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Field Dissiation Kinetics of Paraquat in Acid Soil as Function of Concentration and its Residues in Tea Leaves

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The increasing concern on ecological and public health confined the use of pesticides in agriculture. However the herbicide use is increasing alarmingly to address the issues of labour scarcity and have timely weed management in crop production. Paraquat is toxicity class I herbicide as per EPA classification and is continuously used throughout world as well as in India. Thus, to monitor residues in tea leaves, paraquat dissipation studies were conducted in acid soil under tea in tropical hilly zone. A tea grown field was applied with paraquat dichloride at 2 and 4 kg a.i. ha^{-1} as post-emergent herbicide. The paraquat dissipation in soil followed first-order reaction kinetics and its persistence increased with increase in the application rate. The half-life values calculated was ranged from 25.0 and 27.4 days. Detector response was linear within 0.05-1.0 μg mL^{-1} concentration range at per cent relative standard deviation of 3.14 %. The limit of quantification for soil and tea leaves were 0.08 and 0.05 mg kg^{-1}, respectively. The average recoveries of paraquat from soil and tea leaves were found between 77.8-84.0 % and 82.0-84.0 %, respectively. At both the application rates, residue of paraquat was BDL in soil and tea leaves on 100 day after application.

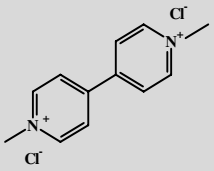
Keywords: Acid soil, Degradation, Paraquat residue, Spectrophotometer, Tea leaves.

INTRODUCTION

Paraquat dichloride belongs to bipyridylium group is a colourless, white, or pale yellow crystalline solids, hygroscopic and odourless [1] in nature and other properties are given in Table-1. Paraquat is extremely persistent in the soil environment and has the field half-lives of greater than 1000 days [1,2]. It is degraded by ultraviolet light, sunlight and soil microorganisms to products which are less toxic than the parent compound. The strong affinity of paraquat to soil particles and organic matter could limit its bioavailability to plants, earthworms and microorganisms [1,2]. However, the bound residues may persist indefinitely and can be transported in runoff with the sediment. Paraquat is not significantly mobile in most soils and that which does not become associated with soil particles can be decomposed to a non-toxic end product by soil bacteria [3]. Although paraquat is highly immobile in soil, limited movement of the chemical may occur if the adsorption capacity of a soil is exceeded, or if paraquat is weakly adsorbed [4]. Increase in soil pH increases its sorption to soil particles and vice versa and the sorption is weaker in highly organic soils and remains active for long time and present upto 29 days in soil with more than 98 % organic matter [5]. Thus the risk of ground water contamination by paraquat is not high until directly applied to the water bodies for aquatic weed control [6].

The major problem in tea cultivation is the weed control and could be achieved through chemical methods using herbicides. Many herbicides are registered for weed control in tea and the commonly used one is paraquat. Paraquat dichloride 24 % SL is the only registered formulation in India with the Central Insecticide Board and Registration Committee (CIBRC) and has been categorized as highly toxic. Although CIBRC has not provided any recommendations, it has approved the use of this herbicide in nine crops including tea. This chemical is also called quaternary ammonium salts and generally known as quats. It destroys plant tissue by disrupting photosynthesis and rup-turing cell membranes, which allows water to escape leading to rapid desiccation of foliage. Paraquat is not metabolized to any degree in plants. Summers [4] found that on plant surfaces, paraquat is degraded by sunlight to the extent of 66 % when exposed to 21 days of sunlight. Though it is tightly bound by the soil, continuous and indiscriminate use may cause bioaccumulation in soil and crops. Hence the paraquat products are classified under restricted use category and registered to control weeds and grasses in many

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF
PARAQUAT USED FOR THE STUDY

Chemical name (IUPAC)	1,1'-Dimethyl- 4,4'-bipyridylium dichloride
Empirical formula	$C_{12}HN_2Cl_2$
Chemical structure	
Molecular weight	257.20
Water solubility	700 g/L @ 20 C
Vapour pressure	Negligible @ room temperature (paraquat dichloride); << 1×10^{-5} Pa at 25 °C
K_{oc}	1,000,000 mL/g
log K_{ow}	4.5 at 25 °C
Melting point	Paraquat dichloride decomposes at approximately 340 °C
Boiling point	Paraquat dichloride decomposes at approximately 340 °C

agricultural and non-agricultural areas [7]. With this background, the present study was carried out find out the persistence, dissipation and residues of paraquat in soil and tea leaves at the time of plucking grown in hilly region of Tamil Nadu.

EXPERIMENTAL

Field experiment: Field experiment to study the persistence and dissipation of paraquat in tea and field soil was carried out during 2011 at the farmer's field at Coonoor, Nilgiris, Tamil Nadu. The experimental farm was located in western zone of Tamil Nadu at an altitude of 1501 m above mean sea level (MSL), 11°15'00"N latitude and 76°40'00"E longitude. The size of each plot was 5 m × 3 m. The spacing between the tea bushes and the rows was 100 cm. The clone variety CR 6017 was used as test species. The test chemical (paraquat dichloride 24 % SL) purchased from the market was applied at two different dosages *viz.*, 2 and 4 kg ai ha^{-1} as post emergence spray in tea plantation field with the help of a knapsack sprayer along with control (water spray alone) and each treatment was replicated thrice. Approximately 500 g of soil samples were drawn randomly from 0-15 cm depth from 5-6 places in each plot. The soil and tea leaves were collected at 0 (2 h), 10, 25, 50, 75 and 100 day time intervals from all the treated and control plots. From each plot the fresh newly emerged tea leaves of about 100 g was collected at random [8] and was subjected to paraquat residue analysis. The soil of the experimental field was sandy clay loam and has pH 4.12, EC 0.21 dS m^{-1} and organic carbon 3.78 %. All the solvents used were of analytical grade and purchased from S.D. Fine Chemicals, Mumbai. For the preparation of stock solution of paraquat and calibration standards and instrumental analysis, HPLC-grade solvents of E-Merck and 0.2 µm filtered milli-Q (Millipore system, USA) water were used.

Paraquat extraction and determination: Paraquat dichloride in soil was extracted with H_2SO_4 under reflux [9] and in tea leaves was extracted with the mixture of methanol and HCl [10] under sonication and centrifugation. The filtered digest of soil is percolated through column of amberlite cation exchange resin [11] slowly and the sorbed paraquat dichloride was eluted using saturated ammonium chloride solution. A portion of the eluted saturated ammonium chloride solution of soil extract and acidified methanol tea leaf extract was treated with alkaline sodium dithionite solution and the intensity of the blue colour developed was measured differentially at 396 nm. The paraquat cation content was obtained by reference to a calibration graph prepared concurrently using blank matrix with series of analysis.

Instrumentation and calibration: The UV-visible spectrophotometer of Varian make; Cary 100 model was used to analyze the paraquat. Before analyzing the samples, the lamda max of the paraquat was identified by scanning the working standards from 190 to 800 nm (Fig. 1) and found two lamda max were 396 nm and 610 nm. Since the peaks were sharp and detection was clear at 396 nm, further analysis of the samples were done at this wavelength. A calibration curve was prepared by plotting the different concentrations of paraquat dichloride (0.01, 0.05, 0.10, 0.5 mg/kg) on X-axis against the absorbance at 396 nm on Y-axis (Fig. 2).

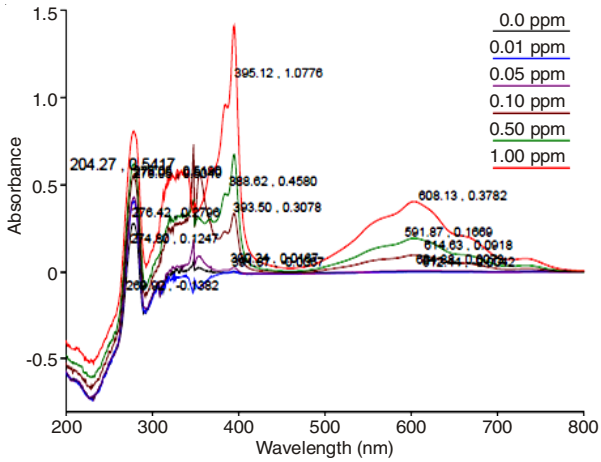


Fig. 1. Scanning chromatogram of paraquat standards from 190 to 800 nm analyzed by UV-Visible Spectrophotometer

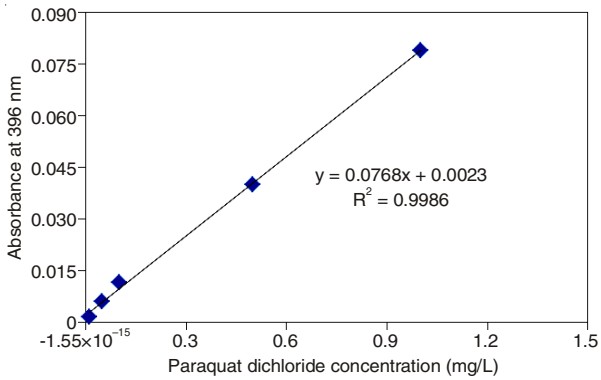


Fig. 2. Calibration curve for paraquat dichloride analytical standards

Method validation and limits of detection: Before proceeding to the persistence analysis of paraquat in soil and tea leaves, the method was validated by fortifying control samples with the known volume of working standards of paraquat. Method validation was done as suggested by Janaki *et al.* [12]. The 5 mL of known concentrations of 0.01, 0.05, 0.10 and 0.50 µg/mL of paraquat dichloride solution were used for

fortification. After 1 h, both fortified soil and tea leaves were subjected to extraction, clean up and spectrophotometric determination as mentioned for paraquat residue extraction from soil and tea leaves. The concentration of paraquat dichloride in different matrix samples (mg kg^{-1}) was calculated as follows:

$$\text{Paraquat content (mg kg}^{-1}\text{)} = \frac{\text{Volume of eluent from column (mL)} \times \text{Concentration in eluent (mg kg}^{-1}\text{)}}{\text{Weight of sample (g)}}$$

$$\text{Paraquat dichloride content (mg kg}^{-1}\text{)} = \frac{100 \times \text{paraquat content (mg kg}^{-1}\text{)}}{72.3*}$$

Note: *Paraquat dichloride contains 72.3 % paraquat cation content.

Data analysis: Rates of dissipation for paraquat in soil were calculated using the method described by Timme *et al.* [13].

RESULTS AND DISCUSSION

Method validation: Validation of the extraction method is a vital prerequisite to ensure quality and reliability of the results for all analytical applications. The linearity, accuracy, precision (RSD), coefficient of determination (R^2), limits of detection (LOD) and limit of quantification (LOQ) were the factors used for validation.

Linearity of the paraquat detection was assessed using the calibration curve of standard solutions (Fig. 2) and found that the coefficient of determination was significant and is more than 0.99**.

Accuracy of the method adopted was evaluated in terms of recovery studies and the recovery ranged from 77.8 to 85.0 % for paraquat from different matrices (Table-2). The average recovery of paraquat from field soil and tea leaves was 80.3 and 83.7, respectively. Since the standard deviation between the replication data was less than 10 %, the method followed for extraction and detection of residues of both the paraquat was found to be precise.

Limit of detection and limit of quantification: Limit of quantification was calculated by taking into account the herbicide concentration in control fortified samples, volume of extractions, size of sample taken for analysis and the minimum amount of that can be determined without ambiguity. While the limit of quantification (LOQ) was found to be 0.08 and 0.05 µg/g for field soil and tea leaves respectively, the limit of detection (LOD) obtained was 0.05 µg/g for both the matrices (Table-2). Similar detection limits of 0.01 mg/kg for paraquat in soil and biological tissues using spectrophotometer was also reported Calderbank and Yuen [14].

Degradation of paraquat in soil: Paraquat as one time application was given to tea cropped field at two rates *viz.*, 2.0 and 2.0 g AI ha^{-1}. Residue was monitored in soil and tea leaves up to 100 days after its application. The initial deposit of paraquat on 0 day was 1.62 and 3.47 mg kg^{-1} of soil at 2 and 4 g AI ha^{-1} respectively (Table-3) and was found that the residue decreased with the advancement of the time. At both the rates of application, it was found that more than 50 % of applied paraquat dissipated from soil on 25th day (Table-3 and Fig. 3). Though the paraquat was strongly adsorbed by the soil and did not degrade rapidly due to the non-availability for the microorganisms [15], the unbound paraquat was readily degraded by soil microorganisms and hence the paraquat residue concentration decreased with the time. The dissipation of more than 90 % of the applied paraquat from soil took 75 days and on day 100 residue becomes below detectable level (0.01 mg/kg). Though paraquat is immobile and tightly sorbed by the soil particles, paraquat initial deposition and further concentration were considerably high in the soil and was detected upto 100 days. This could be attributed to the weaker sorption of paraquat in soil with lower pH [16] and high organic matter; hence the residue remains active and persists in soil upto 100 days. Decrease in the sorption capacity of paraquat to soil with decrease in pH and increase in organic matter was also reported by the Wong *et al.* [5]. Further the residue of paraquat below in soil after 100 days might also be attributed to the loss of soil which sorbed paraquat through erosion influenced by the higher and natural slope (> 10 %) where the tea leaves is grown usually.

TABLE-3
PERSISTENCE AND DISSIPATION OF PARAQUAT IN SOIL UNDER TEA

Days after herbicide application	Residue concentration (mg/kg)		Dissipation (%)	
	2 kg/ha	4 kg/ha	2 kg/ha	4 kg/ha
0	1.624 ± 0.04*	3.470 ± 0.07*	18.8	13.3
10	1.173 ± 0.11	2.857 ± 0.09	41.4	28.6
25	0.887 ± 0.08	1.974 ± 0.10	55.7	50.7
50	0.405 ± 0.09	0.979 ± 0.10	79.8	75.5
75	0.124 ± 0.06	0.161 ± 0.09	93.8	96.0
100	BDL	BDL	–	–

*(±) standard deviation of three replicates

Dissipation parameters for paraquat residue were calculated using first order kinetics equation $\ln C_t = \ln C_0 - k_t$ and where C_t (µg g^{-1}) represents its concentration at time 't' (days), C_0 (µg g^{-1}) represents the initial concentration, k is the first-order rate constant and $t_{1/2}$ is the half-life (DT_{50}) of paraquat. Good linearity was found between log concentration of paraquat residue in soil and time indicating first order rate of dissipation. Paraquat in soil at 2.0 and 4.0 ai kg ha^{-1} dissipated according to equation y = 1.298-0.0127x and y = 2.946-0.028x, respectively (Fig. 3). The DT_{50} values of paraquat in tea grown acid hilly soil calcu-lated from the regression equation was ranged between from 24.95 to 27.39 days at the two rates of application (Table-4). Similar half life of 36-46 days for paraquat with

TABLE-2
AVERAGE RECOVERIES OF PARAQUAT FROM FORTIFIED SOIL AND FRESH TEA LEAVES

Matrix	Concentrations fortified (µg g^{-1})					LOD (µg g^{-1})	LOQ (µg g^{-1})
	0.5	0.1	0.05	0.01	0.005		
Field soil	77.8 ± 5.42*	79.0 ± 3.12	84.0 ± 5.21	BDL	BDL	0.05	0.08
Tea leaves	84.2 ± 5.70	85.2 ± 4.14	81.7 ± 3.64	BDL	BDL	0.05	0.05

*(±) Standard deviation of three replicates; BDL - Below detectable level

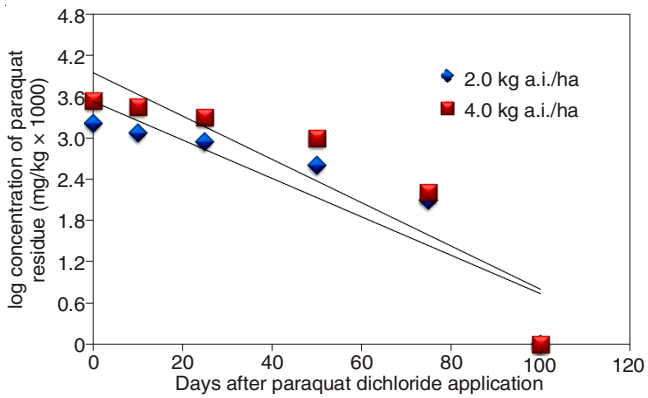


Fig. 3. Degradation of paraquat in soil as a function of concentration *vs.* time

TABLE-4
REGRESSION EQUATION, DEGRADATION CONSTANT, CORRELATION COEFFICIENT AND THE HALF-LIVES ($t_{1/2}$) OF PARAQUAT IN FIELD SOIL

Dose (kg ai ha^{-1})	Regression equation	k (days)	Coefficient of determination (R^2)	Half life (days)
2.0	y = -0.0127x + 1.2977	0.0278	0.871	24.95
4.0	y = -0.028x + 2.9455	0.0253	0.903	27.39

first-order kinetic model was reported by Amondham *et al.* [17] and also found that the degradation of paraquat in soil was faster under field conditions than at ambient laboratory conditions.

Degradation of paraquat in tea leaves: The tea leaves were collected and analyzed for its residue on 0 to 100 days at periodical interval and found that the paraquat residues were below detectable level of 0.05 mg kg^{-1} in tea leaves under both the dose of application throughout the sampling period. Since the paraquat was applied as direct spray on weeds, the residues were not detected in the tea leaves during the initial period. This suggested that the translocation of paraquat from soil to tea plant is very low and might be due to the non-availability of the residue in the root rhizosphere region. At later periods also, the paraquat residue was found to be below detectable level which shown that the uptake and translocation of paraquat by the tea leaves from soil was low due to the hardy nature of the crop and deep root system. The comparative uptake and translocation of ^{14}C-paraquat by tolerant and susceptible soybean cultivar was also reported by the Kim and Hatzois [18].

From this study it was found that the detectable residues (> 0.05 mg/kg) of paraquat was not found on 100th day after its application at any of the dose of application which is well the below the tolerance of paraquat residues in tea fixed by the European Union and Japan as 0.1 and 0.05 mg/kg respectively [19]. Though the tolerance level of paraquat was not yet fixed by the food safety and standards of India (FSSAI) for the tea, the paraquat residues detected in this study, (< 0.05 mg/kg) is well below the tolerance limit of 0.05 and 0.2 mg/kg prescribed by the FSSAI [20] in vegetables and potato respectively. Similarly the residue of paraquat in the present study is also below the tolerance level established for the residues of paraquat, including its metabolites and degradates, in or on the tuberous and corm vegetables of 0.5 and 0.05 mg/kg respectively [20] by CODEX and Fedral Food, Drug and Cosmetic Act (FFDCA).

Conclusion

Based on the present study, it is concluded that the paraquat dichloride at recommended level @ 2.0 kg AI/ha can be used for controlling the weeds in tea plantations with the pre harvest interval of 100 days. However care must be taken to avoid the soil erosion and intercropping as the paraquat residue persist in soil upto 75 days with the detection limit of 0.05 mg kg^{-1} which may have carry over problems to the sensitive crops. Further the erosion of soil immediately after the application of paraquat may contaminate the low lying land and water bodies if the rainfall is heavy. The persistence and dissipation behaviour of paraquat in the soil reveals that the indiscriminate and continuous use of paraquat should be avoided in tea garden which may otherwise contaminate the soil environment through bioaccumulation in the soil and crop produce.

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