e-ISSN: 2248-9126
Vol 5 | Issue 3 | 2015 |123-127. Print ISSN: 2248-9118

Indian Journal of Pharmaceutical Science & Research

www.ijpsrjournal.com

LEACHING OF PROCHLORAZ IN SOIL COLUMN UNDER LABORATORY CONDITION

Chandran Loganayagi and Atmakuru Ramesh*

Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai-601 301, Chennai, Kancheepuram District, Tamil Nadu, India.

ABSTRACT

Laboratory study was conducted in order to determine the leaching potential of Prochloraz using soil column. Prochloraz is an imidazole fungicide that is widely used in agriculture against various plant diseases and also used to control the foliar diseases of cereals. Two soils with different organic carbon content and clay content were used. The Study discusses the mobility and adsorption of prochloraz in two different soils. The soils used were sandy loam and clay loam soil. The size of the soil columns used are 35 cm length x 6.9 cm id. All the columns are sealed and created ≅ 0.3 cm i.d holes at the bottom, for the collection of leachates. Prochloraz was sprayed on the surface of the soil column. The applied dosages are prochloraz @ 1L/ha,2 L/ha, 4L/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 prochloraz at five cm difference in depth. A high performance liquid chromatography with UV detector was used for the quantification of residues. Limit of Quantification for prochloraz was established as 0.001µg/ml. The recovery study conducted for prochloraz at two different concentrations (LOQ and 10 × LOQ) showed mean recovery of 92.7%, 95.9% in water, 91.8%, 93.3% in Sandy loam soil and 89.9%, 91.0% in clay loam soil. Analysis of leachates collected from sandy loam soil columns showed the residues of prochloraz 0.002 – 0.08 µg/mL. Leachates collected from clay loam soil columns showed the residues of prochloraz 0.002 to 0.05 µg/mL. Analysis of sandy loam soil samples showed the residues of prochloraz 0.01 to 0.38 µg/g and clay loam soil samples showed 0.008-0.58 µg/g.

Keywords: Prochloraz, mobility, Soil column, Leaching, organic carbon.

INTRODUCTION

The application of plant protection products is inevitably accompanied by a temporary soil contamination. Sorption and degradation are the main concentration determining processes for pesticides in soils. Environmental pollution results in the contamination of soil and ground water due to the improper use and transport of pesticides. Though the use of pesticides has offered significant economic benefits by enhancing the production and yield of food and fibers and the prevention of diseases, evidence suggests that their use has adversely affected the health of human populations and the environment. Pimentel [1] discussed that during pesticide application, only a small amount of applied pesticides display protective and eradicative action to fight against plant diseases, whereas large amount of pesticides reach the soil and results in the contamination of soil [2,3]. Pesticides have been widely distributed and their traces can be detected in all areas of the environment (air, water and soil). Industrial effluents entering the water bodies are the major source for the environment toxicity. It not only affects the quality of drinking water but also had severe effect on the aquatic ecosystem.

Column test are a common tool to investigate the leaching behavior of contaminated soil. The leaching of pesticides can be linked to a set of main factors including, rainfall characteristics, soil moisture, chemical properties of the pesticides, soil properties, and preferential flow paths [4].

Corresponding Author:- **Atmakuru Ramesh** Email: raamesh_a@yahoo.co.in

Herbicide leaching through soil into groundwater greatly depends upon sorption–desorption and degradation phenomena **[5].** A decrease in pesticide leaching was observed with the increase in dissolved organic matter (DOM) of leachates. The results obtained point to the interest in the use of organic wastes in reducing the pollution of groundwater by pesticide drainage [6]. The use of pesticides for crop protection may result in the presence of toxic residues in environmental matrices. In the aquatic environment, pesticides might freely dissolve in the water or bind to suspended matter and to the sediments, and might be transferred to the organisms' tissues during bioaccumulation processes, resulting in adverse consequences to non-target species **[7].** Leaching through soil has been identified has the major cause for the occurrence of agrochemicals in groundwater. The occurrence of pesticides in groundwater revealed the limitations of our current understanding of transport processes in soils. Leaching studies using soil column often indicate that pesticides should be retained by soil matrix and not to be leached to the groundwater [8]. The main objective was to determine the sorption behavior of Prochloraz compound and their movement in the soil column under laboratory condition.

MATERIALS AND METHODS

Materials

Sandy loam soil
Clay loam soil
Prochloraz
Soil Column
Sieve

Soil Column Preparation

Soil samples collected from the field was dried and sieved through 2 mm sieve. The physicochemical properties such as pH, Electrical conductivity, organic carbon content, water holding capacity and soil texture were determined. Leaching study for prochloraz 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 ≅0.3cm 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 $CaCl_2$ solution and kept undisturbed overnight to drain.

Fungicide Application

Two different experiments were conducted by applying prochloraz @ 1L/ha, 2L/ha, 4L/ha on the surface of the soil column of clay loam and sandy loam soil. After the application of the fungicide 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 UV detector. The concentrations of prochloraz 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 2% hydrochloric 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 prochloraz by an HPLC-UV method.

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% hydrochloric acid, partitioned with 100 mL of methylene chloride thrice and evaporated to near dryness .The residue was re-dissolved in 2 ml of methylene chloride and diluted with 8 ml of iso-octane. 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.

Instrumentation

A high performance liquid chromatograph equipped with a UV detector, at the wavelength 240 nm was used for the quantification of residues of prochloraz. The column used for separation was Agilent zorbox SB-C8 (250 mm x 3.0 mm I.D., x 5 µm particle size) column temperature 40°C and the mobile phase 500 ml of acetonitrile and 500 ml of water used for separation at a flow rate of 1 ml/min.

LIMIT OF DETECTION AND LIMIT OF QUANTIFICATION

Method validation was performed with different known concentrations of prochloraz 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 was conducted by spiking two different known concentrations of Prochloraz at 0.001 µg/ml to 0.01

µg/ml showed mean recovery of 92.7%, 95.9% in water, 91.8%, 93.3% in Sandy loam soil and 89.9%, 91.0% in clay loam soil. From the analytical determinations the limit of detection based on signal-to-noise ratio is 3:1 was established as 0.001µg/ml and limit of quantification 0.001µg/ml was established based on recovery and S/N ratio 10:1.

Table 1. Soil physico-chemical properties

Soil texture	Clay loam soil	Sandy loam soil
Clay (%)	38	25
Silt (%)	30	23
Sand (%)	32	52
pH	6.0	7.02
Organic carbon content (%)	5.2	1.20
CEC(meq/100g)	34.50	35.00
Sol.Salts (milli mhos/cm)	0.22	0.24
Water holding capacity (ml/100g)	28	32
Nitrogen (mg/kg)	2770	2632
Phosphorous (mg/kg)	40	32
Potassium (mg/kg)	120	145
Magnesium (mg/kg)	701	689
Calcium (mg/kg)	3428	3450
Sodium (mg/kg)	12	10
Bulk Density (g/cc)	1.12	1.08

Table 2. Concentration of prochloraz found in leachate in µg/ml

Occasion in days	Sandy loam soil			Clay Loam soil		
	1L/ha	2L/ha	4L/ha	1L/ha	2L/ha	4L/ha
1	0.02	0.04	0.03	0.002	0.006	0.01
2	0.01	0.02	0.05	0.01	0.02	0.02
3	0.01	0.03	0.07	0.04	0.05	0.05
4	0.02	0.03	0.05	0.02	0.02	0.05
5	0.01	0.03	0.06	0.005	0.009	0.04
6	0.02	0.04	0.07	0.01	0.05	0.009
7	0.02	0.06	0.08	0.005	0.01	0.03
8	0.02	0.05	0.06	0.006	0.02	0.03
9	0.008	0.04	0.05	0.01	0.02	0.04
10	0.006	0.03	0.03	0.002	0.01	0.02
11	0.002	0.01	0.04	0.01	0.02	0.05
12	0.003	0.01	0.03	0.004	0.008	0.02
13	0	0.01	0.02	0	0	0.01
14	0	0	0	0	0	0
15	0	0	0	0	0	0

Table 3. Concentration of prochloraz found in the sandy loamsoil column

Column Length in cm	Concentration of prochloraz			Concentration of prochloraz		
	Sandy loam soil column(µg/g)			Clay loam soil column(µg/g)		
0 to 5	0.09	0.25	0.35	0.16	0.39	0.58
5 to 10	0.11	0.21	0.38	0.18	0.31	0.44
11 to 15	0.10	0.24	0.30	0.12	0.31	0.40
16 to 20	0.14	0.22	0.29	0.11	0.19	0.22
21 to 25	0.03	0.04	0.08	0.02	0.05	0.08
26 to 30	0.01	0.03	0.06	0.02	0.02	0.04
31 to 33	0.009	0.01	0.022	0.008	0.02	0.03

Figure 1. Prochloraz Concentration In Leachate Of Sandy Loam Soil Column (µg/mL)

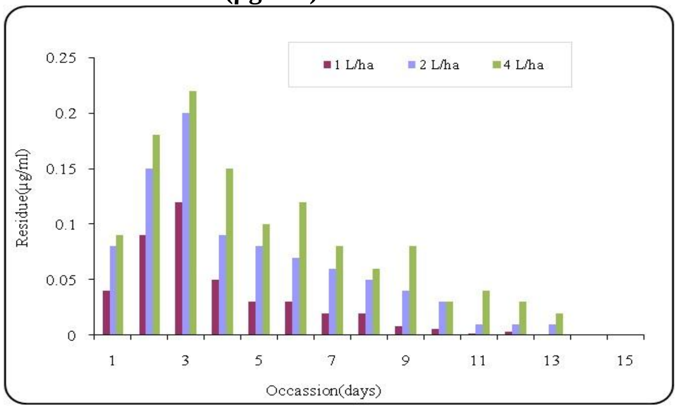


Figure2. Prochloraz Concentration In Leachate Of Clay loam Soil Column (µg/mL)

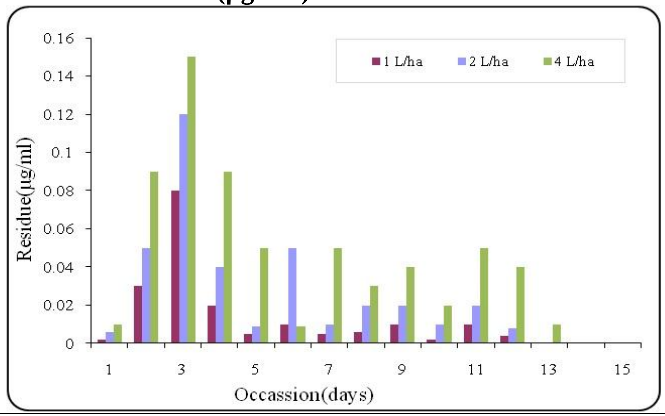


Figure3. Prochloraz Concentration Of Sandy Loam Soil Column (µg/g)

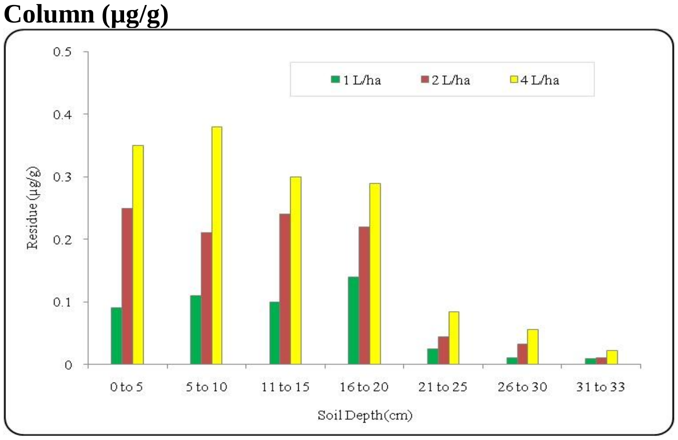
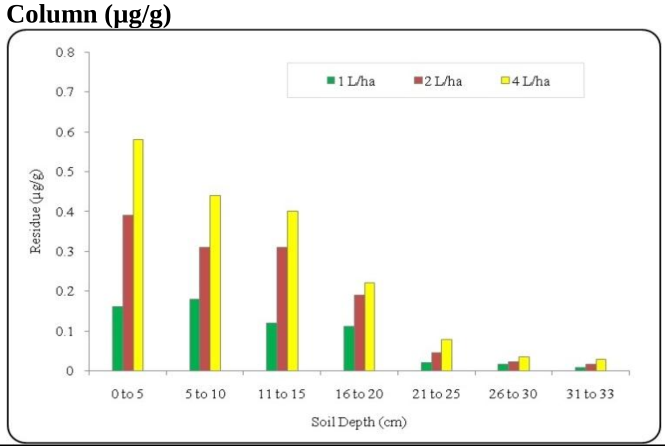


Figure4. Prochloraz Concentration Of Clay Loam Soil Column (µg/g)



RESULTS AND DISCUSSION

Leaching behavior of prochloraz in different soils having different physico-chemical properties are presented in the table 1. The physico-chemical properties of the two soils clearly showed the lower carbon content (1.25%) in sandy loam soil sample collected from IIBAT (India) and higher organic carbon content in clay loam soil (5.2%) collected from Rochelle (US). The clay loam soil column leachates analysed for 12 days at the tested dosages 1L/ha, 2L/ha, 4L/ha showed the residues of prochloraz 0.002 to 0.05 µg/ml. Further analysis of leachates collected on 13th day onwards showed the residues below detectable level. In sandy loam soil leachates analyzed for 13 days showed the residues of prochloraz 0.002 to 0.08µg/ml. Leachates collected on 14^{th} and 15^{th} day showed the residues below the detectable level at the lower dosage. Summarized results are presented in tables 2 and 3. Analysis of soil samples from the clay loam soil column showed the presence of residues of prochloraz in the range 0.008 to 0.58 µg/g, sandy loam soil columns showed the residues of prochloraz in the range 0.01 to 0.38 µg/g. Higher concentration of prochloraz remained in the soil columns and lower amount in the leachates can be attributed due to nature of prochloraz, the higher organic carbon content and clay content. Prochloraz has more adsorption capacity and hence low mobility. Georg Haberhauer et al [9] concluded that organic matter may affect the MCPA movement into the deeper soil. In the case of sandy loam soil, higher concentration of prochloraz was found in the leachate than in soil. Summarized graphical results (Figure. 1 to 4) clearly reveals that 75% of the prochloraz was found in soil after 15 day study in soil columns whereas lower percentage of residues were found in leachate. The movement of pesticide is depends on the adsorption was confirmed by P.C. Abhilash and Nandita Singh [10], their results provide evidence that sugarcane bagasse can accelerate lindane degradation by enhanced microbial activity and prevent pesticide mobility through soil column by adsorption.Glyphosate and AMPA, leach through the soils; thus, both molecules may be potential contaminants of groundwater was concluded by David Landry et al [11]. It has been concluded that laboratory column experiments are a reliable tool for organic compounds with various physico-chemical properties by Ute Kalbe et al [12]. Some pesticides are highly sorbed to soil, and the addition of biochars to soil did not further increase its sorption biochars with high surface areas and low DOC contents can increase the sorption of highly mobile pesticides in soil was discussed by A. Cabrera, L. et al [13]. The use of organic amendment in reducing the pollution of groundwater by pesticide drainage and in the use of solarization and biosolarization in reducing the persistence of pesticides in soil was reported by Jose Fenoll [14]. The sorption of Dissolved organic matter from amendments on soil during the transport process can decrease the mobility of the fungicide by changing the physicochemical properties of the soil surface whose behavior may be dominated by the adsorbed Dissolved organic matter was confirmed by Garcia-Jaramillo at al [15].

CONCLUSION

Before the frequent application of pesticides in agro-ecosystems, their fate and behavior have to be evaluated according to a multistep testing concept. In all these tests, benefits and risks have to be assessed according to the current state of scientific knowledge.

The leaching study conducted in soils of varied organic carbon content with three dosages are 1L/ha, 2L/ha, and 4L/ha. for prochloraz showed that lower concentration found in leachates after 60 cm rain fall reveals the mobility is low. In the soil of lower organic carbon content that is sandy loam soil, percentage of residues retained in the soil was low compared to the soil having higher organic carbon content and clay content that is clay loam soil where the concentration of prochloraz retained in soil was slightly high. Less mobility of prochloraz might be due to its higher adsorption capacity. Even after continuous leaching procedure, only small amount of prochloraz were retained in leachate. This high concentration of prochloraz retained by soil column clearly reveals the less mobility of the prochloraz and there is no possibility of groundwater contamination. This leaching study using soil column indicate that prochloraz was retained by soil matrix and hence this fungicide is safe and not to be leached to the groundwater.

ACKNOWLEDGEMENT

The author thanks the Management for providing necessary facility to conduct this research work.

REFERENCES

1. Pimentel D. Amounts of pesticides reaching target pests, environmental impacts and ethics. *J Agric Environ Ethic*, 8(1), 1995, 17–29.
2. United States Environmental Protection Agency (US EPA). Carbofuran, Final Tolerance Revocations. 40 CFR part 180. *Rules Regul*, 74(93), 2009, 23045 –23095.
3. Bermudez-Couso A, Novoa-Munoz JC, Arias-Estevez M, Fernandez-Calvino D, Influence of different abiotic and biotic factors on the metalaxyl and carbofuran dissipation. *Chemosphere*, 90(10), 2013, 2526 –2533.
4. Julian Klaus, Erwin Zehe, Martin Elsner, Juliane Palm, Dorothee Schneider, Boris Schroder, Sibylle Steinbeiss, Loes van Schaik, Stephanie West, Controls of event-based pesticide leaching in natural soils, A systematic study based on replicated field scale irrigation experiments. *Journal of Hydrology*, 512(6), 2014, 528-539.
5. Edgar Hiller, VeronikaTatarkova, Alexandra Simonovicova, MikulasBartal, Sorption, desorption, and degradation of (4-chloro-2-methylphenoxy) acetic acid in representative soils of the Danubian Lowland, Slovakia. *Chemosphere*, 87(5), 2012, 437-444.
6. Fenoll J, Ruiz E, Flores P, Vela N, Hellin P, Navarro S, Use of farming and agro-industrial wastes as versatile barriers in reducing pesticide leaching through soil columns. *Journal of Hazardous Materials*, 187(1–3), 2011, 206-212.
7. Elsa Teresa Rodrigues, Isabel Lopes, Miguel Angelo Pardal, Occurrence, fate and effects of azoxystrobin in aquatic ecosystems, A review. *Environment International*, 53, 2013, 18-28.
8. Markus Flury, Experimental evidence of Transport of pesticides through field soils-A Review. *Journal of Environmental Quality*, 25(1), 1996, 25-45.
9. Georg Haberhauer, Brigitta Temmel, Martin H Gerzabek, Influence of dissolved humic substances on the leaching of MCPA in a soil column experiment. *Chemosphere*, 46(4), 2002, 495-499.
10. Abhilash PC, Nanditasingh, Influence of the application of sugarcane bagasse on lindane (γ-HCH) mobility through soil column, Implication for biotreatment. *Bioresource Technology*, 99(18), 2008, 8961-8966.
11. David Landry, Sylvie Dousset, Jean-Claude Fournier, Francis Andreux, Leaching of glyphosate and AMPA under two soil management practices in Burgundy vineyards. *Environmental Pollution*, 138(2), 2005, 191-200.
12. Ute Kalbe, Nicole Bandow, Andrea Bredow, Helena Mathies, Christian Piechotta, Column leaching tests on soils containing less investigated organic pollutants. *Journal of Geochemical Exploration*, 147, 2014, 291-297.
13. Cabrera A, Cox L, Spokas K, Hermosin MC, Cornejo J, Koskinen WC. Influence of biochar amendments on the sorption–desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. *Science of the Total Environment*, 470–471, 2014, 438-443.
14. Jose Fenoll, Encarnacion Ruiz, Pilar Flores, PilarHellin, Simon Navarro. Reduction of the movement and persistence of pesticides in soil through common agronomic practices. *Chemosphere*, 85(8), 2011, 1375-1382.
15. Garcia-Jaramillo M, Cox L, Cornejo J, Hermosin MC, Effect of soil organic amendments on the behavior of bentazone and tricyclazole. *Science of the Total Environment*, 466–467, 2014, 906-913.