no.2 as follows

Table 2- LCMS analysis report

Sr. No.	Pesticide	Result mg/kg	LOQ mg/kg
1	Diafenthiuron	BDL	0.01
2	Fenpropathrin	BDL	0.01
3	Fipronil	BDL	0.01
4	Flonicamid	BDL	0.01
5	Imidacloprid	BDL	0.01
6	Profenophos	BDL	0.01
7	Spinosad	BDL	0.01

Though below detection limits, residues of following two compounds are found in low concentrations, the effect of which on soil and leachate was found to be negligible.

Table 3- Quantitation results

Com-- pound	Response time	Response no.	Final concentration
Imidacloprid	5.638	1234	2.7293 ng/ml
Fipronil sulfron	14.534	167	1.2176 ng/ml

Leachates are collected in volumes of about 220 ml from the said columns and are tested for pH, Chlorides and Nitrogen, the results of which are shown in table series 4 as follows

Table 4.1 –Titration results for column 1-Confidor

Day no.	pH	Nitrogen concentration mg/l	Chloride conc. mg/l
1	2.8	ND	79.98
3	2.7	55.01	74.98
10	2.4	53.20	59.98
15	9.2	54.80	49.98
20	8	50.6	64.98
25	8.5	49.98	49.98
30	8.6	48	54.98
33	8	48.02	53.2
35	8.5	43	49.98
38	8.1	BDL	24.99
40	8	BDL	24.99

Table no 4.2- Titration results for column 2-missile

Day no.	pH	Nitrogen concentration mg/l	Chloride Conc. mg/l
1	9	32.2	154.98
5	8.6	35	39.99
10	8.6	34.2	100.4
15	8.6	33.8	90.98
20	8.3	35	86.9
25	8.4	33	85
30	8.2	32.1	84.02
35	8.2	30.08	84.5
40	8.2	30.01	82.3
45	8	29.8	80.2
50	8.2	30	81
55	8.1	30	80
60	8.1	31.2	80
65	8	29.4	75.6
70	7.9	5.6	35
75	7.8	5.5	22.3

Table no.4.3- Titration results for Column 3- Ulala

Day no.	pH	Nitrogen concentration mg/l	Chloride conc. mg/l
1	9.1	91	79.98
3	9	90	84.98
10	9	90.2	99.97
15	8.7	89.5	85.9
20	8.7	89	85
22	8.5	40.3	49.98
24	8.3	BDL	45.7

Table no.4.4- Titration results for Column 4- Profex super

Day no.	pH	Nitrogen concentration mg/l	Chloride conc. mg/l
1	8.2	39.2	92.2
3	8.2	39	90.6
7	8.1	8.4	89.97
9	8.1	8	85.2
10	8.1	7	79.98

From the nitrogen and chloride contents results, we can say that these pesticides have a considerable effect on soils in terms of nitrogen and chlorine and it lasts upto the half lives in a decreasing order due to adsorption phenomenon.

Persistence study was carried out till the half-life of each pesticide. The greater the persistence of pesticide may result in plant uptake in the next cycle so it should be wisely used or replaced by bio-pesticides.

V. CONCLUSION

It can be concluded from present investigation that the chemical pesticides shows persistence in soil and it may affect the soil properties. The pesticides used by the farmers are getting mixed with the soil and due to the persistence of these pesticides in soil there is a chance of plant uptake in the next cycle and may result in severe health issues.

There is a scope to further study of pesticide residue uptake in plants.

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