Research Article
DOI : 10.20425/ijts.0iof.9578

International Journal of Tea Science
Vol. 12 (1&2) 2016

Dissipation rates of some selected pesticides from the soil of tea agroecosystem in Assam, India

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Abstract: An experiment was carried out in Rosekandy Tea Estate, Barak Valley, Assam to investigate the persistence of some selected pesticides (i.e Endosulfan, Fipronil, Paraquat and 2,4-D) on the soil. These pesticides were applied in the soil as per the application rate, where one year old tea plants were growing and the residue were analysed for a period of 50 days. Their degradation kinetics in soil was also studied and described. Soil samples were collected with the help of soil corer. The samples were brought to the laboratory, air dried in room temperature and extracted for analysis with high performance liquid chromatography (HPLC). Among the pesticides 2,4-D was highly persistent with half life of 57.75 days followed by Endosulfan which lost 42.64% of its initial concentration by the last sampling period (i.e 50 days) after the spraying. Fipronil and paraquat lost 65% and 70.32% of initial residue in soil making them the least persistent amongst these pesticides in the studied soil. Considering the impact of pesticide residues on human health, the less persistent pesticides may be used in tea plantations to minimize the potential negative impact of pesticides in the environment. The cost benefit ratios of the use of the pesticides should be also worked out.

Keywords: HPLC, pesticides, residue, tea agroecosystem,

Running title: Selected pesticides from the soil of tea agroecosystem

Introduction

The term pesticide is generic for hundreds of compounds belonging to very different chemical families, with different physiochemical properties, widely used for pest control[6].Tea (*Camellia sinensis* (L.) O. Kuntze) is one of the most important cash crops in India. Pests, pathogens and weeds are severe constraints to productivity and quality of tea[4]. Tea industry in North East India relies heavily on chemical pesticides for the control of pests and diseases in tea which has led to the problem of pest resistance, pest resurgence and environmental pollution[11].

Pesticides may reach soil by direct application to soil surface or during application to crops. The pesticides that are sprayed enter the soil ecosystem, either degrades rapidly or can accumulate in soil and persist for a long period of time thus causing environmental problems[9]. Pesticide residue in soil can diffuse, evaporate or leach causing water pollution and ecological problems[8].

There is lack of data for the level of the pesticide residues in the soil of tea agroecosystem of Barak Valley. The main objective of this study was to assess the rates of dissipation of some commonly used pesticides (i.e. Paraquat, Endosulfan, 2,4-D and Fipronil) in tea agroecosystem in soil.

Materials and Method

This experiment was carried out in the Rosekandy Tea Estate, Barak Valley, Assam by employing the randomized block design. The pesticides used for this study were Paraquat, Endosulfan, 2,4-D and Fipronil. These were diluted in water as per the field application rates i.e. paraquat (15ml/5 l), endosulfan (12.5ml/5 l), 2,4-D (7.5g/5 l) , fipronil (0.2g/5 l) and sprayed on the soil on which one year old tea plants

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ISSN; 0972-544X (print)

were already growing. Soil samples were collected at different intervals i.e., 10, 20, 30, 40 and 50 days after application of the pesticides. Topsoil samples from the experimental plot at 10-20 cm depth were collected randomly from three places from each plot and composited[7]. Soil sample (5 g) was air dried in the laboratory, sieved and 25 g each was weighed to be used for the extraction procedure. A glass column was packed with cotton plug and the sieved soil was loaded along with florisil and sodium sulphate. A solvent mixture of acetone and hexane was used in the ratio of 2:8 for extraction. The solvent was added to the column and it is made to elute slowly. Charcoal was added to the elute and it is made to rest for 5-6 hours. This sample is then filtered through the filter paper through sodium sulphate. It was then concentrated to dryness in a distillation apparatus, and then diluted with hexane to a final volume of 5ml[12]. Now, the samples are ready to be injected in to the HPLC. The analysis was done at the Central Instrumentation Laboratory, Assam University, Silchar.

HPLC Series 200 from Perkin Elmer was used for the study

Detector:	UV
Column:	RP-18
Flow rate:	1ml/min
Injection Volume:	20µl

Results and Discussion

The properties of the experimental soil are given in table 1. The result of the analysis of pesticide residue in soil is shown in the Table 2. A total of five observations were made for a period of 60 days and the sampling was commenced 10 days after the application of the pesticides.

Table 1: Physico chemical properties of the experimental soil.

Sl no	Characteristics	Observation
1	pH	5.3
2	Moisture content	15.15%
3	Water holding capacity	49%
4	Bulk density	0.28 g/cm^3
5	Soil porosity (%)	0.10%
6	Volumetric water content (g/cm^3)	0.04g/cm^3

The concentration of 2, 4-D was found to be highest in all the observations, compared to the other four pesticides (Table 2). After 10 days, the residue was calculated at 49.6 mg/kg which declined to 31.4mg/kg after 60 days. After the last sampling, the total residue loss was recorded to be 57.9 %.

The initial residue of paraquat in the first sampling was 26.28 mg/kg (Table 2), the rate of degradation is at a steady pace with 35.3% of the initial residue lost by the last observation (i.e. 17mg/kg). In case of fipronil, the residue declined to 7.51 mg/kg in the last sampling observation after 60 days of treatment which is 64 % loss of the initial residue (20.9 mg/kg).

The initial concentration of endosulfan was 13.6 mg/kg, however after the third observation, i.e. after 30 days the residue of endosulfan declined steadily from 10.8 mg/kg to9.8 mg/kg in the fourth observation and 7.8 mg/kg at the end of the study period(Table 2). The total residue loss was 42.6% of the initial residue.

The regression equation, R^2 values and half lives of the pesticides are given in Table 3. The calculated half lives of endosulfan, paraquat, fipronil and 2,4-D are 13.36, 34.65, 17.32 and 57.75 days respectively

Table 2: Residue of the pesticides (mg/kg) in the experimental tea agroecosystem soil

Days	Endosulfan	Loss (%)	Paraquat	Loss (%)	Fipronil	Loss (%)	2,4-D	Loss (%)
10	13.6	0	26.28	0	20.9	0	49.6	0
20	12.7	12.6	21.71	17.39	15.6	25.36	48.2	2.03
30	10.8	20.58	10.8	58.9	12.6	39.71	40.2	18.9
40	9.8	27.94	9.8	62.7	8.27	60.43	37	25.4
50	7.8	42.64	7.8	70.32	7.51	65	31.4	36.6

Table 3: Regression equation, R^2 values and half life of the pesticides from the soil

Sl. No.	Pesticide	Regression equation	R^2	K value	$t_{½}$ (days)
1	Endosulfan	y= 0.001x + 0.055	0.934	0.005	13.36
2	Paraquat	y = -0.010x + 3.351	0.990	0.02	34.65
3	Fipronil	y = -0.026x + 3.285	0.976	0.04	17.32
4	2,4-D	y = -0.012x+ 4.038	0.975	0.012	57.75

The degradation kinetics of the selected pesticides (i.e. endosulfan, paraquat, fipronil and 2,4-D) in the experimental soil was studied from the residue of the pesticides over a period of 60 days. In order to model the degradation rate, the order of the transformation reaction is studied by establishing corresponding rate equation as it links to the reaction rate with the rate co-efficient and constant parameters. The rate equation is a differential equation and thus can be integrated to obtain an integrated rate equation linking the concentrations of the reactants (i.e. pesticides) with time. Most of the times, the degradation of pesticides in soil do not follow simple first order kinetics but show a pattern where the pesticides decline at an initial phase rapidly and in a second phase less rapidly[5].

The rate of degradation of the pesticides on soil was determined by plotting the values of LnCt vs time. Straight line was found when the log of concentration was plotted against time with appreciable R^2 values indicating that paraquat (Fig. 1), fipronil (Fig. 2) and 2,4-D (Fig. 3) followed the first order kinetics in the degradation process. The first order rate constant (k) was calculated by the equation $\text{Ln}\,[Ct] = -k + \ln [Ct]_0$. Where, Ct= concentration of pesticide at time t; Ct_0 = initial concentration of pesticide; k = degradation rate constant (s^{-1})

The LnCt vs t graph of endosulfan did not yield a fittable linear curve. The nature of these curves reflects on the non linearity in the rate of degradation at different time span. The plot of 1/ct vs time shows a straight line with appreciable R^2 values for endosulfan (Fig. 4). This indicates that the degradation of endosulfan followed the second order kinetics during the study period of 60 days. The second order rate constant (K_2) was calculated by using the equation $1/[ct]_t = k_2 t + 1/[ct]_0$.

The regression equation, R^2 values and half lives of the pesticides are given in Table 3. The calculated half lives of endosulfan, paraquat, fipronil and 2,4-D are 13.36, 34.65, 17.32 and 57.75 days respectively.

The texture of the soil affects movement of water through soil and therefore affects movement of pesticides. The coarser the soil, faster the movement of the percolating water and less opportunity for adsorption of the dissolved pesticides i.e. coarser the soil texture, greater the chance of the pesticide reaching groundwater. In this present study, the soil texture was sandy loam so the adsorption of the pesticides was less because sand particles have less surface area compared to clay or silt. The organic matter content of the studied soil is 0.57% which favours leaching capacity of the pesticides and reduces adsorption. Leaching and adsorption are inversely related to each other and the soil in which leaching is more than the adsorption implies that the soil possess less organic matter and it is of light texture[2,10].

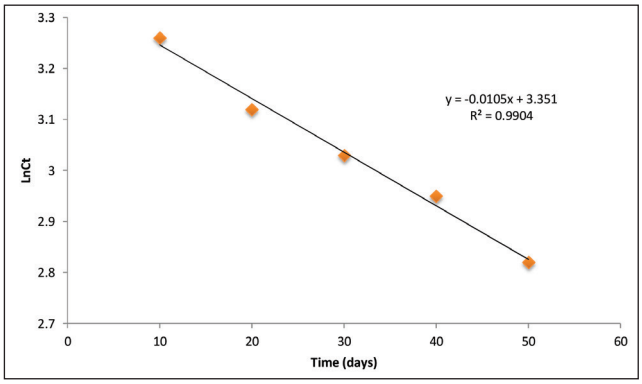

Fig. 1: First order graph (LnCt vs time) for paraquat degradation in soil

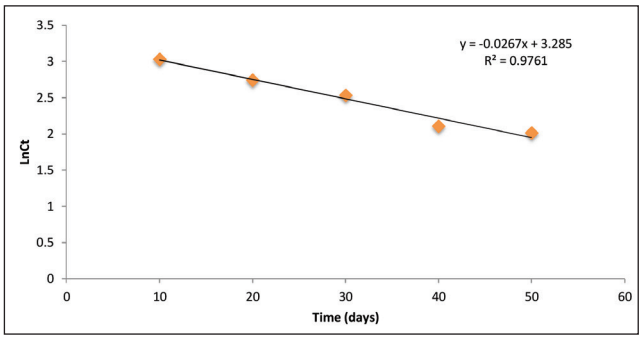

Fig. 2: First order graph (LnCt vs time) for fipronil degradation in soil

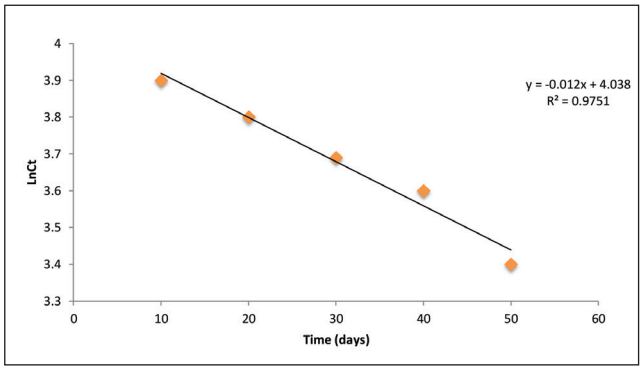

Fig. 3: First order graph (LnCt vs time) for 2,4-D degradation in soil

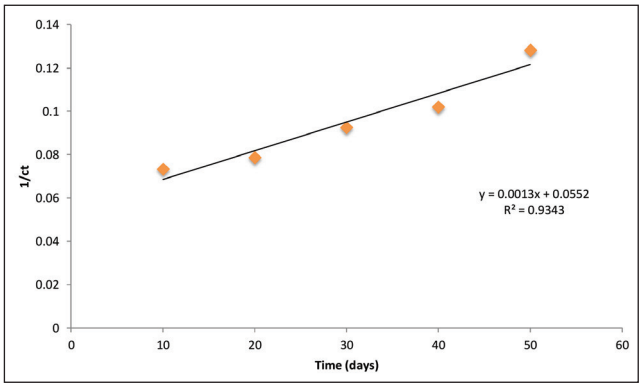

Fig. 4: Second order graph of the residue (1/ct) of endosulfan with time (t)

Table 4: Fortified recoveries of the pesticides from the soil samples

Pesticides	Amount added	Recovery (%)			Average(%)	RSD (%)
		1	2	3		
Endosulfan	1000mg/kg	109.45	103.09	107.93	106.82	3.31
Fipronil	1000mg/kg	106.37	94.19	94.20	98.25	7.02
Paraquat	1000mg/kg	97.8	99.6	102.9	100.1	2.58
2,4-D	1000mg/kg	92.6	92.6	91.7	92.3	0.51

*RSD= Relative Standard Deviation

The method described for sample preparation was validated by a recovery experiment. Samples of untreated soil were fortified with fipronil, endosulfan, paraquat and 2,4-D standard solutions of 1000 ppm. And then, they were processed according to the standard extraction procedure. Three replicates for the concentration were analyzed. The results of the recovery assay are shown in Table 4. The average recoveries of the pesticides ranged from 92.3 to 111.34 % which are within the acceptable range.

From the results of the above study, it can be observed that 2,4-D was highly persistent with a half life of 57.75 days. This persistence is sometimes required as 2,4-D is a herbicide and its very nature requires it to stay for a longer period in the soil for it to be effective. The ability of a pesticide to persist for a certain length of time can be desirable and has been recognized as important in some situations for successful control of pests and diseases. The absorption and desorption of pesticides in soil can influence their bioefficacy against soil borne pests and may also influence the microbial population of the soil. It is important to understand whether a pesticide is mobile in soil or how long it will persist as it can affect the decisions about which pesticide to use or how often to use. It can be suggested that the pesticides under study (i.e.Paraquat, Endosulfan, 2,4-D and Fipronil) followed a gradual degradation process and hence can be safely used in moderation in the tea agroecosystem.

Acknowledgement

The authors are grateful to Manager, Rosekandy Tea Estate, Cachar for allowing the collection of soil samples and also to Central Instrumentation Laboratory, Assam University, Silchar for the HPLC facilities.

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