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Dissipation kinetics and leaching of cyazofamid fungicide in texturally different agricultural soils

N. Singh · S. Tandon

Abstract Dissipation and leaching studies of cyazofamid in two texturally different soils of Tarai region of India at two fortification levels (100 and 200 g a.i. ha^{-1}) were carried out for monitoring residual toxicity and groundwater contamination. Soil was extracted with acetone : methanol (5:1 v/v) followed by cleanup with florisil SPE. Separation was achieved by RP-HPLC on a Discovery® C-18 column using mobile phase acetonitrile: water (60:40 v/v) and detection at 279 nm. Degradation pattern indicated correspondence to monophasic first-order kinetics in soils with half-life values ranging from 4.3 to 4.95 days. The degradation rate was slight different in both types of soils. Persistence was higher in sandy loam compared to silty clay loam soil. Linearity, R^2 of calibration curve, instrument limit of detection/quantitation (LOD/LOQ) was evaluated. Good linearity ($R^2 = 0.99$) of the calibration curves for quantification was obtained over the dynamic range of 0.1–10.0 μg mL^{-1}, and percent relative standard deviation was 1.72 %. Leaching experiment showed that cyazofamid could not leached beyond 15 cm of soil depth. Maximum concentration was at 5–10 and 10–15 cm soil depth. Average recoveries from soils fortified at 0.5–5.0 μg g^{-1} ranged from 78 to 86 %. Instrument LOD values were 0.01 μg mL^{-1}, and method LOQ values were 0.05 μg g^{-1}. A fast, easy and efficient method with acceptable performance was achieved. Results showed that cyazofamid has a short life in soils and low potential to leach down under heavy rainfall conditions. Results confirm that cyazofamid would not build up in the environment and have less possibility of groundwater contamination.

Introduction

Indiscriminate and unjudicious use of pesticides with high residual activity and potential mobility has caused lots of serious environmental problems which were not earlier anticipated as soil and air contamination and pollution. Soil, an important component of the environment, acts as a sink for the pesticides used in agriculture. The buildup of pesticide residues in soil is adversely affecting the soil health as well as polluting the subsoil water (Arora 2006). Presence of pesticide residues in soil may cause detrimental effect on human and animal health and sometime acts as a source of contamination for succeeding crops. From soil, these residues can reach water bodies by leaching and runoff, and as they are inherently toxic molecules on reaching water bodies, they start adversely affecting aquatic environment and non-targeted organism. Presence of pesticides in groundwater is extremely hazardous as groundwater is major source of drinking water.

Cyazofamid, [4-chloro-2-cyano-N,N-dimethyl-5-p-toly-limidazole-1-sulfonamide] a member of phenylimidazole fungicide, has broad spectrum activity against oomycetes and plasmodiophoromycetes with different site of action and specifically active for the control of late blight on potatoes and tomatoes, and downy mildew on grapevine, cucumbers and melons worldwide (Ohshima et al. 2004; Mitani 2001). It has novel and unique mode of action as it kills oomycetes fungi by respiration inhibition. It disrupts

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the energy supply by blocking the electron transfer at the Qi (ubiquinone reducing site) center of complex III of the enzyme cytochrome bc1 complex in mitochondria. It affects all stages in the life cycle of *P. infestans* including germination of cytospores, formation of oospores, zoospores motility and mycelia growth (Mitani et al. 2001a, b, 2002; Yamaguchi and Fujimura 2005).

Work on the analysis on cyazofamid from soil/water/air is very limited, and no work had been reported from Indian soils and conditions. Some literature have reported work on the analysis of cyazofamid pure technical (Xu et al. 2009), photolysis (Zong et al. 2009), soil (Tandon and Singh 2012; Huang et al. 2005), water and air (Fischer et al. 2003), crops (Matsubayashi et al. 1995; Choi et al. 2007; Heimstra and Kok 2007; Lacina et al. 2010) multiresidue in fruits and vegetables (Rial et al. 2003; Pihlstrom et al. 2007; González-Rodríguez et al. 2009; Tseng et al. 2009; European food safety Authority 2012; Lee et al. 2012) animal tissue (Pang et al. 2006a) and food grain (Pang et al. 2006b; Pizzutti et al. 2009).

Pesticide persistence and mobility are largely influenced by the properties of the pesticides. In soil, it is subjected to adsorption, plant uptake, weather condition, application method, movement and degradation depending on the simultaneous influence of physical, chemical and biological processes. The behavior of pesticides in soil, therefore, depends on the characteristics and overall function of the ecosystem as well as physicochemical properties of active ingredients and of its formulated products (Flury 1996; Kerle et al. 2007). In addition to adsorption and biodegradation, it has been recently shown that reduced sulfur species and dissolved organic matter present in soil/sediment are capable of promoting the in situ transformation of otherwise recalcitrant pesticides (Zeng et al. 2011, 2012).

Pesticide leaching or transport through the unsaturated/saturated zone is a function of chemical and soil characteristics, application and water recharge rate (Hancock et al. 2008). Leaching of pesticides is predicted to be greatest for shallow soils and for persistent compounds with low sorptivity (Webb et al. 2008). Estimation of fungicide residues is very useful to determine the persistence and its effect on crop and the quality of food and feed. The information of degradation rate and leaching behavior in soil helps to access and predict the residual toxicity and groundwater pollution, as a whole, environmental behavior of pesticide. Recommendations for the use of a pesticide on a crop cannot be made until studies of its persistence and leaching have been carried out. Information on degradation rate and downward movement also helps to assess and predict the environmental behavior of the pesticide (Laskowski et al. 1983).

The work on persistence and leaching behavior of cyazofamid has not been reported in Indian soils and subtropical conditions. The registration of cyazofamid is proposed for use is under consideration by Central Insecticide Board, DPPQS, India. Thus, study pertaining to its persistence and leaching behavior in soil is essential to get an idea about its extent of residue, thereby predicting the risk of residual toxicity and groundwater pollution. The focus of these studies has been to measure the rate of degradation of the active ingredient as well as to assess the potential for leaching of this compound into the soil. Therefore, a sensitive analytical method capable of estimation of its microquantities in soil is required. Thus, the present studies were undertaken to find the persistence and leaching behavior of cyazofamid in different soils of Tarai region of Uttarakhand, India.

Materials and methods

Instruments

Water's model Gradient HPLC system with varying wavelength equipped with UV detector, 7725i rheodyne injector 20-µL loop and HP 3395 series integrator recorder, P.C. controlled double beam (PMT detector) UV–Visible spectrophotometer Model 2101 (Systronics, India), rotavapor (Buchii, Switzerland) and SPE miniplastic florisil columns (6.0 × 0.75 cm id) packed with 500 mg florisil packing material (Varian/Supelco, USA) were used. For estimation and separation Discovery® C-18, 5 µm, (15 cm × 4.6 mm, stainless steel) column (Sigma-Aldrich) was used for analysis.
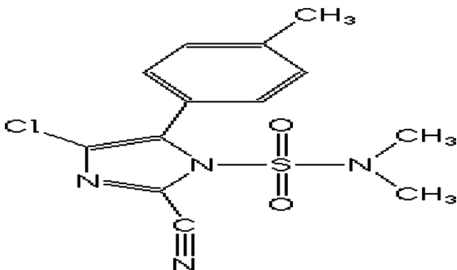
Chemicals and glasswares

Analytical grade (AR) cyazofamid of 99.3 % pure was obtained from courtesy M/s Ishihara Sangyo Kaisha (ISK) Biosciences Corporation, Japan. The structure and some physicochemical properties of cyazofamid are given in Table 1. All the glasswares used were of Corning, Pyrex or Borosil make. Solvents used were of 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.

Sampling

Soils samples representing the major soil type of Tarai region of Uttarakhand were collected at different depths viz 0–15, 15–30, 30–45 and 45–60 cm from five randomly selected spots with the help of tube auger from the N. E. Borlaug Crop Research Centre, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, India. Surface soil of 0–15 cm was used for persistence study,

Table 1 Structure and physicochemical properties of cyazofamid

Structure	
Molecular formula	$C_{13}H_{13}ClN_4O_2S$
Molecular mass	324.8
Melting point	152.7 °C (99.1 %)
Appearance	White, odorless solid powder (99.1 %)
Solubility in water@ 20 °C (mg L^{-1})	5 0.121 7 0.107 9 0.109
Partition coefficient (log Pow)	3.2 at 25 °C
Octanol–water partition coefficient	1.58×10^3 at pH 7 & 20 °C
Dissociation constant (pKa)	Does not dissociate in water. No pKa in the pH range of 2–12
Adsorption/ desorption (Kd and Koc in L Kg^{-1})	Loamy sand (Ohio): Kd = 9.99/6.96 and Koc = 1,524/1,062 Sandy loam (UK): Kd = 43.31/87.00 and Koc = 1,444/2,900 Sandy loam (UK): Kd = 14.11/13.49 and Koc = 1,176/1,124 Sand (Germany): Kd = 5.14/4.14 and Koc = 815/657

USEPA (2004)

and soil from different depths was used in leaching study. To bring the uniformity and destroy unwanted weed seeds present in the soil, it was moistened to field capacity for a period of 7 days in plastic bucket. After incubation, the soil was air-dried, powdered, passed through 2-mm sieve and stored in polythene bags in deep freezer till analysis. Soil were analyzed for its physicochemical properties like pH, CEC, organic carbon, $CaCO_3$ percent, moisture content, water holding capacity and proportion of sand silt and clay fraction by standard analytical procedure (Jackson 1973).

Persistence Studies

Shade air-dried powdered 2 kg of 2 mm size soil samples was taken from both the soils in glass trays. Three treatments consisting of control and cyazofamid were applied.

Table 2 Metrological data for the month of experiment

Month	Week	Temperature (°C)	Relative humidity (%)		
		Max.	Min.	Max.	Min.
February, 2010	3	25.3	10.1	88	47
	4	24.6	11.8	86	48
	5	28.5	12.5	87	42
March, 2010	1	30.6	13.2	86	36
	2	34.2	16.2	88	33
	3	30.9	13.7	71	19
April, 2010	1	37.8	15.0	76	20

Both soils were fortified and mixed thoroughly with 20 and 40 mL of 5 µg g^{-1} cyazofamid solution equivalent to recommended [100 g a.i. ha^{-1} (T_1)] and double recommended [200 g a.i. ha^{-1} (T_2)] application doses of fungicide, respectively. Each treatment was replicated thrice, and 15 % soil moisture was maintained throughout the experiment. The metrological data during the persistence studies is given in Table 2. Representative samples of 50 g were drawn from fortified soils by randomized sampling in triplicate from each treatment at regular intervals (0, 1, 3, 5, 7, 10, 15 and 30 days after treatment) and were processed for estimation of cyazofamid residues as given below. Control samples for both soils were also kept with similar moisture but without treatment or without fortification of cyazofamid.

The experiment was laid in completely randomized block design (CRD) fashion, and all the treatments were replicated thrice. Data were subjected to analysis to determine standard deviation among the replicates (Gomez and Gomez 1984).

Leaching studies

The leaching studies were performed at ambient temperature 25 ± 2 °C in columns made from polyvinyl chloride (PVC) of 60 cm length with 10 cm i.d. One end of PVC columns were covered with double layer of muslin cloth and then sequentially filled the soil from the bottom and packed with 7.2 kg (2.0 kg for 45–60 cm, 1.9 kg for 30–45 cm, 1.7 kg for 15–30 cm and 1.5 kg for 0–15 cm depth) sandy loam and 7.0 kg (1.9 kg for 45–60 cm, 1.8 kg for 30–45 cm, 1.7 kg for 15–30 cm and 1.6 kg for 0–15 cm depth) silty clay loam soils with control columns for reference. For maintaining similar column length of different soil layers, different soil weights were used because of difference in the bulk density of both soils. The upper part of the each column was uniformly covered with glass wool to assist uniform dispersion of the water across the column surface and to minimize the surface disturbance. Columns were saturated overnight by flowing water

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from above and keeping them dipped in water in a bucket, excess water was drained out by 1- day drainage cycle, and columns were covered with aluminum foil to prevent loss of water by evaporation. PVC funnel was attached to the bottom of each column to collect the leachates into 500-mL flasks.

For monitoring vertical movement and leaching loss of cyazofamid, the T_1 (0.1 kg ha^{-1}) and T_2 (0.2 kg ha^{-1}) treatments were applied to surface of column. The fungicide was allowed to equilibrate with the soil for 2 h before the leaching process was initiated. The addition of water was divided into 24 hourly applications of 120 mL for five days (equivalent to 1,400-mm annual rain fall) so that infiltration rate of soil does not exceed the annual rainfall limit. Soil columns receiving respective amount of water only served as control. After five days, when addition of water was completed, the soil columns were allowed to drain for 24 h and were cut into two halves and the soils was cut into 5-cm segments, pooled, air-dried and processed for analyzing cyazofamid residue as described below. Water eluted daily from the columns was collected and processed for fungicide quantity. The experiment was laid in CRD fashion, and all the treatments were replicated thrice. Data were subjected to analysis to determine standard deviation among the replicates.

Recovery

Shade-dried powdered soil was spiked with 0.5, 2.0 and 5.0 µg g^{-1} of cyazofamid. Soil was maintained at 15 percent moisture. All the experiment was done in triplicate. The soil was extracted, cleaned up and analyzed following the procedure as described below.

Extraction procedures

Extraction was done according to method developed by Tandon and Singh (2012). Soil sample (50 g) was mixed with 100 mL of acetone: methanol (5:1 v/v) in conical flask, and the content was shaken for 30 min on a rotatory shaker, centrifuged and filtered. The procedure was repeated twice with 50-mL of solvent system. The clear supernatant obtained was pooled into a 250-mL conical flask. The combined organic layer was dried over anhydrous sodium sulfate, and the content was filter through Whatman No. 1 filter paper. The residue on funnel was rinsed twice with 5 mL of solvent. The extract was evaporated at 45 ± 1 °C to dryness under reduced pressure with help of Buchii Flash Evaporator. Residues were dissolved in 1 mL of dichloromethane and subjected to cleanup.

The cleanup was done using florisil SPE cartridge which was prewashed with 5 mL of dichloromethane. One milliliter sample was loaded on florisil cartridge, and sample was eluted with 1.5 mL dichloromethane. The eluted sample was dried under the stream of nitrogen and re-dissolved in 1 mL acetonitrile and used for HPLC analysis. The samples were filtered through 0.22-µm PTFE disk filter prior to HPLC.

Chromatographic conditions and calibration curve

The λ max of cyazofamid was obtained on UV–VIS spectrophotometer using following conditions: bandwidth 0.5 mm, range 200-400 nm, mode scan, scan speed: slow. The operating chromatographic conditions for the RP-HPLC were Discovery® C-18 column (150 × 4.6 mm i.d. × 5.0 µm particle size). The column was maintained at room temperature of 27 ± 1 °C. The operating parameters were mobile phase acetonitrile: water (60:40, v/v) with isocratic mode at a flow rate of 1 mL min^{-1} and UV detection of 279 nm. The sample injection volume was 20 µL.

A calibration curve was plotted between different concentration of cyazofamid and peak area. A stock solution of cyazofamid (100 µg mL^{-1}) was prepared while working solutions from 0.05 to 10.0 µg mL^{-1} were prepared by serial dilution of the stock solution with acetonitrile. The linearity of the HPLC assay and calibration curve was evaluated in triplicate at six concentration levels consisting of 0.1, 0.5, 1.0, 2.0, 5.0 and 10.0 µg mL^{-1} cyazofamid.

Data analysis

The experimental data were subjected to analysis to determine standard deviation among the replicates. The amount of pesticide residues that remained at different intervals was fitted to first-order exponential decay equation

$$C_t = C_o\, e^{-kt} \tag{1}$$

where C_t—the concentration (µg g^{-1}) after time, t (day), C_o—initial concentration (µg g^{-1}), k—rate constant (day^{-1}).

The half-life was computed using Eq. (2)

$$t_{1/2} = [0.693/k] \tag{2}$$

where k is rate constant in days.

Results and discussion

The physicochemical properties of the soils and soil composition showed that textures of soils were silty clay loam and sandy loam type (Tables 3, 4). Validation of the extraction procedure in terms of percent recovery the

average values of recoveries of cyazofamid from both spiked soil samples ranged from 78 to 86 %. (Table 5)

The retention time of cyazofamid under the set conditions was found to be 7.6 min. The chromatograms obtained showed no interfering peak at the retention time of the cyazofamid, i.e., at 7.6 min showing good specificity of the method. Detector response was linear to the concentration as the value of coefficient of determination (R^2) was 0.999 giving good accuracy. The percent RSD was 1.72 showing good precision of the method. The limit of quantification for method and limit of detection for instrument were 0.05 μg g^{-1} and 0.01 μg mL^{-1}, respectively.

Dissipation in soils

The amount of residue at different time interval estimated by HPLC is tabulated in Table 6. The temperature and

Table 3 Physicochemical properties of soils of experimental field (0–15 cm)

Parameters	Soil 1	Soil 2
Particle size distribution		
Sand (%)	9.80	50.07
Silt (%)	60.20	31.85
Clay (%)	30.00	18.08
Texture class	Silty clay loam	Sandy loam
Moisture content	38.0 ± 2	32.5 ± 2
Bulk density (mg m^{-3})	1.23 ± 0.15	1.07 ± 0.10
pH	7.06 ± 0.1	6.94 ± 0.1
Organic carbon (%)	1.2	0.75
Electrical conductivity at 19 °C (dS m^{-1})	0.496 ± 0.011	0.451 ± 0.012
Water holding capacity (%)	151.95 ± 1	142.82 ± 1
CaCO$_3$ (%)	0.502 ± 0.08	0.521 ± 0.08

Soil 1 = silty clay loam; soil 2 = sandy loam

Table 5 Percent Recovery of Cyazofamid in Soil

S. No	Silty clay loam		Sandy loam	
	Amount loaded (ppm)	Percent recovery (±SD)	Amount loaded (ppm)	Percent recovery (±SD)
1	0.5	78.0 ± 0.06	0.5	80.6 ± 0.04
2	2.0	82.6 ± 0.02	2.0	83.0 ± 0.05
3	5.0	86.0 ± 0.02	5.0	85.5 ± 0.01

Average of three replicates

relative humidity during the study period varied from 12 to 34 °C and 19 to 88 %, respectively (Table 2). Percent dissipation values at different time intervals were calculated considering the amount of fungicide recovered on 0th day (1 h after application) as 100 %. The persistence of cyazofamid in silty clay loam soil applied at 0.1 kg ha^{-1} in soil decreased from 100 to 67.67 % from 0th day (1 h. after application) to 3rd day, and then, it gradually fell up to 36.11 % till 7th day, on 10th day of application, the persistence decreased to 19.44 %. In sandy loam soil application at 0.2 kg a.i. kg ha^{-1}, it degraded from zero percent to 12.50 % from 0th day (1 h. after application) to 1st day and then further degraded to 33.12 % till 3rd day of application, on 7th day it further reduced to 63.12 %. Residues was below detectable limit (<0.01 μg g^{-1} soil) on 15th day of application in both silty clay and sandy loam type of soils at both (0.1 and 0.2 kg ha^{-1}) treatments.

It is evident from Table 7 that residue of cyazofamid dissipates with almost the same rate in silty clay loam and sandy loam soil with almost same dissociation constant rate ($k = 0.13$ and 0.16) up to 10 days leaving no detectable residue on 15th day of application. Slight difference/almost same dissipation rate (0.13 and 0.16) in both soils would be attributed to the fact that the pH of the soils was almost same beside high temperature also favoured in rapid degradation.

Table 4 Physicochemical properties of soils of experimental field depthwise

Sl. No.	Properties	Silty clay loam soil (cm)			Sandy loam soil (cm)		
		15–30	30–45	45–60	15–30	30–45	45–60
1.	Sand (%)	15.60	21.44	24.42	52.10	53.00	53.44
2.	Silt (%)	55.61	53.66	51.37	31.80	31.62	31.98
3.	Clay (%)	28.79	25.00	24.21	16.10	15.38	14.58
4.	Organic carbon (%)	1.01	0.84	0.64	0.60	0.51	0.44
5.	pH	7.09 ± 0.1	6.46 ± 0.1	6.01 ± 0.1	7.01 ± 0.1	6.58 ± 0.1	6.14 ± 0.1
6.	Electric conductivity (1: 2 d Sm^{-1})	0.304 ± 0.011	0.270 ± 0.013	0.126 ± 0.012	0.441 ± 0.012	0.445 ± 0.011	0.435 ± 0.011
7.	CaCO$_3$ (%)	0.497 ± 0.06	0.464 ± 0.05	0.298 ± 0.08	0.501 ± 0.08	0.488 ± 0.07	0.481 ± 0.04

Table 6 Persistence of cyazofamid in soils

Persistence ($\mu g\ g^{-1}$) $\pm$ SD				
Days	Silty clay loam		Sandy loam	
	100 g a.i. ha^{-1}	200 g a.i. ha^{-1}	100 g a.i. ha^{-1}	200 g a.i. ha^{-1}
0	0.72 ± 0.05 (100)	1.25 ± 0.07 (100)	0.82 ± 0.03 (100)	1.60 ± 0.06 (100)
1	0.59 ± 0.03 (81.94)	1.05 ± 0.05 (84.00)	0.71 ± 0.06 (86.80)	1.40 ± 0.04 (87.50)
3	0.48 ± 0.05 (67.67)	0.85 ± 0.02 (68.00)	0.53 ± 0.05 (65.62)	1.07 ± 0.06 (67.07)
5	0.32 ± 0.06 (44.44)	0.65 ± 0.06 (52.00)	0.39 ± 0.02 (48.75)	0.80 ± 0.05 (50.45)
7	0.26 ± 0.02 (36.11)	0.40 ± 0.01 (32.00)	0.29 ± 0.03 (35.36)	0.59 ± 0.07 (37.40)
10	0.14 ± 0.03 (19.44)	0.20 ± 0.08 (16.00)	0.19 ± 0.04 (23.17)	0.39 ± 0.02 (24.37)
15	ND	ND	ND	ND

Values are mean of three readings

Values in parenthesis show percent persistence of fungicide

At the both application rates of cyazofamid, the values of logarithm of residue (C) were plotted against time (t) the distribution of points followed straight line pattern in both soils suggesting that dissipation of cyazofamid could occur through a single distinct phase conforming to first-order kinetics (Figs. 1, 2). The computed value of coefficient of determination (R^2) for the degradation of cyazofamid in silty clay loam at both concentrations was 0.992 and 0.974 and in sandy loam was 0.999 which is statistically significant ($P = 0.05$). This signified that the kinetics of cyazofamid degradation rate followed monophasic first-order degradation kinetics in both soils.

The half-life ($t_{1/2}$) value of cyazofamid calculated from the slope of the regression equation in silty clay loam at application dose 0.1 and 0.2 kg a.i. ha^{-1} was found to be 4.30 and 4.47 days while, for sandy loam soil, it was 4.74 and 4.98 days, respectively (Table 7).

Among the soils, irrespective of the factors, the dissipation of cyazofamid was more in silty clay loam than sandy loam soil. This may be due to high organic matter, high pH and moisture content of silty clay loam. Thus, the breakdown of cyazofamid appears to be soil dependent and reflects the number of organisms present in the soil capable of degrading the compound. Aerobic degradation of cyazofamid in soil occurs via hydrolysis to CCIM (4-chloro-5-p-tolylimidazole-2-carbonitrile). This compound is further degraded to CCIM-AM (4-chloro-5-p-tolylimidazole-2-carboxamide) and then to CTCA (4-chloro-5-p-tolylimidazole-2-carboxylic acid) (USEPA 2004). The half-life values are slightly higher in higher rate of application of cyazofamid in our study. This could be attributed to limitation in number of reaction sites in soil and toxic effects on microorganisms or enzyme inhibition.

The degradation of cyazofamid in soil depends upon soil texture, temperature and pH. Under aerobic condition in different soils, its half-life ranges from 3.5 to 6.5

(USEPA 2004). Degradation studies of cyazofamid in soils showed that the first-order DT$_{50}$ were found in the range of 3.8–15.1 days at 20 °C (Norwegian Food Safety Authority 2007). Dissipation studies conducted in Manitoba, Ontario and New York indicated rapid dissipation of cyazofamid, with DT$_{50}$ ranging from 2.0 to 8.0 days. The rate of degradation increases with increase in pH of soil, and degradation rate was slower in loamy sand ($t_{1/2} = 6.1$–6.4 days, pH 6.5) than in sandy loam ($t_{1/2} = 4.3$–4.4 days, pH 6.9 and 3.7–4.0, pH 7.6) and sandy soil ($t_{1/2} = 4.9$–6.0 days, pH 5.9) (New York State Department of Environmental Conservation 2006). Dissipation of cyazofamid from turf was rapid (half-lives of 18–19 days). By 120 days after the last of three applications, 94–98.8 % of the applied cyazofamid had degraded (primarily in the form of bound residues) (Wiedmann 2009). Cyazofamid persistence under field condition was less, half-life calculated was 4.5 days, and soil aerobic microbes played important role in degradation of fungicide (Suciu et al. 2011).

In our study, soil has high organic matter content, neutral pH and adequate moisture, which is necessary for the growth and development of microorganism and these factors plays major role for rapid degradation of fungicide. Other studies also confirm the fact that at high pH rate, degradation of cyazofamid was higher compared to low or acidic pH. Organic matter and moisture content also play significant role as it harbors more aerobic organisms which is capable of degrading the compound. High temperature during the experimental period also favoured in rapid degradation. Environmental factors play important role in the degradation of pesticides. High temperature and humidity favor rapid degradation of pesticide in soil as these factors favor high microbial population and activity. In general, microbial activity increases in warm, moist and well-aerated soils, and rate of degradation decreases when there is low (temperature,

Table 7 Dissipation kinetics of cyazofamid residues in soils

Properties	Silty clay loam		Sandy loam	
	100 g ha^{-1}	200 g ha^{-1}	100 g ha^{-1}	200 g ha^{-1}
k (days^{-1})	0.161 ± 0.024	0.155 ± 0.025	0.146 ± 0.024	0.139 ± 0.006
Half-life $t_{1/2}$ (days)	4.30	4.47	4.74	4.95
R^2	0.992	0.974	0.999	0.998
Regression equation	$y = -0.071x + 0.122$	$y = -0.077x + 0.130$	$y = -0.063x + 0.086$	$y = -0.065x + 0.209$
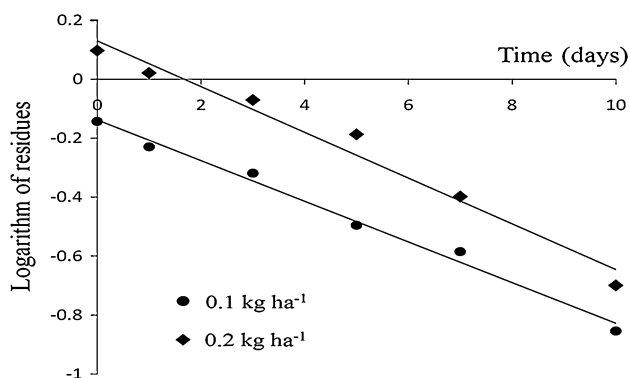
Fig. 1 Logarithm of cyazofamid residues in silty clay loam soil at two application dose
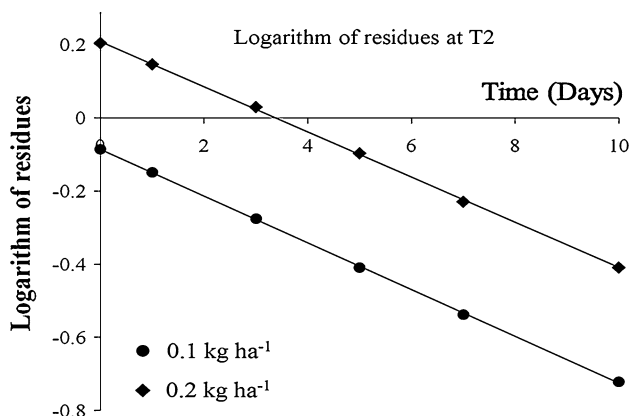
Fig. 2 Logarithm of cyazofamid residues in sandy loam soil at two application dose

moisture and aeration) in soil. (Matsumura 1989; Tiryaki and Temur 2010; Tandon et al. 2012a; b)

Dissipation was faster in silty clay loam compared to sandy loam, which would be attributed to the fact that silty clay loam soil is rich in organic carbon content; hence, more microbial activity would be in soil and microbes play significant role in degradation of fungicide. Beside this, it has higher percentage of clay; the fungicide is more adsorbed on its active sites and it will react with the molecule and would degrade (hydrolysis) or form bound residues.

Leaching

The residues of cyazofamid in different fractions of leachate for both soils which were collected from 1 to 5 days showed no residues in the leachates for both concentrations.

Distribution of fungicide residue in soils at different sections after passing 0.6 liter of water showed that the surface applied cyazofamid was not distributed equally throughout the whole column length but concentration varied at different soil depths. At both application doses, in silty clay loam soil, highest concentration was recorded in 5–10-cm section, whereas in sandy loam soil, it was in 10–15-cm section. No residue was found beneath 15-cm layer of soils. Leaching of fungicide was more in sandy loam as compared to silty clay loam soil. Cyazofamid remains only in top soil, i.e., up to 15 cm length of column in both soils at both concentration doses showing its mobility to be very low in the soil columns (Table 8). This phenomenon might also be correlated with the amount of organic matter present in the soil (McLaughlin and Johnson 1997). It was evident that soil with sand facilitates more permeability and adsorption was relatively less which favored leaching. The presence of organic matter affects the movement of pesticide because of its high absorption capacity toward soil. Since sandy loam soil was deficient in organic matter, there was more movement of the fungicide as compared to silty clay loam soil. Leaching study reveals that mobility of surface applied cyazofamid was very less in both types of soils and show strong affinity for adsorption to soil.

After leaching and processing of the soil sample out of total 78.5 and 157.0 µg cyazofamid added on both types of soil column, the recovery of cyazofamid in silty clay loam soil was 21.15 µg (26.94 %) and 41.72 µg (26.57 %) while recovery in sandy loam was 30.95 µg (39.42 %) and 59.38 µg (37.82 %), respectively. Loss of cyazofamid in silty clay laom soil was 57.35 µg (73.06 %) and 115.28 µg (73.43 %), while in sandy loam soil, it was 47.55 µg (60.58 %) and 97.62 µg (62.18 %) was observed. Low

Table 8 The concentration of cyazofamid ($\mu g\ g^{-1}$) in the different soil depth

Soil Depth (cm)	Silty clay loam ($\mu g\ g^{-1}$) ± SD		Sandy loam ($\mu g\ g^{-1}$) ± SD	
	0.1 kg ha^{-1}	0.2 kg ha^{-1}	0.1 kg ha^{-1}	0.2 kg ha^{-1}
0–5	0.751 ± 0.031	0.981 ± 0.021	0.684 ± 0.026	1.298 ± 0.021
5–10	0.960 ± 0.024	2.587 ± 0.030	1.049 ± 0.022	1.766 ± 0.019
10–15	0.404 ± 0.023	0.604 ± 0.028	1.165 ± 0.018	2.493 ± 0.023
15–20	–	–	–	–
20–25	–	–	–	–
25–30	–	–	–	–
30–35	–	–	–	–
35–40	–	–	–	–
40–45	–	–	–	–
45–50	–	–	–	–
50–55	–	–	–	–
55–60	–	–	–	–

Values are mean of three readings

recovery of cyazofamid is due to the fact that it had half-life of 4.3–4.9 days in silty clay and sandy loam soils, beside other factors such as chemical hydrolysis, interaction among mineralization, formation of biotic and abiotic products viz., different metabolites as well as formation of bound residues also influenced in the low recovery of the fungicide.

Pesticide transport through the unsaturated/saturated zone is a function of chemical and soil characteristics, application and water recharge rate. Leaching studies done by other workers indicated that cyazofamid, and its metabolites had very low mobility in different soils and major residues and were confined to top 0–5 cm section of columns (Wiedmann 2009; Food Safety Commission 2004). Mobility of cyazofamid on four unaged different soils showed that more than 98 % of the applied compound remained on the top 10 cm with very limited leaching and less than 1 % of applied test material was present in the leachate (New York State Department of Environmental Conservation. 2006; Pest Management Regulatory Agency Canada 2006). Adsorption/desorption studies in four types of soil viz. US loamy sand, UK loamy sand, UK sandy loam and Germany sand, the Kf values indicate a medium to high degree of adsorption for the cyazofamid compound. The values of Kf and Koc varied from 4.6 to 65 and 736 to 2,172, respectively, indicating a high degree of adsorption (Norwegian Food Safety Authority 2007). A number of factors influences leaching of soil-applied pesticide, i.e., chemical nature of the pesticide compound, adsorption of pesticide to soil colloids, soil texture, soil permeability, volume of water flow, water solubility of pesticide, soil pH and inorganic and organic soil colloids (Anderson 1996). The result of our study indicates that cyazofamid is tightly adsorbed on the top layer of the soil, and hence, there is low movement of the fungicide. Suciu et al. (2011) also found that cyazofamid is strongly bound to the organoclays particles under laboratory conditions.

The results indicated that as silty clay loam soil was rich in organic carbon and had high clay content, this could be the reason for the higher retention of cyazofamid fungicide on the top soil compared to sandy loam soil in which more concentration was in deeper layers.

Conclusion

The fate of pesticide as well as its mobility in soil environment appears to be controlled by many biotic and abiotic factors. Degradation is dependent upon the chemical nature of the fungicide compound as well as the chemical and physical properties of the soil. The dissipation study of cyazofamid shows that it has first-order degradation kinetics in soil. Cyazofamid in silty clay loam soil and sandy loam has short half-life and does not persist for long period in soils indicating its short persistence. Under simulated rainfall condition, cyazofamid could not leached beneath 15 cm of soil depth in both types of soil. Strong affinity for adsorption to soil results in less hazards for environment as no possibility of groundwater contamination.

It could be concluded from the study that cyazofamid fungicide has short persistence in soils and leaves almost no residues, and hence, pesticide buildup in environment is negligible. There was very little movement of cyazofamid into the soil. It have high affinity for binding with the soil particles, and hence, there are remote chances of leaching through soil profile to pollute the groundwater.

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