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Dissipation Kinetics Study of Clopyralid in Water

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The study was undertaken to study the dissipation kinetics of clopyralid in water under laboratory conditions. Water was fortified with clopyralid at 150 μg a.i. per liter and sampling was done at different time interval after application. Residue was estimated by reversed phase HPLC with UV detector at 229 nm. Dissipation study showed that clopyralid degraded with decay rate (λ = 0.06 ± 0.02/days) in water and no detectable residue was found on 30th day of application. Dissipation in water followed monophasic first order kinetics. The half life of clopyralid in the water was found to be 11.55 days. The limit of detection was 5 ng/mL of water and the RSD was 1.87 %.

Keywords: Clopyralid, Dissipation, Water, HPLC, First order kinetics.

INTRODUCTION

Besides direct pollution of the environment, industrial agriculture has placed an extremely heavy burden on world water resources. One of the main causes of pollution of the Earth's surface water with pesticides and herbicides is washing by rain which transfers the substances from treated fields to large water-supply basins and thus into surface water (lakes, rivers, streams and drinking water) [1].

Clopyralid (3,6-dichloropicolinic acid) is a selective, auxins type herbicide of pyridine carboxylic acid group used to control broad leaf weeds of the family polygonaceae, compositae, legmuminosae and umbelliferae in sugarbeet, fodder beet, oilseed rape, brassicas, onions, strawberries, flax and grassland (lawn and turf also) [2]. Clopyralid is highly water-soluble and degradation is entirely through microbial metabolism in aquatic sediments. The half-life of clopyralid in water ranges from 8 to 40 days [3]. Clopyralid is not registered for use in aquatic systems. According to Leitch and Fagg [4] 12 g of clopyralid (0.01 % of that applied) leached into the water stream during the first significant rainfall after the application that occurred 3 days later. Bergstrom *et al*. [5] found clopyralid is not susceptible to hydrolysis or other types of chemical degradation and a maximum of 0.02 % of applied clopyralid was lost to runoff from clay soils in Sweden. A 3 year study carried out to assess the effects on the downstream water quality showed that clopyralid was 0.31 % of the amounts applied showing its persistence in water [6]. Field study on water quality showed that clopyralid, declined to below detection limits before monitoring was concluded and not detoriating the quality of water [7]. At different pH range (1.0 to 9.0) clopyralid solutions was found to stable for at least a period of two months [8]. Donald *et al.* [9] estimated the annual calculated concentration of different herbicides including clopyralid in drinking water and found concentrations of the individual chemicals were well below their respective tolerance limits.

The clopyralid herbicide is not registered in India for use commercially but likely to be used in near future. Thus, viewing the above facts of high leachability of this compound study was conducted to look into the dissipation of clopyralid in water under Indian environmental conditions.

EXPERIMENTAL

Technical grade clopyralid of 95 % pure and its formulation (clopyralid 10 % SL) were obtained from M/s Willowood, Hong Kong. The technical compound was re-crystallized prior to use. All the solvents used were of analytical (AR) or HPLC grade. Triple distilled water was prepared in the laboratory by double distillation of single metal distilled water in all quartz double distillation assembly. Ground water was taken for dissipation study and characterized for its physicochemical properties

Beckman HPLC, Systronics UV-visible spectrophotometer, Buchii flash evaporator.

Recovery: For recovery experiment 200 mL water was taken and fortified with 10 mL of 0.5-2.0 ppm solution of technical grade of clopyralid.

Extraction: The extraction procedure used during experiment of clopyralid from water was done according to the method given by Singh *et al*. [10]. Fortified water sample (50 mL) was transferred to separating funnel and acidified with conc. sulfuric acid to pH below 2. Acidified solution was extracted with 75 mL (40 mL + 20 mL + 15 mL) of chloroform in 03 steps. Organic layers was collected and pooled into 250 mL round bottom flask. Organic layer was dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure at 40 ± 1 °C using Buchi Flash Evaporator. The residue was dissolved in 5 mL acetonitrile and subjected to HPLC analysis. The samples were filtered through 0.2 μm PTFE disc filter prior to HPLC. An untreated water sample processed as above was used as control.

Dissipation studies: For experimental purpose water was fortified with recommended application dose (300 g a.i./hac) as used in the field condition for controlling weeds. 2 L water was taken in glass bottle in triplicate. The water was fortified with clopyralid formulation at 0.15 ppm (equivalent to 300 g a.i./hac application rate). The solution was shaken properly.

Sampling: 50 mL sample was drawn for dissipation study at different time intervals *i.e.* 0 (1 h), 1, 3, 5, 7, 10, 15, 30 and 45 days after fortification. Water was shaken every time before sampling. The method applied for extraction and cleanup were the same as standardized earlier for recovery of water.

HPLC: The Beckman model 322 HPLC system with fixed wavelength UV detector was used for residue analysis. The operating parameters were Discovery C-18, 5 μm, (150 × 4.6 mm) column, mobile phase 0.02 % acetic acid in 9: 1 v/v methanol:acetonitrile in isocratic mode at a flow rate of 1 mL/min and UV detection at 229 nm.

RESULTS AND DISCUSSION

The physico-chemical properties of water was pH 7.37, hardness 899.64 ppm, electrical conductivity 0.97 mS, total dissolved solids 342.00 ppm, alklanity due to hydroxyl and carbonate ions are 3.33 and 5.18 g/L as equivalent of $CaCO_3$, respectively, free CO_2 6.10 ppm and dissolved O_2 5.32 ppm.

The retention time of clopyralid under the above condition was found to be 9.8 min [11]. The per cent recovery from water sample ranged between 89-92 % (Table-1). The amount of residue at different time interval estimated by HPLC is given in Table-2. The amount of clopyralid recovered from soil at different time intervals were fitted to a first order kinetic equation.

$$C = C_0e - \lambda t$$

where C = amount of clopyralid recovered from soil at time t; C_0 = amount of clopyralid recovered at t = 0; λ = degradation constant; t = time in days.

It is evident from Table-2 that residue of clopyralid in water dissipates with rate 0.06 ± 0.02 days^{-1} up to 15th days leaving no detectable residue on 30th day of application with half life 11.55 days. The limit of detection of clopyralid in water by the above method was 5 ng/mL (Fig. 1).

TABLE-1
PER CENT RECOVERY OF CLOPYRALID FROM WATER

S. No.	Amount (ppm)	Recovery (%)
1	0.50	88.95 ± 0.04
2	1.00	90.76 ± 0.02
3	2.00	92.22 ± 0.02

TABLE-2
DISSIPATION OF CLOPYRALID IN WATER

Days of application	Persistence (mg/L)	Dissipation (%)
0 (1 h)	0.1379 ± 0.004 (100.0)	0
1	0.1327 ± 0.006 (96.22)	3.77
3	0.1292 ± 0.002 (93.69)	6.30
5	0.0933 ± 0.003 (67.65)	32.34
7	0.0738 ± 0.005 (53.51)	46.48
10	0.0522 ± 0.004 (37.85)	62.14
15	0.0376 ± 0.003 (27.26)	72.73
30	ND	–
45	ND	–

Values in parenthesis show % persistence of the herbicides.
N.D (no detection) ≤ 5 ng/mL

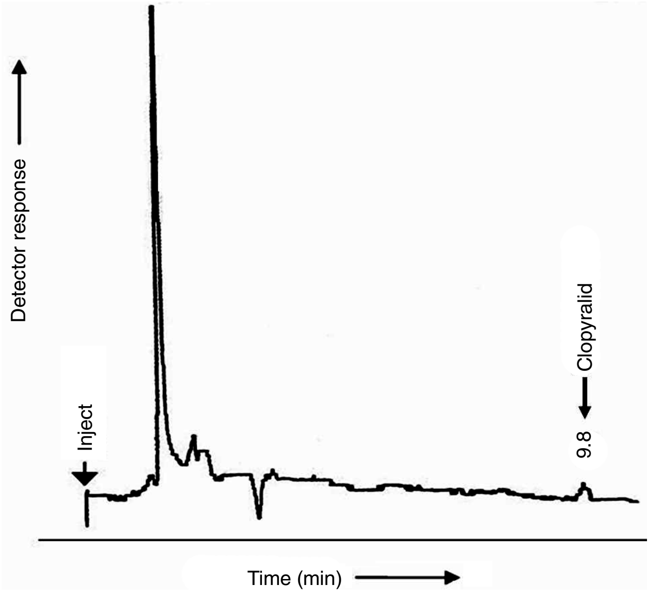

Fig. 1. Standard clopyralid chromatogram

The values of logarithm of residue (C) were plotted against time (t). The distribution of points followed straight line pattern in water (Fig. 2) showing a monophasic first order kinetics. Coefficient of determination (R^2) values for the degradation

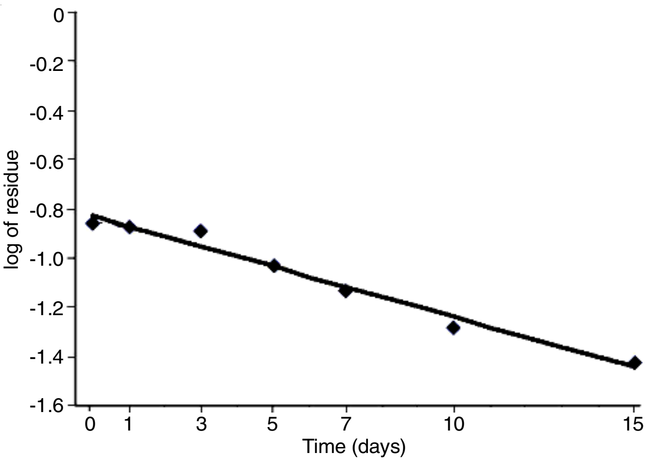

Fig. 2. Plot of log of clopyralid residue in water *versus* time (@300 g a.i. ha^{-1})

of clopyralid in water was 0.9749, which is statistically significant. This also signified that the kinetics of clopyralid degradation rate followed first order degradation kinetics. Baloch-Haq *et al*. [12] found that under practical farming conditions contamination of groundwater in excess of the 0.1 µg/L limit for drinking water is highly unlikely by clopyralid. In groundwater (from wells) collected from Poland, Germany and Sweden residues of clopyralid were detected sporadically but their level was well below the EC limits and possibility of contamination of groundwater were very less [13,14].

From the study it may be concluded that clopyralid has less persistence in water therefore there are remote chances of contaminating the water bodies. Further studies are necessary under field conditions or river or runoff water and sediments for final conclusions.

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