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Soil Persistence of Diuron Applied to Cotton Cultivation in Red and Black Soils

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Authors' contributions

"This work was carried out in collaboration among all authors. Author MMF designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors TR and TA managed the analyses of the study. Author MM managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Persistence of diuron applied to cotton as preemergence spray at varied rates of application (0.5, 0.75, 1.0 kg ha^{-1}) was studied in field experiments conducted simultaneously in red and black soils at Professor Jayashankar Telangana State Agricultural University, Rajendranagar during *kharif*, 2018. In both red and black soils, persistence of diuron was observed beyond 120 days after application and the concentration of diuron in the top soil (0-15 cm) was higher in black soils compared to red soils from 0 Days to 120 Days. Higher dose of diuron showed greater soil persistence in both red and black soil. Diuron dissipation in soil followed first order kinetics in both the soils. Field half life of diuron was higher in black soil was 53.3-77.0 days at different rates of application than in red soil (53.3-69.3 days).

Keywords: Diuron; persistence; half life; herbicide residue.

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1. INTRODUCTION

Weeds are one of the major constraints in cotton production which may reduce the yield up to 80% [1]. Critical period of weed competition in cotton was found to be 15-60 days after sowing [2]. In widely spaced crops such as cotton, weeds get ample opportunity to compete with cotton plants for the scarcely available soil moisture and nutrients in the early stages of crop growth. Pre-emergence herbicides are the most important weed management interventions in weed-free establishment of the crop. So, the application of pre-emergence herbicides provides a foundation for season long weed management.

At present, pendimethalin and alachlor are the two pre-emergence (PE) herbicides registered for use in cotton besides diuron. As alachlor is being phased out of use by 2020, pendimethalin will remain as sole preemergence herbicide registered for use in cotton [3]. Further, it is a well-known that, utilising the same herbicide/herbicides with same mode of action over years can have adverse effects like development of resistance in weeds and poor bio-efficacy over long periods of time. Further, continuous usage of same herbicide may also negatively influence different properties of soil like soil enzyme activity and soil microbial population. Even though diuron is registered for use in cotton, its current usage is very low owing to its long residual life and phytotoxicity in the applied crop as well as crops sown in rotation on same field. These situations demand use of an alternate pre-emergence herbicide to be used in rotation with pendimethalin for effective weed management. So, there emerges a need to re-evaluate diuron, registered for pre-emergence use in cotton, keeping in view the safe practise of rotating herbicides with different modes of action.

Diuron is a broad spectrum herbicide belongs to the phenylurea group of herbicides that kills plants by blocking electron transport at photosystem II, thus inhibiting photosynthesis.

Diuron has a prolonged soil residual life making it more suitable for cotton crop due to its slow initial growth. Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl urea ($C_9H_{10}Cl_2N_2O$). Diuron is relatively stable in the environment; however, it can be hydrolysed under acidic and alkaline conditions or at high temperatures. It has a low solubility in water (42 mg litre^{-1}) at 25 °C and a high adsorption rate onto the soil particles (K_{OC} = 418 – 560). This pesticide has a low n-octanol-water partition coefficient (log K_{OW}), of 2.87 [4,5,6]. Therefore, it can be regarded as being highly persistent in the soil and poses a risk to water bodies and sediments through leaching processes. Even though, information on persistence of diuron in red and black soils is very scanty under Telangana. Hence, the field trial was conducted to evaluate the persistence of diuron applied at varied doses at different intervals of time in cotton cultivated in red and black soils.

2. MATERIALS AND METHODS

2.1 Experimental Site and Meteorological Information

A field experiments were carried out at College Farm, College of Agriculture, Professor Jayashankar Telangana State Agricultural University, Rajendranagar, Hyderabad, Telangana state. The farm is geographically located at 17^{o}19' N latitude and 78^{o}23' E longitude at an altitude of 542.6 m above mean sea level (MSL). The climate of the region is semi-arid. More than 80% of rainfall is received from South-West monsoon (June-October). Bothe the field trial sites are located in same experimental farm within few hundred meter distance. Red soil experiment site was sandy clay in texture with neutral pH, non-saline and classified as Typic Haplustalf. Black soils site was classified as Vertic Haplustept with clay loam texture, slightly alkaline pH and non-saline.

Field experiments were laid out in a Randomized Block Design comprising of seven treatments which were replicated thrice. “First Class BG II” cotton hybrid seeds of Bayer company were sown at a seed rate of 2.5 kg ha^{-1}. Seeds were sown at a spacing of 90 x 60 cm. Thinning was done within two weeks of sowing to maintain optimum plant population. Pre-emergence herbicides, diuron 80% WP (“Karmex” of Adama India Pvt. Ltd) at 0.5 kg ha^{-1}, 0.75 kg ha^{-1} and 1.0 kg ha^{-1}; and pendimethalin 38.7% CS at 677 g ha^{-1} were sprayed with knapsack sprayer fitted with flat fan nozzle at two days after sowing. Spray volume applied was 500 lha^{-1}. Pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop ethyl 5% EC 50 gm ha^{-1} were sprayed at 2-3 leaf stage of the weeds. Polyfilm was spread one day before sowing and seeds were sown by making holes on film at designated spacing. Mechanical weeding was done at 20, 40, 60 DAS with power weeder (Honda F300) and an unweeded control was maintained without any weeding from sowing to harvest.

2.2 Soil Sampling and Extraction of Diuron Residues from Soil

Soil samples were collected from the cotton field two hours after the spray of herbicide diuron. Diuron was extracted by the standard procedure [7]. Soil sample (25 g) was weighed into an Erlenmeyer flask and to this 50 ml of methanol was added and kept for shaking for a period of one hour. The soil slurry was filtered through filter paper and resulting aliquot was evaporated in a rotovapor at 40°C. The residue was then redissolved in 3 ml of methanol and filtered through a 0.45µm Millipore filter directly into glass vials and stored at 4°C until further use.

2.3 Instrumentation

Herbicide diuron and its metabolites were analyzed by HPLC using a Waters Alliance® e2695 Separations Module (Milford, MA, USA) equipped with degasser, quaternary solvent organizer pump, autosampler and a Waters 2998 photodiode array detector. Separations were performed using a XTerra C-18 column (4.6 x 250 mm, 5 µm) from Waters Corporation. Data acquisition and treatment were performed using an Empower 2.0® software package. Ideal analytical conditions able to promote separation of diuron was obtained using a mobile phase composed by water and acetonitrile (55:45 v/v) at 0.86 mL min^{-1}. Sample injection volume was 20 µL with detection done at 254 nm. Column and injector temperature were maintained at 30°C and 20°C, respectively. Diuron analysis was carried out on HPLC with UV detector after extraction from soil, clean-up and reducing the volume. Equal volumes of different standard concentrations of diuron *viz.,* 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 µg mL^{-1} were injected and their corresponding peak areas were recorded.

3. RESULTS AND DISCUSSION

Under the given conditions of HPLC, diuron was resolved at 12.65 min as a single sharp peak. Analytical calibration graph (Fig. 1) equation obtained by plotting peak areas of diuron standards in the range of 0.05 µg mL^{-1} to 0.5 µg mL^{-1} on ‘y’ axis versus concentrations of diuron on ‘x’ axis. A straight line equation y = 317585x + 3419.5 was obtained from the resultant graph. This showed good linearity with the correlation coefficient of 0.997 (r^2 = 0.997).

Following data shows the response of diuron standards in HPLC at different concentrations. Linearity was drawn on the basis of this data.

Table 1. Response of diuron standards in HPLC at different concentrations

Concentration (µg/ml)	Peak areas
0.05	16589
0.1	34578
0.2	69155
0.3	103733
0.4	128320
0.5	160400

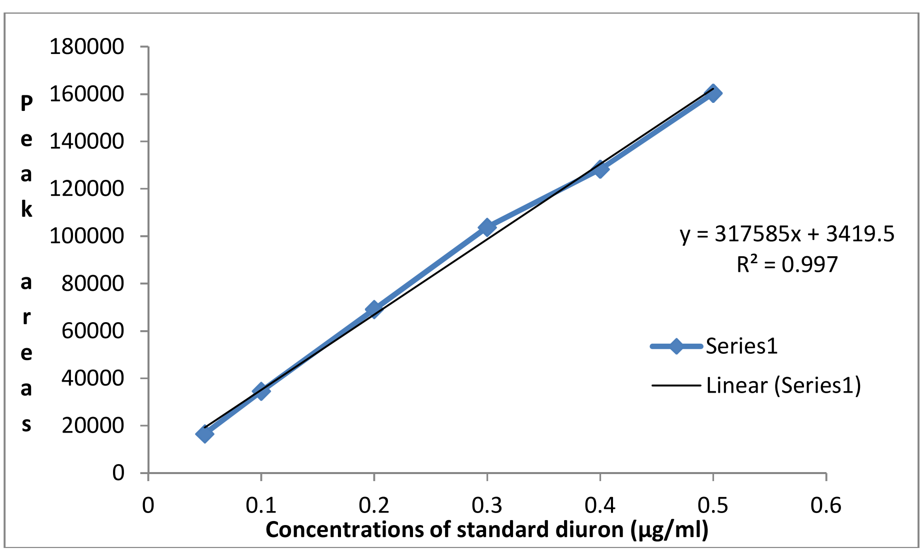

Fig. 1. Calibration curve of diuron standards

The LOD and LOQ reported for diuron was 0.0163 μg g^{-1} and 0.05 μg g^{-1} respectively.

The persistence of diuron was determined in samples collected at 0, 7, 15, 30, 60, 90 and 120 days after application in 0.5 kg ha^{-1}, 0.75 kg ha^{-1} and 1.0 kg ha^{-1} doses. The data obtained from the study was subjected to regression analysis to determine the half life (DT_{50}).

While studying the degradation pattern of the diuron it was observed that it follows the first order kinetics and mathematically represented as

$$C_t = C_0.e^{-kd} t. \quad (1)$$

The linearized form of this equation is

$$\log (C_t / C_0) = - 0.4343\, K_d\, t. \quad (2)$$

3.1 Dissipation of Diuron in Red Soil

Diuron persistence in red soil (Table 2) was observed from the day of application to beyond 120 days after application (harvest). On 0 Days (at two hours after diuron pre-emergence spray), highest concentration of diuron was recorded in 1.0 kg ha^{-1} (0.395 μg g^{-1}), followed by 0.75 kg ha^{-1} (0.306 μg g^{-1}) and 0.5 kg ha^{-1} (0.263 μg g^{-1}). Concentration of diuron decreased as the time progressed from the day of application to 7, 15, 30, 60, and 90 DAYS and harvest. Lowest concentration of diuron residue was recorded at 120 DAYS from plots which received diuron 0.5 kg ha^{-1} (0.056 μg g^{-1}) followed by 0.75 kg ha^{-1} (0.065 μg g^{-1}) and 1.0 kg ha^{-1} (0.084 μg g^{-1}). The graph showing persistence of diuron at different days after application in red soil was plotted by taking concentration of diuron on 'y' axis and time intervals on 'x' axis (Fig. 2). Different curves of fit were tested to predict the dissipation behaviour of the diuron. Among the models tested (linear, polynomial, logarithmic and exponential) the exponential model was found to give better fit for field dissipation of the diuron at 0.5, 0.75 and 1.0 kg ha^{-1} doses. Mathematically, diuron dissipation followed a first-order (or more correctly for field dissipation, pseudo first-order) decay process.

Applying first order kinetics equation, the dissipation trends of diuron at different doses of application are as following.

For 0.5 g/ha dose $\quad y = 0.2240e^{-0.013x}$ R^2 = 0.957 (3)

For 0.75 g/ha dose $\quad y = 0.2663e^{-0.011x}$ R^2 = 0.963 (4)

For 1.0 g/ha dose $\quad y = 0.3353e^{-0.010x}$ R^2 = 0.974 (5)

DT_{50} of diuron in soil was calculated from the exponential equations obtained from the dissipation curves. The field half-life of diuron 1.0 kg ha^{-1} was longer (69.3 days) than when diuron applied at 0.5 kg ha^{-1} and 0.75 kg ha^{-1} whose half lives were 53.3 and 57.8 days respectively.

3.2 Dissipation of Diuron in Black Soil

Diuron persisted in black soil beyond the period of harvest (120 days) at the rates of application tested in the experiment (Table 3). The initial concentration of diuron recorded (at 2 hours after application) in the top soil was 0.316 μg g^{-1}, 0.367 μg g^{-1} and 0.474 μg g^{-1} in 0.5 kg ha^{-1}, 0.75 kg ha^{-1} and 1.0 kg ha^{-1} treatments respectively. However, from 0 DAYS the concentration of diuron recorded in soil reduced as the time progressed *i.e.* 7, 15, 30, 60 and 90 DAYS till harvest. Terminal concentration of diuron residue (recorded at 120 DAYS) was 0.067 μg g^{-1} (0.5 kg ha^{-1}) and 0.078 μg g^{-1} in 0.75 kg ha^{-1} dose and 0.101 μg g^{-1} in 1.0 kg ha^{-1} dose. Graph showing persistence of diuron in black soil was plotted by taking concentration of diuron on 'y' axis and time intervals (DAYS) on 'x' axis (Fig. 3). Dissipation of diuron in black soil also followed first order kinetics, where the increase in the dose of application increased the diuron persistence in soil.

Kinetics equation of diuron at different doses of application in black soils are

For 0.5 g/ha dose $\quad y = 0.3033e^{-0.013x}$ R^2 = 0.987 (6)

For 0.75 g/ha dose $\quad y = 0.3302e^{-0.012x}$ R^2 = 0.982 (7)

For 1.0 g/ha dose $\quad y = 0.3977e^{-0.009x}$ R^2 = 0.956 (8)

The field half-life of diuron was longest (77.0 days) in soil where diuron was applied 1.0 kg ha^{-1} compared to the other doses of application i.e. 0.5 kg ha^{-1}(53.3 days) and 0.75 kg ha^{-1} (63.0 days).

Table 2. Concentration of diuron (µg g^{-1}) in soil at different intervals in red soil

Treatment	Days after herbicide application						
	0	7	15	30	60	90	120
Diuron 80% WP 0.5 kg ha^{-1} as PE *fb* pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop p ethyl 5% EC 50 g ha^{-1} as PoE.	0.263	0.196	0.177	0.145	0.115	0.084	0.056
Diuron 80% WP 0.75 kg ha^{-1} as PE *fb* pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop p ethyl 5% EC 50 g ha^{-1} as PoE.	0.306	0.236	0.212	0.172	0.134	0.122	0.065
Diuron 80% WP 1.0 kg ha^{-1} as PE *fb* pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop p ethyl 5% EC 50 g ha^{-1} as PoE.	0.395	0.321	0.244	0.206	0.177	0.124	0.084

Table 3. Concentration of diuron residue (µg g^{-1}) in soil at different intervals in black soil

Treatment	Days after herbicide application						
	0	7	15	30	60	90	120
Diuron 80% WP 0.5 kg ha^{-1} as PE *fb* pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop p ethyl 5% EC 50 g ha^{-1} as PoE.	0.316	0.292	0.241	0.191	0.125	0.085	0.06
Diuron 80% WP 0.75 kg ha^{-1} as PE *fb* pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop p ethyl 5% EC 50 g ha^{-1} as PoE.	0.367	0.307	0.264	0.212	0.149	0.122	0.07
Diuron 80% WP 1.0 kg ha^{-1} as PE *fb* pyrithiobac sodium 10% EC 62.5 g ha^{-1} + quizalofop p ethyl 5% EC 50 g ha^{-1} as PoE.	0.474	0.385	0.293	0.237	0.201	0.135	0.10

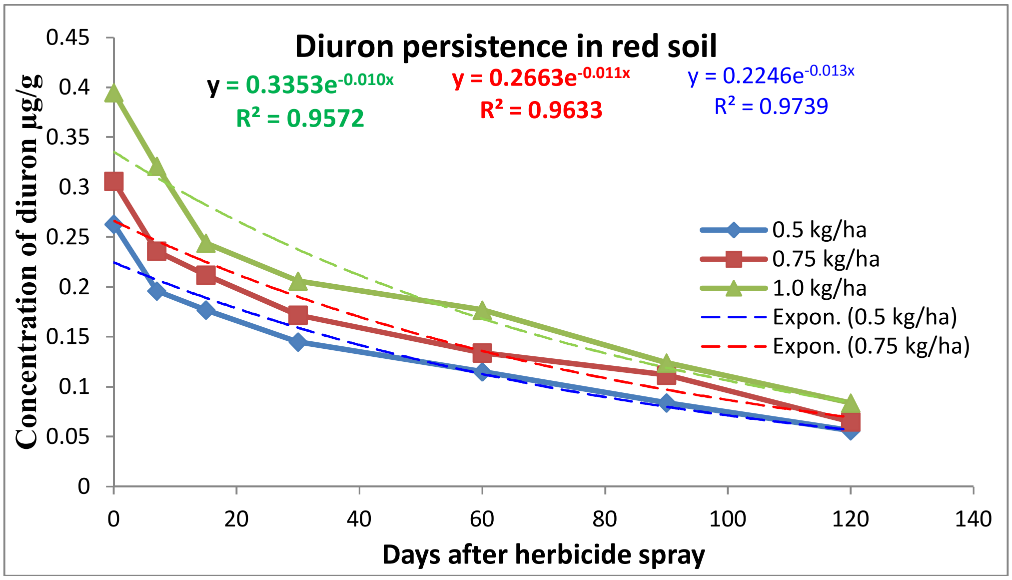

Fig. 2. Persistence of diuron (µg g^{-1}) at different intervals in red soil

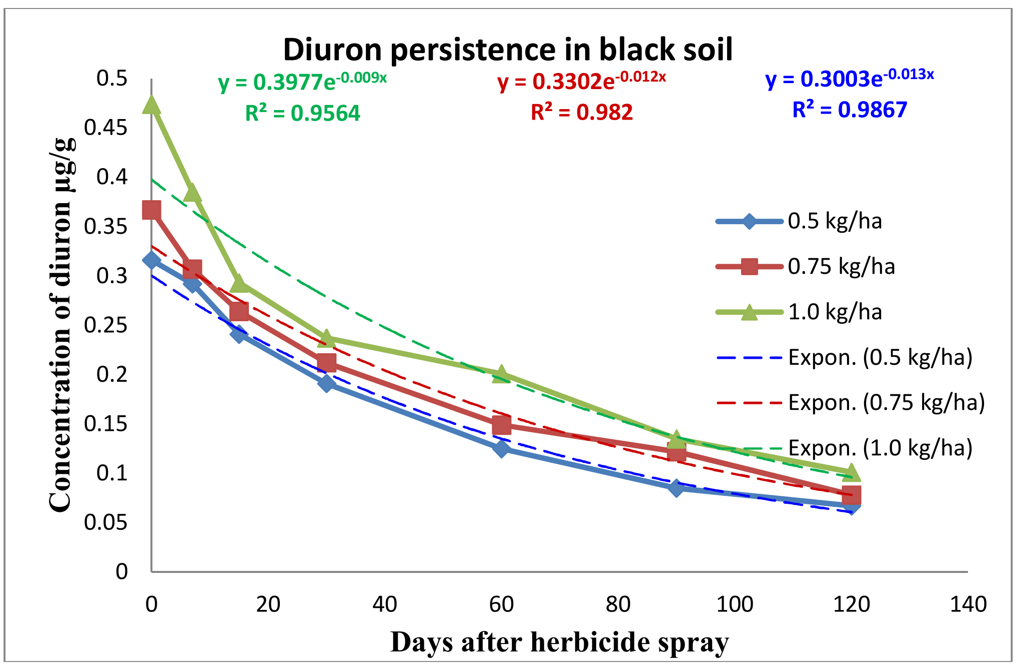

Fig. 3. Persistence of diuron (µg g^{-1}) at different intervals in black soil

In the environment, diuron can be transformed abiotically *via* hydrolysis and photodegradation reactions, but under natural conditions these reactions occur at very low rates. The dissipation of diuron from the environment is thus mainly due to biotic processes, the aerobic microbial metabolism being the major form of diuron transformation. The main reactions involved are N-demethylation and hydrolysis of the amide bond. In most cases, mono and di methylated compounds and 3,4-dichloroaniline appear as the main products of microbial metabolism [8].

Diuron degradation data fit a first-order reaction kinetics model, yielding half-lives in soils ranging from 40 to 267 days [9]. Other researchers [10] studied diuron dissipation in soil in Belgium, in an area where this herbicide was applied for the first time and in another area where it was applied consecutively during 12 years. They reported a half-life of 81 days in the first case with a reduction to 37 days in the second case. First order reaction kinetics in dissipation of soils applied herbicides was earlier reported [11,12]. From the day of application to 15 days of application, the concentration of diuron was comparatively higher in black soils than in red soil. it may be due to the higher organic matter content present in the soil [13].

Half-life of diuron in red soil ranged from 53.3 – 69.3 days and in black soil 53.3 – 77 days (or DAYS). Most studies on the persistence of diuron residues in soil reported that the half-life of diuron ranged from 90 – 365 days, depending on the application rate and various other factors such as, adsorption rate on soil particles, pH, organic matter and rainfall [14].

Prolonged persistence of soil applied herbicides when used double the recommended rates compared to normal application rates, especially when applied to soils with low organic carbon status [15,16]. Lower amount of clay content in red soil might be other potential reason of poor persistence of diuron with respect to black soil. Other researchers [17] stated that clay minerals can strongly adsorb certain aqueous phase organic compounds containing polar functional groups, suggesting the potential contributions of clay minerals to the retention of organic contaminants and pesticides in soils and subsoils.

4. CONCLUSION

In both red and black soils, persistence of diuron was observed beyond 120 days after application and the concentration of diuron in the top soil (0-15 cm) was higher in black soils compared to red soils from 0 DAYS to 120 DAYS. Higher dose of diuron showed greater soil persistence in both red and black soil. Diuron dissipation in soil followed first order kinetics in both the soils. DT_{50} of diuron was more in black soil (53.3-77.0 days) than in red soil (53.3-69.3 days). Higher doses of diuron showed larger DT_{50} values in both soils.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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