Journal Crop and Weed, 11(2):144-150(2015)

Persistence and metabolism of dithiopyr in different soils of West Bengal

S. ROY, A. BHATTACHARYYA AND [1]A. CHOWDHURY

Department of Agricultural Chemicals
Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741252, Nadia, West Bengal
[1]Institute of Agricultural Science, University of Calcutta, Bullyganj, Kolkata, West Bengal

Received : 11.12.2014, Revised : 04.07.2015, Accepted : 15.07.2015

ABSTRACT

A laboratory experiment was performed to understand the persistence behaviour of the herbicide dithiopyr in three different soils of West Bengal, India. Estimation of dithiopyr residues revealed its dissipation following first-order kinetics. The half-life ($T_{1/2}$) values were in the range of 13.75-31.03 days for T_1 and 21.20-41.24 days for T_2. The dissipation of dithiopyr was maximum in coastal soil with the shortest $T_{1/2}$ (13.75 and 21.20 days) and the higher persistence was recorded in Gangetic alluvial soil. Formation of three metabolites of dithiopyr viz. dithiopyr monoacid, reverse monoacid and diacid were also quantified and their structures were confirmed by Gas chromatography-Mass spectrometry (GC-MS). The metabolites were detected in soils at 7-30 days after application with varying rates of formation reaching maximum between 30-90 days followed by a decreasing trend. Among the metabolites, only diacid could be detected till 120 days. The degradation pathway of dithiopyr in soil involved pH induced abiotic hydrolysis of the methylthioester groups to form the monoacids and diacid which was more favourable under alkaline condition as observed in coastal soil (pH = 8.50) compared to the Terai soil (pH = 5.20) and the least in Gangetic alluvial soil (pH = 6.90).

Keywords **:** Dithiopyr, metabolism, persistence, soil pH

The fate of pesticide in soil has received much attention due to considerations ranging from pest control efficacy to non-target organism exposure and offsite mobility. Factors affecting pesticide movement like diffusion, mass flow, volatilization and transport on adsorbed particles has been described with regard to the potential contamination of the groundwater (Yaron, 1989). Presence of organic matter plays an important role in persistence, adsorption and degradation of herbicides in soil (Nag and Das, 2009). The pathways of degradation and kinetics have been particularly well studied for many insecticides and herbicides. The mechanism of pesticide degradation in soil may be either abiotic or biotic in nature. Microorganisms are the major scavengers in nature, responsible for recycling most natural waste materials including herbicides/ pesticides into harmless compounds by evolving new genes and encoding enzymes that use these compounds as their primary substrates (Parsek *et al*., 1995). However, the biodegradation product may also exhibit a higher toxicity in soil, water and groundwater (Giacomazzi and Cochet, 2004). Careful use of pesticides can restrict their off-site migration, avoiding (or at least minimising) adverse impacts on non-target organisms in the environment. Among the abiotic pesticide degradation processes important in soil include hydrolysis, oxidation, reduction and photolysis (on soil surface). Investigations on the significance and mechanism of soil hydrolysis have been conducted for several pesticides (Chapman and Cole, 1982; Lehmann and Miller, 1989). Pesticides which are resistant to hydrolysis and photolysis can be transported over great distances, for example, organochlorine insecticides have been detected in the Arctic regions (Unsworth *et al*., 1999).

Dithiopyr [S,S′-dimethyl 2- (difluoromethyl)-4-(2-methyl propyl)-6- (trifluoromethyl)-3,5-pyridinedicarbothioate] is a pre-emergent soil applied herbicide belonging to the class of fluoroalkylated pyridine herbicides (Lee *et al*., 1991) and introduced in the Indian sub-continent by Rhom and Hass company as a commercial formulation Scoop1E. This thio-pyridine compound is effective as pre-emergence and early post-emergence control of crabgrass and other susceptible annual grasses and broadleaf weeds in established lawns and ornamental turf (USEPA, 1991). The compound possesses low water solubility (1.38 mg/l). The effect of various environmental variables like volatilization, chemical, photochemical and biological transformation on dithiopyr loss and its persistence in the turfgrass ecosystem has been studied (Hong and Smith, 1996). The dissipation behaviour of dithiopyr in soil following its pre- or post-emergence applications in wheat crop was also investigated (Saikia and Kulshrestha, 2003). The adsorption-desorption, persistence, and leaching behavior of dithiopyr under laboratory condition revealed its strong adsorption in alluvial soil leading to a greater persistence problem in soil. The leaching and mobility experiments indicated that dithiopyr was

Email: roysankha@yahoo.co.in

highly immobile in alluvial soil (Gupta and Gajbhiye, 2002) and also in golf course greens rooting medium (Hong and Smith, 2001) and the chances of its movement into surface water or ground water will be negligible. Transformation of dithiopyr *in vitro* was mediated *via* rat liver microsomal oxygenases (and not *via* esterases) to produce the corresponding monoacids as the predominant metabolites (Feng and Solsten, 1991). But very limited information is available on the nature of transformed products of the herbicide in soil. To explore further, the present investigation was conducted to understand the persistence and metabolism in soils from three different agro-climatic zones of West Bengal under laboratory condition.

MATERIALS AND METHODS

The analytical grade dithiopyr (I), three metabolites [*viz*. monoacid (II), reverse monoacid (III) and diacid (IV)] and the commercial formulation Scoop 1E (12% EC) were supplied by M/S Rhom and Hass, USA. The purity of the chemicals was confirmed by TLC and GLC. Solvents used in the study were analytical grade and freshly distilled prior to use. All inorganic reagents were laboratory grade.

Collection and processing of soil

Field soils were collected from three different agro-climatic regions of West Bengal *viz.* a) Gangetic alluvial soil, from Kalyani, District- Nadia; b) Terai soil from Hilla Tea Estate, District- Jalpaiguri; and c) Coastal soil from Canning, District- 24-Paraganas (South). Selected physico-chemical properties of the soils are given in table- 1. Soil texture was determined by the hydrometer method and pH was measured in soil + deionised water (1 + 2.5 by weight). The organic carbon content of soil was determined by oxidation with dichromate (Nelson and Soemmers, 1982). The CEC of soil was estimated by extracting the soil with buffered barium chloride solution at pH 8.1, adjusted with triethanolamine, following the method of Bascomb as outlined by Dewis and Freitals (1984).

Table 1 : Physicochemical properties of the experimental soils

Soil	Location	Texture (%)			CEC	pH	Organic
		Sand	Silt	Clay	(meq 100^{-1} g soil)		matter(%)
A	Kalyani	26.40	35.10	38.50	13.20	6.90	1.32
B	Jalpaiguri	20.80	46.50	32.70	9.00	5.20	1.73
C	Canning	11.20	36.30	52.50	10.10	8.50	1.21

Preparation of standard solutions

An accurate amount (10 mg) of analytical standard of dithiopyr (I) and its metabolites [monoacid (II), reverse monoacid (III) and diacid (IV)] dissolved in methanol. The solution for dithiopyr was diluted to 1 µg ml^{-1} by measuring an appropriate aliquot of the stock solution into a 100 ml volumetric flask using iso-octane. The stock solution (1ml) of the metabolites (II, III and IV) were taken into separate 100 ml pear-shaped flasks addition of diazomethane (1ml) and kept at room temperature for 30 minutes. The material was dried completely under a nitrogen stream, resuspended in 25 ml of iso-octane and transferred to a volumetric flask (100 ml). The flask was rinsed two more times with 25 ml iso-octane each time and added to the flask. The volume was made up with iso-octane making a 1 µg ml^{-1} methylated solution of each compound which was further diluted to 0.1µg ml^{-1}. The mass spectrum of the methylated products of each standard compound was determined by GC-MS for structural confirmation of the dithiopyr metabolites.

Application of dithiopyr

Samples of processed (air dried and sieved) soil (100 g) were taken in amber colored glass bottles. Scoop 1E was applied individually in two doses equivalent to 1000 g a.i. ha^{-1} (*i.e.* 0.50 µg g^{-1}) and 2000 g a.i ha^{-1} (*i.e.* 1.0 µg g^{-1}) using sterilized distilled water assuming 2×10^6 kg soil ha^{-1} to a depth of 15 cm. The control soil set received only sterilized distilled water. The calculated amount of sterilized distilled water was then added to the soils to maintain 80% of maximum water holding capacity (WHC). The bottles were weighed and plugged with non-adsorbent cotton plug and kept at 28 (±1) °C. The weight loss due to evaporation of soil moisture was refilled by periodic addition of water during the incubation period. Samples (in three replicates) were processed for analysis of dithiopyr at intervals of 0 (2h after application), 7, 15, 30, 60, 90 and 120 days after application.

Extraction and clean-up of soil samples

200 ml Acetonitrile - water (95:5 V/V) was added to each replicated soil sample, shaken vigorously for 2h on a mechanical shaker and filtered through a

Buchner funnel using Whatman No. 1 filter paper under vacuum with repeated washing with the same solvent. The acetonitrile was evaporated from the filtrate using a rotary vacuum evaporator. The concentrated soil extract was transferred completely to a separatory funnel where 1-2 ml 1M NaOH, 10 ml saturated NaCl solution and 50 ml petroleum ether (PE) was added for liquid-liquid partitioning. The upper PE phase containing dithiopyr was collected by passing over anhydrous sodium sulphate. The process was repeated twice and the combined PE fraction (Fraction A) was concentrated. The lower aqueous phase containing the acid metabolites of dithiopyr was drained to a separatory funnel and partitioned after adding 1-2 ml of 6M HCl, 50 ml of diethyl ether (DE). The lower aqueous layer was discarded and the upper DE fraction (Fraction B) was collected over anhydrous sodium sulphate.

Methylation of Fraction B

p-tolyl sulphonyl methyl nitrosamide (10 g) was dissolved in 30 ml diethyl ether, cooled with ice and a solution of 0.4 g potassium hydroxide in 10 ml 96% ethanol was added to it (Meon, 1979). In case of any precipitate, more ethanol was added until it just dissolved. After 5 minutes the ethereal diazomethane solution was distilled from a water bath. The ethereal solution contains 0.32- 0.35 g diazomethane. Fraction B containing the acid metabolites of dithiopyr was cooled in ice and ethereal solution of diazomethane was added in small portion until gas evolution ceases and the solution acquired a pale yellow color. The solution was evaporated to dryness.

The concentrated fractions [fraction A & B (methylated)] were transferred on the top of two separate glass columns (65 cm length, 2.5 cm i.d.) packed with florisil (80-120 mesh) in PE and were eluted with 30 ml 5% DE in PE which was discarded. The column containing fraction A was further eluted with 150 ml 50% DE in PE and concentrated for analysis by GC-ECD. The column containing fraction B (methylated) was finally eluted with 200 ml of 0.5%, 10% and 50% acetone in n-hexane. Elutes thus obtained were collected separately and designated as E_1, E_2, and E_3. The methylated metabolites of dithiopyr were quantified by GC-ECD and their identity was further confirmed by GC-MS.

Gas chromatographic (GC) analysis

A Hewlett Packard 5890A gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) was used for quantification of dithiopyr and its methylated esters. The GC conditions [slightly modified from those reported by Saikia and Kulshrestha (Saikia and Kulshrestha, 1999) were as follows: Separation on a glass column (6 ft length, 2 mm i.d.) packed with 3% OV 101 on chromosorb W.H.P. A temperature programme consisted of an initial temperature of 150 ^{0}C that was increased at a rate of 5 ^{0}C per minute to 200 ^{0}C, then 10 ^{0}C per minute to 250 ^{0}C and held for 5 minute. The detector temperature was 300 ^{0}C, the injector temperature 220 ^{0}C and the carrier gas nitrogen flow rate was maintained @ 50 ml per minute. Under the above operating conditions the retention times of dithiopyr (I) was 12.7 min. The retention times of the compound II, III and IV were 8.4, 7.7 and 5.6 minutes.

Gas chromatography-Mass spectrometry (GC-MS) analysis

GC-MS spectra of the methylated metabolites of dithiopyr were obtained on a Hewlett Packard 5890A GC equipped with 5970A quadrupole mass spectrometer with a J & W DB-210 (30 m × 0.53 mm i.d.) capillary column with splitless injection. The temperature programme was as follows: Initial 100 ^{0}C, 3 min hold, increase @10 ^{0}C min^{-1} to 250 ^{0}C, hold for 5 min. The carrier gas used was helium (0.014cm^3 s^{-1}). The ionization potential of 70 eV was used to obtain the mass spectra. Under above operating condition the retention times of dithiopyr monoacid (II), reversemonoacid (III) and diacid (IV) were 14.6 min, 13.7 min and 10.3 min respectively.

Validation of the method

Known quantities of dithiopyr dissolved in diethyl ether were added to untreated (control) soil samples (100 g) at five fortification levels in the range of 0.01-2.0 µg g^{-1} (Table 2). Dithiopyr was extracted

Table 2: Recoveries of dithiopyr from different soils

Soil	Average % recovery (of three replicates) of dithiopyr from soil fortified at various levels (µg/g)					Mean recovery (%) ± SD
	0.01	0.05	0.50	1.00	2.00	
A	95.29	93.36	93.67	94.15	95.88	94.47 ± 0.08
B	96.33	93.78	92.39	92.55	91.96	93.40 ± 2.34
C	95.70	93.83	94.87	95.94	94.78	95.02 ± 1.11

following the method as mentioned above and analyzed by GLC. Recovery of the fortified dithiopyr was calculated to understand the suitability and reliability of the adopted method.

RESULTS AND DISCUSSION

Method validation and recoveries

The analytical method employed is simple and rapid that is used in routine scale in our laboratory for monitoring of agricultural products. This method allows the reliable determination of dithiopyr with very good accuracy. The response of detector to dithiopyr concentration was linear $Y = 4.51 \times 10^5 x + 340.62$ in the range of 0.002-0.02 ηg (0.001-0.1 µg ml^{-1}); with a very high correlation coefficient (r = 0.989). This linearity was checked with standard solutions of dithiopyr prepared by dilution either in hexane or in extracts of soil from control samples. In the latter case, the response of the detector was checked again in the same range of 0.002-0.02 ηg (0.001-0.1 µg ml^{-1}). The regression lines were $Y = 6.38 \times 10^6 x + 2010.95$ and $Y = 5.49 \times 10^6 x + 1179.09$ and the correlation coefficients (r) were 0.999 and 0.995 respectively. Quantification of dithiopyr in samples was made by comparing the detector response (area) for the samples to that measured for the calibration standard within the linear range.

The recovery data are summarized in table- 2. Average recovery percentage from spiked samples of soil ranged from 92.34-94.40%. All the control samples were found free of dithiopyr residues. A comparable recovery of dithiopyr from soil, wheat grain and straw (80 – 99 %) was also obtained by Saikia and Kulshrestha (1999). Estimation of the method's sensitivity, the limit of detection (LOD) and limit of quantification (LOQ) were performed for soil in accordance with the method of Their and Zeumer (1987). The results of recovery experiments were used to calculate the parameters of regression line $w = a_0 +]_q$. In this equation w is the measured concentration of each fortification level q and the slope] is the estimated value of sensitivity S. LOD value for determination of dithiopyr in soil was 0.0007µg g^{-1}. This value was calculated on the basis of standard deviations of the blanks at the lowest for each matrix fortification level, with f = 6 degrees of freedom at 95% confidence level. Consequently, the methods LOQ value under these conditions was 0.002µg/g for the determination of dithiopyr in soil. All values were within the accepted range for residue determination, satisfying the three requirements LOQ e" LOD, S e" 0.7 and V d" 0.2 (20%). The

Table 3 : Dissipation of dithiopyr residues in different soils following application @1000 g a.i. ha^{-1} (T_1) and 2000 g a.i. ha^{-1} (T_2)

Soil	Dose	Concentration remaining in soil (µg/g ± SD) on different days after application (Data are average of three replicates)							$T_{1/2}$	Regression equation
		0	7	15	30	60	90	120	Days	Y = a + bX
a	T_1	0.461± 0.007	0.392± 0.004 *(14.97)	0.324± 0.001 (29.72)	0.235± 0.005 (49.02)	0.120± 0.005 (73.97)	BLOQ	BLOQ	31.03	Y = 2.661 - 0.0097 X
	T_2	0.971± 0.099	0.804± 0.008 (17.20)	0.703± 0.008 (27.60)	0.518± 0.009 (46.65)	0.356± 0.004 (63.34)	0.198± 0.021 (79.61)	BLOQ	41.24	Y = 2.964 0.0073 X
b	T_1	0.469± 0.007	0.357± 0.003 (23.88)	0.280± 0.004 (40.30)	0.168± 0.005 (64.18)	0.082± 0.003 (82.52)	BLOQ	BLOQ	24.08	Y = 2.643 0.0125 X
	T_2	0.965± 0.014	0.803± 0.012 (16.79)	0.597± 0.010 (38.14)	0.412± 0.011 (57.31)	0.254± 0.005 (73.68)	BLOQ	BLOQ	31.35	Y = 2.953 0.0096 X
c	T_1	0.448± 0.010	0.287± 0.005 (35.94)	0.200± 0.007 (55.36)	0.096± 0.002 (78.57)	BLOQ	BLOQ	BLOQ	13.75	Y = 2.633 0.0219 X
	T_2	0.942± 0.015	0.631± 0.010 (33.02)	0.462± 0.009 (50.96)	0.268± 0.011 (71.55)	0.125± 0.007 (86.73)	BLOQ	BLOQ	21.20	Y = 2.911 0.0142 X

*Note: *Figures in the parentheses indicate % dissipation of dithiopyr; BLOQ = below limit of quantification*

measurement of spiked dithiopyr samples stored at -20ºC showed that the storage of matrix under the conditions did not affect the amount of dithiopyr residues.

Persistence of dithiopyr in soil

The residues of dithiopyr in three different soils of West Bengal following application @ 1000 g a.i. ha^{-1} (T_1) and 2000 g a.i. ha^{-1} (T_2) are shown in table-3. The initial residues of dithiopyr determined after 2h from the application (0 day) ranged from 0.448-0.469 µg g^{-1} for T_1 and 0.942-0.971 µg g^{-1} for T_2. The molecule was dissipated by about 15 – 36 % within 7 days, 28 – 55 % within 15 days and 47 – 79 % within 30 days. The minimum time required for the herbicide to reach below the LOQ (*i.e.* 0.002 µg g^{-1}) was 60 days in coastal alkaline soil (c) with T_1, while the maximum time was 120 days in alluvial soil (a) with T_2 dose. Gupta and Gajbhiye (2002) also reported the herbicide to persist beyond 90 days.

The dissipation was found to follow first order reaction kinetics in all the three soils and the computed regression equations are presented in table-3. The regression analysis between the time after application and the dithiopyr residues in the soil at the corresponding time indicate the dissipation of dithiopyr in soil with time after application which could be well approximated by the first order equation: Log R = Log K_2 – (Log K_1) T, where Log R = Log residues in µg/g at any time T; Log K_2 = Log of initial residue in µg g^{-1}; Log K_1 = Slope of the linear plot or the rate of dissipation of residues with time; T = Time elapsed in days. The highest rate of dissipation was found in soil c (b = 0.014 – 0.022) and the lowest in soil a (b = 0.001 – 0.007) as shown in table- 3.

The dissipation half-lives ($T_{1/2}$) of dithiopyr in soil were calculated from the equation: $T_{1/2}$ = log2 / log K_1. The $T_{1/2}$ values were found in the range of 13.75-31.03 days for T_1 and 21.20-41.24 days for T_2. However, Saikia and Kulshrestha (2003) reported that the half-life value of dithiopyr in wheat cropped soil in the range of 17.3 – 25.0 days (Feng and Solsten, 1991).

Metabolism in soil

Dithiopyr was found to degrade in soil to different metabolites of which dithiopyr monoacid (II), reversemonoacid (III) and diacid (IV) were monitored by GC-ECD. All the three metabolites were detected in all the soils (Fig. 1a & 1b). The metabolite II was first detected 7 days after application of dithiopyr. The maximum concentration of Metabolite II was reached 30 days after application in soil a and soil b in the concentration range from 0.120-0.140 µg g^{-1} for T_1 and 0.245-0.282 µg g^{-1} for T_2 but in case soil c the maximum concentration of the metabolite II (0.140 – 0.282 µg g^{-1}) was observed at 15th day after application of dithiopyr.

Metabolite III was detected 15 days after application in all the three soils with different rates of formation. The maximum concentration of the metabolite III was noticed 60 days after application in soil a & b in the range of 0.145-0.152 µg g^{-1} for T_1 and 0.297-0.303 µg g^{-1} for T_2 while in soil c the maximum concentration of the metabolite III (0.148 – 0.292 µg g^{-1}) was observed on 30th day (Fig. 1a & 1b).

The formation of metabolite IV was first recorded in soil c at 15th day and onwards reaching the maximum (0.253 – 0.505 µg g^{-1}) on 60th day. However, in case of soil a and soil b, IV was detected 30 days after application of dithiopyr and reached the maximum concentration (0.244-0.258 µg g^{-1} for T_1 and 0.499-0.509 µg g^{-1} for T_2) on 90 days after application of dithiopyr. The metabolite IV persisted till 120 days with a decreasing trend in all the three soils irrespective of dose.

The formation of the metabolites (II – IV) in all the treated soils was confirmed by GC-MS analysis of the three different elutes (E_1-E_3) of column fraction-B. The mass spectral data are presented in table- 4. The MS data of the compound II and III showed molecular ion peak (M^+) at m/z 385. The mass fragmentation pattern of the compound II and III are identical but the retention time of the compound II in GC column is 14.4 minutes where as for the compound III it is 13.7 minutes which was further compared with authentic samples and found the same. So from the above MS data and RT comparison of the metabolites II and III, it was confirmed that the metabolite II was dithiopyr monoacid [O,S$^{\text{£¢}}$- dimethyl-2-(difluoromethyl)-4 -(2-methylpropyl) –6-(trifluoromethyl)-3,5-pyridinedicarbothioate] and compound III was dithiopyr reverse monoacid [,S O$^{\text{£¢}}$- dimethyl-2-(difluoromethyl)-4 -(2-methylpropyl) –6-(trifluoromethyl)-3,5- pyridinedicarbothioate]. The molecular ion peak of the compound IV was at 369(M^+) and from the MS spectral data and comparison with the authentic samples it was

confirmed that the compound IV was dithiopyr diacid [O, O$^{\text{£¢}}$ - dimethyl-2- (difluoromethyl)-4 – (2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarboxylate].

Table 4: GC-MS data of the methylated metabolites of dithiopyr

Column fraction	Methylated metabolite	Retention time (RT)	Molecular ion (m/z)	Mass fragmentation pattern
I	**II**	14.4 min	385 (M^+)	366 (M^+-F), 354 (M^+-OCH_3), 338 (M^+-SCH_3), 318 (M^+-SCH_3 -HF), 306 (M^+-SCH_3 –$HOCH_3$), 300 (M^+-SCH_3 –F_2), 286 (M^+-SCH_3 –$HOCH_3$ -HF), 267 (M^+-SCH_3 –$HOCH_3$ –HF -F).
II	**III**	13.7 min	385 (M^+)	366 (M^+-F), 354 (M^+-OCH_3), 338 (M^+-SCH_3), 318 (M^+-SCH_3 -HF), 306 (M^+-SCH_3 –$HOCH_3$), 300 (M^+-SCH_3 –F_2), 286 (M^+-SCH_3 –$HOCH_3$ -HF), 267 (M^+-SCH_3 –$HOCH_3$ –HF -F).
III	**IV**	10.3 min	369 (M^+)	349 (M^+ -HF), 338 (M^+ -OCH_3), 327 (M^+ -C_3H_6), 312 (M^+ -C_4H_9), 307 (M^+ -C_3H_6 –HF), 292 (M^+ -C_4H_9 -HF).

Based on the assigned structures of the metabolites, a pathway of dithiopyr degradation in soil has been proposed (Fig. 2). Although the transformation of the methylthioester functional groups in dithiopyr to the monoacids was mediated *via* rat liver microsomal oxygenases (and not via esterases) through an initial sulphur oxidation of the methylthioester group followed by nucleophilic displacement reaction (Feng and Solsten, 1991), but in case of the soils under present investigation it might be mediated. The pH induced abiotic hydrolysis was more favoured under alkaline condition as observed in the coastal soil, c (pH = 8.50 with the highest concentration of the monoacids: 0.129 – 0.271 µg g^{-1}) followed by acidic condition in terai soil (pH = 5.20 with moderate concentration of the monoacids: 0.126 – 0.252 µg g^{-1}) and the least under the neutral alluvial soil (pH = 6.90 with concentration of the monoacids: 0.120 – 0.250 µg g^{-1}). The observation on alkaline hydrolysis is strongly supported by the fact that alkaline potassium hydroxide was conveniently used for the selective hydrolysis of the thioester groups of dithiopyr to the corresponding carboxylic acid (Mehrsheikh *et al*., 1991). In addition, the rate of conversion of the herbicide was not directly related with the organic matter content of the soils (Table 1) which further substantiated the involvement of abiotic process for cleavage of the thioester linkage in dithiopyr rather than biological transformation.

Transformation of thiazopyr to its monoacid metabolite resulted in loss of herbicidal activity (Feng *et al.,* 1995) and the concept was engineered in plants to confer resistance to thiazopyr via an esterase deactivation mechanism (Feng *et al*., 1997).

GLC coupled with ECD allows a rapid and highly sensitive determination of dithiopyr and the resulting degradates in soil. As a result, the dissipation behavior and degradation times of dithiopyr and its major metabolites in soil could be ascertained. The degradation of the herbicide in soil followed first order nature. The dissipation rate was influenced by the pH of the soil. Dithiopyr residues dissipated at much faster rate in Coastal soil having alkaline pH ($T_{1/2}$ ~ 14-21 days) followed by acidic Terai soil ($T_{1/2}$ ~ 24-31days) and neutral Gangetic alluvial soil ($T_{1/2}$ ~ 31-41 days). Therefore, the residual herbicidal activity of dithiopyr was predicted in the order of Gangetic alluvial soil > Terai soil > Coastal soil.

ACKNOWLEDGEMENT

We thank M/S Rhom and Hass for supplying technical product and financial assistance. The infrastructure facility provided by Bidhan Chandra Krishi Viswavidyalaya is also thankfully acknowledged.

REFERENCES

Chapman, R.A. and Cole, C.M. 1982. Observations on the influence of water and soil pH on the persistence of insecticides. *J. Env.. Sci. Health*. **B17:** 487-504.

Dewis, J. and Freitals, F. 1984. *Physical and Chemical Methods of Soil and Water Analysis*. Oxford and IBH Publ. Co., New Delhi.

Feng, P.C.C., Ruff, T.G. and Kosinski, W.G. 1995. Metabolic deactivation of the herbicide thiazopyr by animal liver esterases. *Xenobiotica*, **25**: 27-35.

Feng, P.C.C., Ruff, T.G., Rangwala, S.H., and Rao, S.R. 1997. *Pesticide Biochem. and Physiology*, **59:** 89-103.

Feng, P.C.C. and Solsten, R.T. 1991. In vitro transformation of dithiopyr by rat liver enzymes: Conversion of methylthioesters to acids by oxygenases. *Xenobiotica*, **21** : 1265-71.

Giacomazzi, G., Cochet, N. 2004 Environmental impact of diuron transformation: a review. *Chemo.,* **56**: 1021-32.

Gupta, S. Gajbhiye, V.T. 2002. Adsorption-desorption, persistence, and leaching behavior of dithiopyr in an alluvial soil of India. *J. Env Sci. Heal.*, **B37** : 573-86.

Hong, S., Smith, A. B. 1996. Abiotic and biotic degradation of dithiopyr in golf course greens. *J. Agri. Food Chem.,* **44** : 3393-98

Hong, S. Smith, A.E. 2001. Sorption and mobility of dithiopyr in golf course greens rooting medium. *J. Env. Sci. Hea.* **B36**: 529-43.

Lee, L.F., Stikes, G.L., Sing, L.Y.L, Miller, M.L., Dolson, M.G., Normansell, J.E. and Auinbauh, S.M. 1991. Synthesis of a new class of pyridine herbicide. *Pest. Sci.*, **31:** 555-68.

Lehmann, R.G. and Miller, J.R. 1989. Soil catalyzed hydrolysis of fluroxypyr-methylheptyl ester. *Weed Res.*, **29**: 385-89.

Meon, S. 1979. The influence of infection by Meloidogyne javanica on growth hormones in tomato plants. *Nematologica*, **25** : 143-45.

Mehrsheikh, M.E., Clizbe, L.A., Singh, H. and Purdum, W. 1991. Synthesis of ^{14}C labelled monoacidic metabolites of dithiopyr. *J. Labelled Compounds and Radiopharmaceuticals*, **29** : 9-13

Nag, S.K. and Das, S.K. 2009. Persistence of atrazine in soil under fodder sorghum. *J. Crop Weed*, **5** : 131-35.

Nelson, D.W. and Soemmers, L.E. 1982. Total carbon, organic carbon and organic matter. In *Methods of Soil Analysis* (Part 2). 2nd Edn, (Ed.) ASA, Madison, WI, USA.

Parsek, M.R., McFall, S.M. and Chakrabarty, A.M. 1995. Microbial degradation of toxic, environmental pollutants: Ecological and evolutionary considerations. *Biodet. Biodeg.*, **35** : 175-88.

Saikia, N. and Kulshrestha, G. 1999. New gas chromatographic method for residue determination of dithiopyr in soil, wheat grain and straw. *J. Chrom A*, **864***:* 351-53.

Saikia, N. and Kulshrestha, G. 2003. Dissipation of herbicide dithiopyr in soil and residues in wheat (*Triticum aestivum* L) grain under Indian tropical conditions. *Pest Man. Sci.*, **59:** 114-18.

Their, P. and Zeumer, H. 1987. Introduction and Instructions In. *Manual of Pesticide Residue Analysis*; Eds. DFG, Dt Forchungsgemeinschaft, Pesticides committee, **1**, VCH: New York.

Unsworth, Wauchope, Klein, Dorn, Zeeh, Yeh, Akerblom, Racke and Rubin. 1999. Pesticides report 41. Significance of the long range transport of pesticides in the atmosphere *Pure App. Chem.,* **71** : 1359-83.

USEPA. 1991. *United States Environmental Protection Agency,* Office of Pesticides and Toxic Substances: 540/FS-91-137., Fact Sheet Number: 223.

Yaron, B. 1989. Effects of Agriculture on Groundwater. *Agric. Ecosys. Env.,* **26** : 275-97.