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The Influence of Filter Mud Compost and *Tithonia diversifolia* Leaves on the Dissipation of Diuron in Soils within the Nzoia River Drainage Basin, Kenya

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Abstract The aim of the study was to evaluate the environmental impact of filter mud compost and *Tithonia diversifoila* amendments on the dissipation of diuron in sugarcane cultivated soils. Filter mud compost is the by-product of sugarcane processing, while *T. diversifoila* is a common local plant that grows within the study region. The dissipation of diuron was significantly enhanced with DT_{50} of 15 and 16 days ($p < 0.05$) in soils amended with filter mud compost and *T. diversifoila*, respectively compared to 26 days in non-amended soils. Residues of 0.93 %, 1.83 % and 5.40 % of the initial applied diuron were recorded at the end of the experiment in the three treatments, respectively. The residues of 3,4-dichlorophenylmethylurea metabolite were 22.93 %, 25.92 % and 30.93 %, while 10.19 %, 12.19 % and 15.46 % of 3,4-dichloroaniline metabolite remained in soil after 112 days in the three treatments, respectively.

Keywords Diuron · Dissipation · Filter mud compost · *Tithonia diversifolia*

Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is a non-selective pre- and post-emergence phenylurea herbicide widely employed in both agricultural and non-agricultural areas. In Kenya, diuron has been used for over 20 years to control weeds in sugarcane fields within the Nzoia River Drainage Basin (NRDB), where it is applied at the rate of 5 kg a.i/ha. As a result, it has been detected in surface and ground water bodies raising a lot of environmental concerns based on its high toxicity (Sebai et al. 2010; Bois et al. 2011). The slow dissipation of diuron from soils coupled with its high water solubility (42 mg/L at 20°C) exacerbates the contamination potential by this chemical (Field et al. 2003). Microbially facilitated degradation is major dissipation route of diuron (Sebai et al. 2010). Diuron is moderately recalcitrant in soil due to its relative chemical stability and strong adsorption to soil with reported half-lives of 1 month to 1 year (Castillo et al. 2008). Amending the soil with organic materials like compost and manure increases microbial populations hence a faster rate of biodegradation of pesticides (Getenga 2003; Cayuela et al. 2009). Pesticides can also be adsorbed onto organic matter present in the organic amendment, hence minimizing its bioavailability to degrading microbes in the liquid phase (Kravvariti et al. 2010). However, microbial degradation has been reported to occur more extensively in the solid phase due to constant re-establishment of equilibrium as the dissolved substrate is being metabolized (López-Piñeiro et al. 2010). The capability of extracellular enzymes produced by microbes to transform the adsorbed pesticides may enhance degradation in solid phase (Kravvariti et al. 2010). In addition, alteration of the pH of microsites by exudates produced by microbes renders hydrophobic xenobiotics more hydrophilic and thus enhances their degradation (López-Piñeiro et al. 2011).

In a study by Mukherjee (2009), atrazine degradation was enhanced in soils amended with farm yard manure, rice straw and saw dust. Another study by Herrero-Hernandez et al. (2011), reported enhanced dissipation of tebuconazole fungicide in soils amended with spent mushroom substrate. Most of these studies were conducted in temperate regions; yet, information on the use of organic amendments in tropical soils, especially within the NRDB is scarce (Daam and Brink 2010). A laboratory study by

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Getenga (2003) reported enhanced biodegradation of atrazine in soils amended with municipal compost, while a field study by Lalah et al. (2009) conducted within the NRDB reported slight enhancement of hexazinone dissipation in soils amended with sugarcane barggase. However, the influence of filter mud compost (FMC) and *Tithonia diversifolia* leaves (TD) on the dissipation of diuron within the study area is unknown. Filter mud compost is the waste product in vacuum and press filters of the sugar industry which is about 3 %–8 % of processed sugarcane (Jamil et al. 2008). Sugarcane farming is the major agricultural activity within the NRDB in Kenya resulting in production of approximately 240,000 tonnes of filter mud annually. Utilization of this organic material will provide an environmentally friendly management strategy of disposing this waste product. *T. diversifolia* is a local plant that rapidly grows on the hedges and boundaries of sugarcane farms with an average of 10 tonnes harvestable biomass per hectare yearly. The low nutrient levels of most tropical soils under continuous monoculture together with erosion and desertification, makes the use of FMC and TD important in restoring the soil structure, improving crop yields and minimizes the impact of inorganic fertilizers (Cabrera et al. 2010). Simultaneous application of FMC, TD and diuron to soils may lead to potential interaction of this pesticide with the amendment which could modify the dissipation behaviour and persistence of diuron in soils. Therefore, the objective of this study was to investigate the influence of filter mud compost and *T. diversifolia* leaves on the dissipation of diuron under field conditions.

Materials and Methods

Analytical grade reagents and HPLC grade solvents were purchased from Sigma Aldrich through Kobian Kenya Limited (Nairobi, Kenya). High purity pesticide standards (>99 %) were purchased from the laboratories of Dr. Erhenstofer GmbH (Augsburg, Germany). These were; diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), 3,4-dichloromethylphenylurea (DCPMU) and 3,4-dichloroaniline (DCA) and 1,3-dimethyl-2-nitrobenzene (DMNB) of purity 99.5 % was (surrogate standard). Whatman extraction thimbles (30 × 100 mm) and octadecyl cartridges (C_{18}-E, Phenomenex) were purchased from Kobian Kenya Limited. A LC-20AT Shimadzu liquid chromatograph equipped with a SPD-10A VP Shimadzu UV–vis detector and a 250 × 4.6 mm Shim Pack ODS (VP-2) 5 µm column was used for HPLC analyses. A Shimadzu IR-408 double beam Infrared spectrometer was used for structure elucidation.

The study was conducted in a sugarcane (*Saccharum officinarum*) field within the Nzoia River Drainage Basin (NRDB) in Kenya. The soil classified as sandy loam, had acidic pH (4.9), low organic matter and nitrogen (3.0 % and 0.16 %), respectively. Filter mud compost (FMC) and *T. diversifolia* (TD) used in this study were obtained from Nzoia Sugar Company within the NRDB. Filter mud compost was found to have a pH of 6.3, 3.0 % N and 12.9 % organic carbon, while the properties of TD leaves were 2.94 % N and 24.84 % organic carbon.

A set of three field experiments were conducted which consisted of eight plots in a complete randomized design for the application of filter mud compost, *T. diversifolia* and a control (without amendments). Experiments were conducted using poly vinyl chloride (PVC) tubes of 6 cm diameter and 45 cm length (Lalah et al. 2009). Diuron was applied at the rate of 5 kg (a.i.)/ha which is equivalent to 1.413 mg/pipe. Filter mud compost was applied at the rate of 30 tonnes/ha which is equivalent to 8.48 ± 0.10 g/pipe, while *T. diversifolia* was applied at the rate of 5 tonnes/ha, equivalent to 1.4 ± 0.1 g/pipe. These are equivalent to the field application rates used. A 10 mL aliquots containing 1.413 ± 0.001 mg diuron was spiked into each pipe using a pipette after filling the pipe to three quarters level with soil and adding the organic amendments equivalent to the above concentrations. Soil was then added leaving about 4 cm to avoid losses through surface run-off.

The average daily rainfall in Nzoia during the first two months of the study (January and February, 2011) was 16.8 mm, whereas higher average daily precipitation of 202.85 mm was recorded during the months of March and April. The average daily soil temperature at the top 0–20 cm was 27.18°C and median wind speed of 123.1 km/h. The average daily evaporation rate recorded was 6.46 mm with a mean daily sunshine of 7.5 h. The average daily relative humidity during the experimental period was 58.5 % at 9 a.m. and 32 % at 3 p.m. Soil samples were collected immediately after application (day zero), followed by 1, 7 and 21 days, then monthly for a period of 112 days. Each time the whole pipe was removed and the samples were immediately taken to the laboratory and air dried under shade in a fume hood to reduce moisture (Lalah et al. 2009). Dry samples were weighed and passed through a 2 mm sieve after removal of coarse materials. The weight of soil in each pipe was between 1,100 ± 2 and 1,000 ± 3 g and initial concentration of diuron at day zero was between 12.85 ± 0.01 µg/g and 13.96 ± 0.03 µg/g. Diuron was extracted from soils by accurately weighing 50 ± 2 g of dry soil and transferred into a cellulose thimble. Extraction was done with 150 mL of analytical grade methanol under reflux for 8 h (Field et al. 2003). The extracts were evaporated to dryness at 45°C and re-dissolved in 5 mL of HPLC grade methanol. The sample extracts were then diluted to 250 mL with double distilled water. Clean up procedure was done using solid phase extraction (SPE) method by percolating the sample through a C_{18} SPE cartridge that had already been conditioned by passing 10 mL methanol and 10 mL double distilled water successively. The column cartridge was dried with a vacuum manifold and analytes eluted with HPLC grade methanol. The clean extracts were dried over anhydrous Na_2SO_4 in a florosil column that had been conditioned with 10 mL of HPLC grade methanol. The final volume of the extract obtained was 10 mL which was filtered through 0.45 µm nylon membrane prior to HPLC analysis. A Shimadzu LC-20AT liquid chromatograph equipped with a SPD-10A VP Shimadzu UV–vis detector and a 250 × 4.6 mm Shim Pack ODS (VP-2), 5 µm column were used for analysis. Structural elucidation of pesticides and their transformation products was done using a Shimadzu IR-408 double beam Infrared spectrometer (Hiroaki et al. 2001). Samples were evaporated to dryness and the residue ground with analytical grade potassium bromide (1:10 ratio of sample to KBr). The powder mixture was then pressed to form a translucent pellet through which the beam of the spectrometer was passed and the IR spectrum obtained (Doran et al. 2000).

Method performance was checked using samples spiked with 0.01–20 µg/mL of surrogate standards and recoveries calculated. External calibration standards were prepared in concentration ranges of up to 20 µg/mL. A midpoint calibration standard was injected after every 10 samples, throughout the analysis, to check for instrument response and drift (Field et al. 2003). Procedural blanks were analyzed in order to check for contamination in reagents and glassware. The precision and repeatability of the method was determined in sample extracts by spiking the samples with known concentrations of standards and passing through the same extraction method in six replicates (Orata et al. 2009) while the accuracy of the method was evaluated in triplicate by performing recovery tests of samples with concentrations of 0.5, 1 and 5 µg/mL. To determine the accuracy of the HPLC analysis step, standard addition experiments were performed. The limit of quantification (LoQ) of target chemicals was evaluated for each sample based on the average blank concentrations plus 5 times its standard deviation of 10 blanks (Bois et al. 2011). This value was then verified by the concentration in a standard that yielded a standard to noise (S/N) ratio of (10:1) (Field et al. 2003). The detection limit (LoD) was the injected amount that resulted in a peak with a height at least 3 times as high as the baseline noise level. Structural elucidation of metabolites formed during pesticide degradation in soils was done by infrared spectroscopy. Pesticide dissipation half-lives were determined by regression using first-order rate equation (Caracciolo et al. 2005). Statistical analysis was done using SPSS version 17.0. Analysis of variance (ANOVA) was used to evaluate the effect of different treatments on the dissipation of diuron from soil. Pair wise multiple comparisons were performed by *t* test at 95 % confidence limit (López-Piñeiro et al. 2010).

Results and Discussions

The chromatograms of the extracts presented satisfactory chromatographic resolution as shown in Fig. 1. The analytical curves and the related linear regression data indicated that the response of the UV detector was linear for all the standards analysed as shown in Fig. 1 with correlation coefficients (r^2) above 0.99 within the specified range. The detection and quantification limits of the various pesticides analyzed for Diuron, DCPMU and DCA were 0.010 ± 002, 0.005 ± 0.001, 0.020 ± 0.002 µg/mL and 0.10 ± 0.003, 0.05 ± 0.001 and 0.05 ± 0.002 µg/mL respectively.

Results of the recovery tests were good with values 78.5 ± 0.01 %, 91.6 ± 0.4 %, 82.6 ± 0.3 % and 92.2 ± 0.05 % for DCA, Diuron, DCPMU and DMNB (a surrogate standard for phynylurea pesticides) respectively. Results from the dissipation studies of diuron in soils amended with filter mud compost and *T. diversifolia* leaves are presented in Fig. 2. The dissipation behaviour of diuron in all treatments showed an initial rapid rate within the first 7 days of application, followed by a slower rate up to 81 days after which the curves leveled off attaining a plateau. In the final phase, availability of diuron residues in soil may have been the limiting factor due to diuron having been strongly bound to soil particles (Getenga et al. 2004). After 112 days, the concentration of diuron residues remaining were 5.40 %, 1.83 % and 0.93 % for soils without amendments, soils amended with *T. diversifolia* and filter mud compost, respectively. The dissipation half-

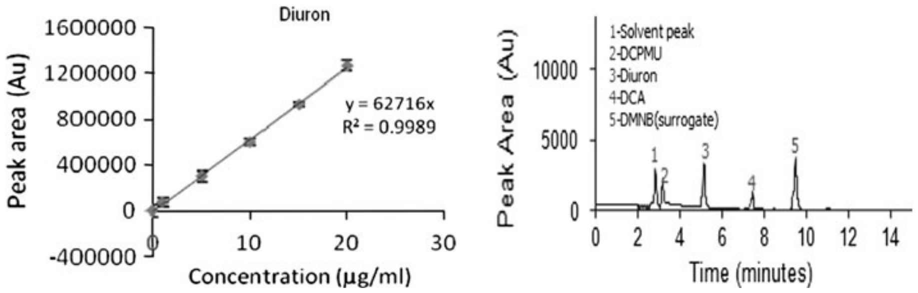


Fig. 1 Chromatograms showing separation of analytes in HPLC and calibration curve of diuron

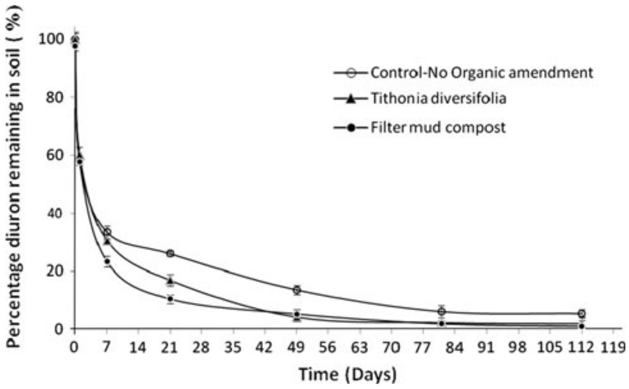


Fig. 2 The dissipation behaviour of diuron in soils amended with filter mud compost and *T. diversifolia*

Table 1 Statistical results for diuron dissipation from soil under different amendment regimes

The paired treatments	Level of significance	Conclusion
Unamended soil – soil amended with *T. diversiflia*	0.027	Significant
Unamended soil – soil amended with filter mud	0.022	Significant
Soil amended with filter mud – soil amended with *T. diversifolia*	0.076	Not significant

lives were obtained by first order kinetics and the linear curves are shown in Fig. 3. The dissipation half-lives (DT_{50}) obtained using the linear equation from each graph were 16 days and 15 days in soils amended with *T. diversifolia* and filter mud compost, respectively compared to 26 days in non-amended soils. The data obtained were subjected to one way ANOVA and the comparisons were performed by the paired *t* test. These results show significant enhanced dissipation ($p < 0.05$) of diuron from soils amended with the two organic materials (*T. diversifolia* and filter mud compost) as shown in Table 1.

However, there was no significant difference ($p > 0.05$) in diuron dissipation between the two organic amendments. Accelerated dissipation of diuron from soils amended with organic materials may be attributed to upset of nutrient balance (C/N ratio) resulting in utilization of the pesticide to regain the optimum nutrient balance, thus enhancing pesticide biodegradation (Lalah et al. 2009). Additionally, soils from the study site were deficient in nitrogen (0.16 %) and therefore, addition of T. *diversifolia* and filter mud compost with percentage nitrogen of 3.0 and 2.94, respectively probably decreased the C/N ratio creating a shortage in soil carbon. Soil microorganisms may have resorted to the use of diuron as a carbon and energy source resulting in enhanced degradation of the herbicide (López-Piñeiro et al. 2011). The metabolites of diuron formed during degradation in soils with different amendment regimes were identified and their concentrations determined. The identified transformation products were 3,4-dichlorophenylmethylurea (DCPMU) and 3,4-dichloroaniline (DCA) with retention times of 3.2 and 7.2 min, respectively. A plot of percentage metabolites formed relative to the amount of diuron applied to the soil was plotted against time and results are presented in Fig. 4a, b. Results from the study indicate the presence of 2.65 % of DCPMU in technical grade diuron. In soils amended with filter mud compost, 17.53 % of DCPMU had been formed after 1 day of application. This metabolite accumulated in soil reaching 32.88 % after 49 days and declined reaching 22.93 % at the end of the experimental period of 112 days with a concentration of 2.89 ± 0.05 μg/g. Diuron metabolite, DCA, of 1.62 % appeared in soils 7 days after application and accumulated throughout the experimental period reaching 10.19 % after 112 days with a concentration of 1.28 ± 0.02 μg/g as shown in Fig. 4a. On the other hand, DCPMU metabolite formed in soils amended with *T. diversifolia* leaves after day one of application was 4.52 %. This metabolite accumulated up to 32.67 % after 81 days and then declined to 25.92 % with a concentration of 3.27 ± 0.03 μg/g at the end of 112 days. There DCA metabolite of 0.62 % appeared after 7 days of application and accumulated up to 12.19 % with a concentration of 1.53 ± 0.02 μg/g after 112 days as shown in Fig. 4b. Results from the studies show that diuron degradation was occurred immediately in soils after amendment with filter mud compost with formation of 17.53 % DCPMU metabolite after 1 day compared to soils amended with *T. diversifolia* leaves which recorded 4.52 % DCPMU. Similarly, 1.62 % and 0.62 % of DCA metabolite appeared

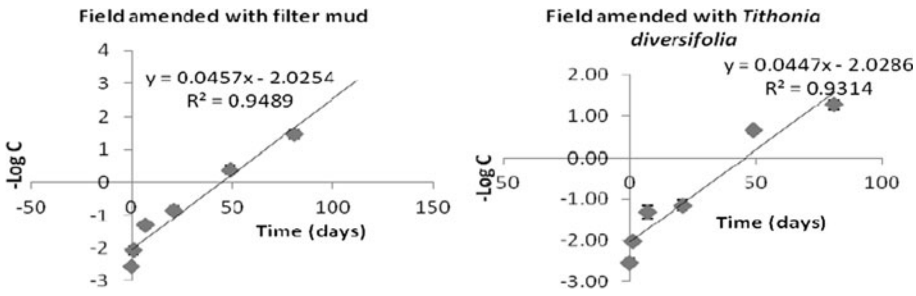


Fig. 3 Graphs showing the dissipation kinetics of diuron in soils amended with organic materials

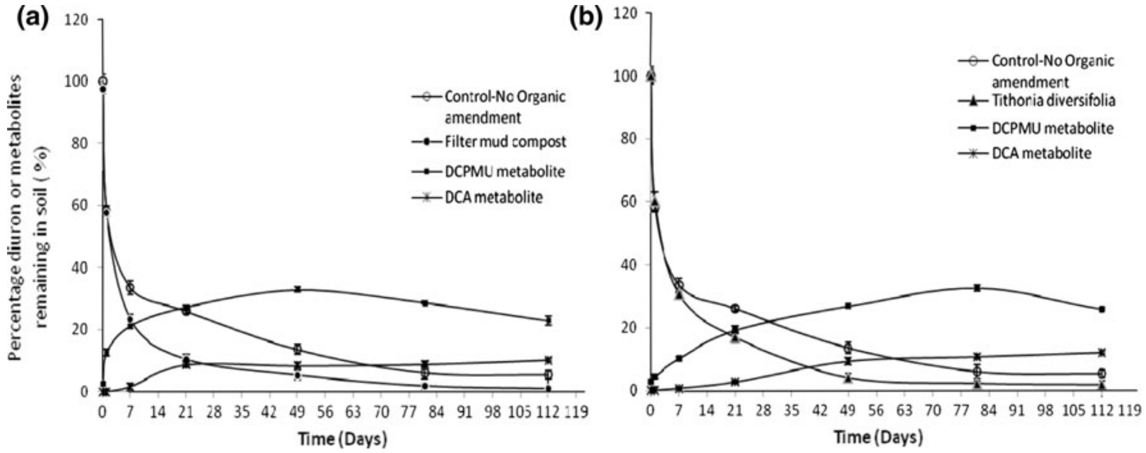


Fig. 4 Diuron metabolites formed in soils amended with filter mud compost (**a**) and *T. diversifolia* leaves (**b**)

Fig. 5 The proposed degradation pathway of diuron in soils from Nzoia

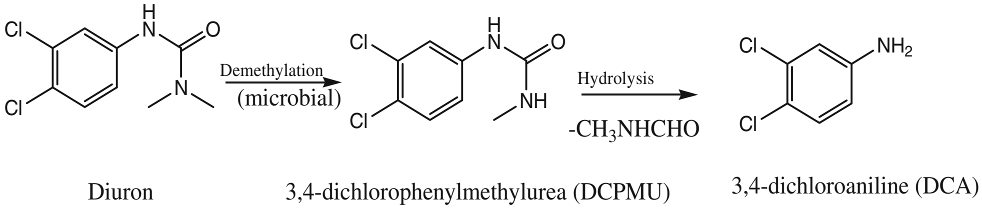
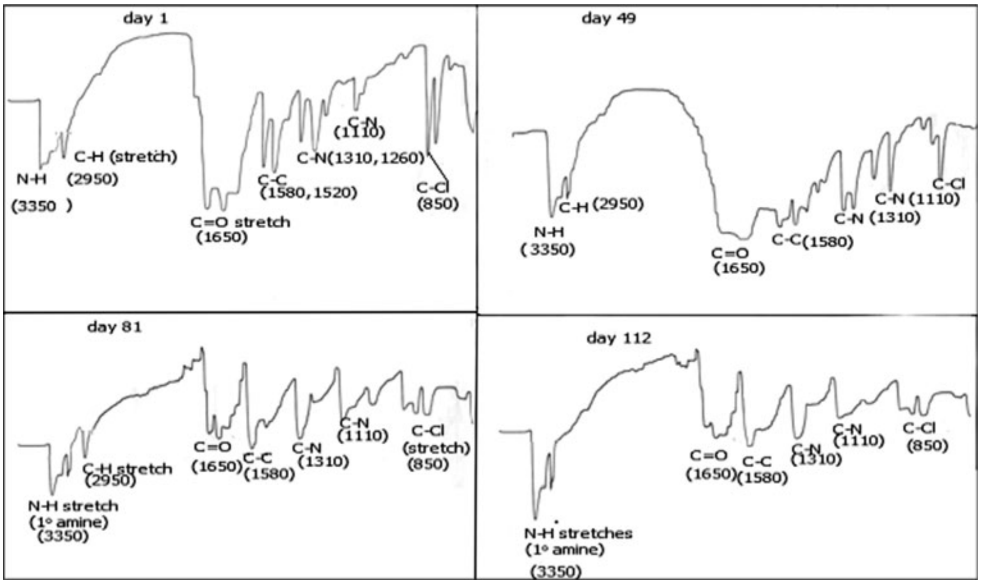


Fig. 6 Infra-red spectra of diuron and its transformation products in soils within Nzoia



after 7 days of application in the two treatments, respectively. The faster degradation rates observed in soils amended with filter mud composed may be attributed to the possible presence of microorganisms in the compost which acted on the pesticide immediately after application. From Fig. 4a, b, the proposed degradation route of diuron in soils from Nzoia may be through an initial demethylation to form 3,4-dichlorophenylmethylurea (DCPMU) followed by microbial hydrolysis of the urea side chain to give dichloroaniline (DCA) as shown in Fig. 5. Both transformation steps were believed to occur by microbial processes since this is the major route of diuron degradation in acidic soils (pH of 4.9) (Caraciollo et al.2005). The proposed degradation pathway was confirmed by Infrared spectroscopy and the spectra are presented in Fig. 6. The spectra of samples collected at day 1 shows the presence of a medium intensity absorption band at 3,350 cm^{-1}.

This indicates the presence of an amine which is supported by absorption bands at 1,310 and 1,260 cm^{-1} showing an aromatic amine. The presence of an aliphatic amine is represented by an absorption band at 1,110 cm^{-1}. The increase in the intensity of the N–H absorption band at 3,350 cm^{-1} at day 49 compared to day 1 shows the accumulation of an amine. The two absorption bands at 3,350 and 3,330 cm^{-1} show the presence of a primary amine. A strong absorption band at 1,650 cm^{-1} indicates the presence of a carbonyl in the sample collected at day 1. The intensity of this absorption band decreased with increase in diuron residence time in soil up to 112 days showing the possible loss of the urea side chain in diuron and DCPMU as shown in Fig. 6. Absorption bands at 850 and 810 cm^{-1} indicate the presence of a halide which is present in all the samples analyzed. This confirms the proposed degradation pathway.

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