A Liquid Chromatographic Method for Determination of Acetamiprid and Buprofezin Residues and Their Dissipation Kinetics in Paddy Matrices and Soil

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Abstract

The present study was conducted to investigate the residue status of two insecticides (acetamiprid and buprofezin) and their dissipation kinetics in three matrices viz. paddy grain, straw and soil. The extraction protocol for residues of these two insecticides was executed using acetonitrile solvent. The analytical method was validated, which showed good linearity with the limit of quantification (LOQ) value of 0.01 and 0.02 mg kg^{-1} for acetamiprid and buprofezin respectively. The recovery range was 79.67-98.33 % concerning all the matrices in both the insecticides. Acetamiprid (20% SP) and Buprofezin (25% SC) were applied separately in the paddy field in two doses: single dose (recommended dose) and double dose along with untreated control throughout the experiment. Residue analysis of these two insecticides in paddy (grain and straw) and soil was accomplished employing high-pressure liquid chromatography (HPLC) with a UV detector. The dissipation data showed that acetamiprid exhibited higher dissipation in comparison with buprofezin. However, their persistence was found slightly higher in soil. The dissipation dynamics in the rice and soil were discussed with biological half-lives of both the insecticides. Consumer risk assessment study was also made considering its fate to the consumers.

Introduction

Rice (*Oryza sativa*) is one of the prime staples for people in low- and lower-middle-income countries that feeds over half of the world's population (Sen et al. 2020). It, being the most consumed cereal in Asia, has profuse economic importance in national and international markets (Bajaj and Mohanty 2005; Burlando and Cornara 2014). India occupies the largest area (43.5 Mha) under rice cultivation and ranks second in production (163.52 MT) in the world (IRRI 2020). The fruitful cultivation of paddy is often drastically thwarted due to preponderance of insect pests (Thongphak et al. 2012). There are nearly twenty insects considered to be rice pests of economic importance including stem borers, gall midge, defoliators and vectors like leafhoppers and planthoppers that hamper rice ecosystem balance causing direct ravages and disease transmission (Ane and Hussain 2016). To combat these pests, synthetic insecticides are generally applied as frontline defence strategies. Acetamiprid (IUPAC name: N-[(6-chloro-3-pyridyl)methyl]-N'-cyano-N-methyl-acetamidine) is a systemic, odourless, neonicotinoid insecticide, developed and marketed by Nippon Soda Co. Ltd., Japan, under the trade name MOSPILAN for the control of sucking insects, generally recommended by Central Insecticide Board (CIB) and Registration Committee (RC) for solo use in rice, cotton, chilli, okra and cabbage in India (DPPQS 2020). This insecticide is a nerve poison that acts as a nicotinic acetylcholine receptors (nAChRs) agonist, which makes it extremely effective in managing insect pests like aphids, jassids, whiteflies, leafhoppers, thrips, bugs and borers (Tomizawa and Casida 2005). Another novel insecticide, Buprofezin (IUPAC name: (2Z)-3-Isopropyl-2-[(2-methyl-2-propanyl)imino]-5-phenyl-1,3,5-thiadiazinan-4-one), developed and marketed by Nihon Nohyaku Co. Ltd., Japan, under trade name APPLAUD, which is an insect growth regulator which is recommended for solo use in rice, cotton, chilli, okra, mango and grape in India (DPPQS 2020). This thiadiazine-like compound acts on the nymph stages of planthoppers, leafhoppers, mealybugs, scales, and whiteflies, and drastically hampers chitin synthesis (Ishaaya et al. 2007; De Cock and Degheele 1998).

Injudicious application of these insecticides may pose a serious threat to human beings because of the residues present there. Various residue analysis methods for acetamiprid and buprofezin were followed using standardized chromatographic protocols (GC/ GC-MS/ LC/ LC-MS) (Wartono et al. 2018; Wu et al. 2012; Sanyal et al. 2008; Lee and Jang 2010). Analysis of buprofezin residues was done earlier in soil (Yu et al. 2016) and various crops like vegetables (Valverde-Garcia et al. 1993), rice (Melo et al. 2020), tea (Chen et al. 2017), grapes (Oulkar et al. 2009) etc. A similar type of analysis was carried out for acetamiprid in crops like paddy (Saha et al. 2017), fruits and vegetables (Obana et al. 2002) and soil (Gupta and Gajbhiye 2007). However, there exists hardly any study of persistence-dissipation of these two insecticides under tropical climate. As both of these insecticides are well utilized in rice, there should be a study of the residue dynamics of these insecticides in different matrices.

The current research paper, therefore, conveys the dissipation dynamics of acetamiprid and buprofezin in paddy (grain and straw) and soil for different doses of applications. In view of the above, the authors have validated the method for residue analysis of these two insecticides in the matter of the precision in results using HPLC, and tried to comprehend their actual residue status in various matrices and concluded with consumer safety issues.

Materials And Methods

Chemicals and reagents

Acetonitrile (HPLC grade) was purchased from J.T. Baker (New Jersey, USA). Analytical Reagent (AR) grade chemicals - Anhydrous sodium sulfate (Na_2SO_4), Sodium chloride (NaCl), Sodium citrate dibasic sesquihydrate ($C_6H_6Na_2O_7.1.5H_2O$), Sodium citrate tribasic hydrate ($C_6H_5Na_3O_7.xH_2O$) were acquired from Thomas Baker, Mumbai, India. Ultrapure water (HPLC grade) was taken from Sartorius water purification system (Sartorius AG, Goettingen, Germany). Primary secondary amine (PSA, 40 µm) was procured from Agilent Technologies, Bangalore, India.

Apparatus

Mixer Grinder (Bajaj India Pvt. Ltd., Mumbai, India), homogenizer (Heidolph 900, Germany), Mettler Toledo electronic balance (with an accuracy of 0.01 mg), vortex mixer (Geni 2T, Imperials Biomedicals, Mumbai, India), centrifuge (Kubota, Germany), microcentrifuge (Microfuge Pico, Kendro, D-37520, Osterode, Germany), Mechanical shaker and ultrasonic bath (Oscar electronics, Mumbai, India), P.P Centrifuge tubes of 50 ml capacity, Click lock centrifuge tubes of 2 ml capacity, Volumetric flasks of 10 ml and 50 ml capacity (Grade A), Volumetric pipettes of 1 ml, 5 ml and 10 ml capacity (Grade A), Micropipette (100–1000 µ1), and Micro tips HPLC auto-sampler vial (2 ml) were used.

Reference standard

The certified reference materials (CRMs) of both acetamiprid (having 99.9 % purity) and buprofezin (having 99.1 % purity) were obtained from Krishi Rasayan Exports Pvt. Ltd., India. Standard stock solutions were prepared by dissolving 10 (± 0.1) mg of CRMs in 10 ml of methanol resulting in a final concentration of

1000 μg ml^{-1}. A working standard mixture of 10 μg ml^{-1} was prepared in methanol by duly mixing the individual standard stock solutions followed by subsequent dilution, from which the calibration standard solutions of 1, 2.5, 5, 10, 25 and 50 ng ml^{-1} were made. The matrix-matched standards of the same concentrations were made using the control rice extracts acquired from the sample preparation procedure.

Field experiment

The field trial was conducted on Swarna variety of kharif paddy at Uttar Banga Krishi Viswavidyalaya, Pundibari, Cooch Behar under Terai agro-climatic zone of West Bengal, during July to November in 2018 following Randomized Block Design (RBD). The meteorological conditions and soil properties during the study period are shown in Table 1.

Table 1
Meteorological and soil physico-chemical parameters of the site of experiment

Sl. No.	Parameters	Result	Methods of determination
Meteorological conditions			
1	Av. temperature (max) °C)	36.25	Modified Blaney-Criddle method (Zhan and Lin 2009)
2	Av. temperature (min) °C)	18.58	Modified Blaney-Criddle method (Zhan and Lin 2009)
3	Av. rainfall (max) (mm)	9.79	Rain gauge method (WMO 2009)
4	Av. rainfall (min) (mm)	1.75	Rain gauge method (WMO 2009)
5	Av. relative humidity (max) (%)	93.27	Psychrometer method (Gorse et al. 2012)
6	Av. relative humidity (min) (%)	43.53	Psychrometer method (Gorse et al. 2012)
Soil properties			
1	Sand (%)	16.77	Hydrometer method (Bouyoucos 1962)
2	Silt (%)	44.12	Hydrometer method (Bouyoucos 1962)
3	Clay (%)	39.25	Hydrometer method (Bouyoucos 1962)
4	pH (soil: water ratio 1: 2.5)	5.57	Digital pH meter (consisting of glass and calomel electrodes) (Jackson 1973)
5	$EC_{1:2}$ (dS m^{-1}) at 25°C	0.10	Conductivity meter (Richards 1954)
6	Organic Carbon (%)	0.51	Wet oxidation method using $K_2Cr_2O_7$ (Walkley and Black 1934)
7	Available N (Kg/ha)	206.40	Kjeldahl method/ alkaline potassium permanganate oxidation method (Subbiah and Asija 1956)
8	Available P (Kg/ha)	8.17	Olsen's sodium bicarbonate method (Olsen et al. 1954)
9	Available K (Kg/ha)	177.80	Neutral normal ammonium acetate method (Stanford and, English 1949)
10	S (Kg/ha)	32.63	Calcium chloride extraction method (William and Steinbergs 1962)
11	Zn (ppm)	1.07	DTPA extraction method (Lindsay and Norvell 1978)
12	Cu (ppm)	3.41	DTPA extraction method (Lindsay and Norvell 1978)
13	Fe (ppm)	9.01	DTPA extraction method (Lindsay and Norvell 1978)
14	Mn (ppm)	9.27	DTPA extraction method (Lindsay and Norvell 1978)
15	Bulk density	1.33	Core method (Blake 1965)
16	CEC (cmol (p^+) kg^{-1})	17.34	Ammonium acetate method (Chapman 1965)
17	Texture	Silty clay loam	Texture triangle hydrometer method (Bouyoucos 1962)
18	Order	Entisol	Soil taxonomy classification method (USDA 1999)

Acetamiprid 20% SP formulation (under Trade name SPARK manufactured by Hindustan Agro Chemicals) was applied in the paddy field in two doses: single dose (SD i.e. 20 g a.i. ha^{-1}) and double dose (DD i.e. 40 g a.i. ha^{-1}) along with untreated control throughout the experiment. Similarly, Buprofezin 25 % SC (under Trade name BANZO manufactured by Biostadt India Limited) was sprayed over the rice field in dosages of 200 g a.i. ha^{-1} as single dose (SD) and 400 g a.i. ha^{-1} as double dose (DD) in addition to untreated control. Each experiment was conducted in 20 m^2 plots in triplicates. These two insecticides were applied thrice since the start of tillering to panicle initiation stage at an interval of 3, 7 and 15 days. The residues of the pesticide formulation were investigated in paddy (grain and straw) and soil.

Sampling

To investigate the dissipation of pesticide formulation (acetamiprid 20% SP and buprofezin 25% SC) in paddy (grain and straw) and soil, pesticide formulations were sprayed once in the tillering stage of rice. In order to achieve valid detection of residues even at 10–15 days after spraying, the treatment dosages for the dissipation study were set as 20 g a.i. ha^{-1} and 40 g a.i. ha^{-1} for acetamiprid, and 200 g a.i. ha^{-1} and 400 g a.i. ha^{-1} for buprofezin. Sufficient quantities of paddy grain, straw and soil (about 500 g each) samples were collected from 10–12 randomly chosen sampling points in each plot at 0 (2 hours after spraying), 1, 3, 5, 7, 10 and 15 days after spraying. The soil was randomly sampled to a depth of 0–15 cm in each plot using a soil-sampling apparatus. All samples were stored in a deep freezer (-20°C) till analysis.

Sample preparation and analysis

The soil samples were made free from stones and weeds, pulverized thoroughly and passed through 2 mm sieve to get fine powder. Rice straw samples were chopped to small pieces, and grains were detached by a threshing machine followed by grinding by a vegetation disintegrator to make coarse powder.

The samples of soil (10 g), grain (5 g) and straw (2 g) were kept separately into a centrifuge tube (50 ml capacity), followed by addition of ultrapure water (5 ml) and acetonitrile (10 ml for the paddy samples and 20 ml for the soil samples). The tubes were continuously shaken for 30 minutes by an oscillator (air bath). Then, NaCl (3 g) was added and subjected to oscillation by a vortex mixer for 1 min. The mixture was then centrifuged (5 minutes, 3800 rpm), and the supernatant acetonitrile layer (1 ml) was transferred into a centrifuge tube (2 ml capacity) containing PSA (50 mg). The centrifuge tube was shaken for 1 minute on a vortexer and then again centrifuged for 3 minutes at 10000 rpm. The supernatant was passed through a 0.22 µm polypropylene filter and collected into an autosampler vial for HPLC analysis.

HPLC Operating conditions

Analytical determinations were attained using the chromatographic (HPLC) conditions as given below:

Model : Shimadzu LC-2010CHT

System software : Empower 2 (version 5.1).

Column : Perfectsil C18 stainless steel column, 250 × 4.6 mm, 5µm

Detector : UV detector

Wavelength : 254 nm

Flow rate : 0.8 ml/min

Mobile phase : ACN : Water (0.1% orthophosphoric acid) (50 : 50)

Temperature : 35°C

Injection volume : 10 µl

Typical run time : 20 minutes

Typical retention time : 4.7 minutes (Acetamiprid), 10.7 minutes (Buprofezin)

Method validation

Analytical method validation was performed following standardized guidelines given by the European Commission (SANTE 2017).

Calibration curves and linearity

The calibration curve was prepared by establishing six concentration points with calibration standards in the range of 0.02–0.50 µg ml-1 in solvent as well as in the extract of matrix (control). The linearity curve was plotted by the concentrations against the responses (area of the peak) (Figs. 1 and 2).

Selectivity and sensitivity

Sensitivity was evaluated by the limit of quantification (LOQ) in different matrices (soil, grain and straw).

Recovery study

Recovery was performed at 0.01, 0.02, 0.05, 0.10, 0.50 mg/kg levels for acetamiprid and at 0.02, 0.03, 0.05, 0.1 and 0.5 mg/kg for buprofezin. The matrix effect was assessed by post-extraction spiking at 0.02, 0.03, 0.05, 0.1 and 0.5 levels in comparison to solvent standard response.

Dissipation kinetics and waiting periods

Dissipation for acetamiprid and buprofezin was studied by plotting the data to the first order kinetic equation:

$A_t = A_0 e^{-kt}$ (1)

Where, A_t = the concentration at time t, A_0 = the initial concentration, k = the rate constant for dissipation of insecticides, and t = the time.

Calculation of half–life ($t_{1/2}$) was required to an analysis by the following equation:

$t_{1/2} = \ln 2/k$ (2)

The Pre-harvest intervals (PHI) can be calculated in terms of the time (days) required to dissipate of the initial deposition after insecticides sprayings to below the maximum residue limit (MRL). Straw as such cannot be used for direct consumption by human beings, but it can be used for mushroom production, conversion to the sugar syrup and yeast protein, which is further consumed by human beings. Hence, determination of PHI for both the products are necessary. Each pesticide has its own PHI ,which also varies from crop to crop. In first-order kinetics, it was calculated by the following equation:

PHI = [log(intercept) – log(MRL)]/slope (3)

The residue data, after plotting against time (days) were fitted to TableCurve 2D, which is a commercially available software and one of the popular choices among researchers for curve-fitting and data modelling of research data. The specialized models used in the 2D curve can contain most mathematical constructs, special functions, including series convergence and conditional statements, differentiations, integrations, and parameter constraints. Unlike most curve fitting programs, TableCurve 2D's user-defined functions are compiled in custom mode curve fitting for quicker performance, at the speed as with the built-in equations. $(1 + 1)^{st}$ order kinetics were followed during calculation in the 2D curve. According to FSSAI, the MRL values of 0.01 mg kg^{-1} and 0.05 mg kg^{-1} for acetamiprid and buprofezin respectively are considered.

Consumer food safety assessment

The food safety of acetamiprid and buprofezin in paddy grain was determined as per the reported literature (Majumder et al. 2020). The maximum permissible intake (MPIs) were estimated by multiplying the acceptable daily intake (ADI) by the average body weight of child (approx. 16 kg). The ADI of acetamiprid and buprofezin was 0.025 and 0.01 mg kg^{-1} body weight day respectively (EU 2020). Dietary exposures were calculated by multiplying the acetamiprid and buprofezin residue present in each sample (mg kg^{-1}) with consumption (per person) of 0.270 kg day^{-1} of cereals (rice) (ICMR-NIN 2020).

Results And Discussion

Method validation

To satisfy the specification of MRLs for acetamiprid and buprofezin residue in paddy grain by the Food Safety and Standard Authority of India (FSSAI), the method was validated as stated in the SANTE guideline validation system (SANTE 2017). The percentage recovery was determined at five levels in all the matrices (paddy grain, straw and soil). The percentage recoveries for acetamiprid at 0.01, 0.02, 0.05, 0.10 and 0.50 mg kg^{-1} were 82.33–98.33 %, 80.33–89.67 % and 79.67–81.67 % in grain, straw and soil respectively. In case of buprofezin, percentage recovery data at 0.02, 0.03, 0.05, 0.10 and 0.50 mg kg^{-1} were varying from 80.00 to 93.67 % (Table 2). The coefficient of determination (R^2) were more than 0.987 for both the pesticides within the calibration range of 0.02–0.5 mg/kg for solvent standards as well as matrix standards. The average matrix effect (ME) percentage of acetamiprid and buprofezin were less than 5.00 % for paddy grain, 6.00 to 7.20 % for straw and 5.70 to 7.40 % for soil. The LOQ of acetamiprid was 0.01 mg kg^{-1} and for buprofezin 0.02 mg kg^{-1} in paddy grain, straw and soil sample. The method optimized data in the present research satisfied the EU protocols (SANTE 2017) for the determination of acetamiprid and buprofezin residue in the matrices of paddy grain, straw and soil.

Table 2
Percent recovery of acetamiprid and buprofezin from paddy grain, straw and soil

Sample Types	Acetamiprid			Buprofezin		
	Fortification level (mg kg^{-1})	**Recovery (%)**	**% RSD**	**Fortification level (mg kg^{-1})**	**Recovery (%)**	**% RSD**
Paddy grain	0.01	82.33	1.86	0.02	81.33	3.09
	0.02	85.67	1.35	0.03	82.33	0.70
	0.05	90.33	1.28	0.05	86.67	2.40
	0.10	93.33	1.64	0.1	91.33	1.67
	0.50	98.33	1.17	0.5	93.67	2.22
Paddy straw	0.01	84.67	0.68	0.02	82.33	0.70
	0.02	80.33	1.90	0.03	81.33	1.88
	0.05	82.00	2.11	0.05	84.33	1.37
	0.10	86.33	0.67	0.1	89.00	1.12
	0.50	89.67	1.70	0.5	91.67	0.63
Soil	0.01	81.67	1.41	0.02	81.33	1.88
	0.02	81.00	1.23	0.03	80.00	1.25
	0.05	81.67	2.83	0.05	83.67	1.83
	0.10	79.67	1.92	0.1	87.33	1.75
	0.50	81.33	1.88	0.5	90.33	0.64

Residues of acetamiprid and buprofezin

After the final spray, the initially deposited residues of acetamiprid were found to be 0.36 and 0.75 mg kg^{-1} in paddy grain, 0.31 and 0.71 mg kg^{-1} in paddy straw and 0.29 and 0.63 mg kg^{-1} in soil for single and double doses respectively (Table 3). Acetamiprid was degraded at a faster rate up to 5 days after application (DAA) in paddy grain and straw, whereas in case of soil, it was very slow, *viz.* initially degraded at a slower rate (up to 5 DAA), and however, all residues reached below detectable limit (BDL) in all the matrices on 15 DAA.

Table 3
Acetamiprid residue persistence in paddy grain, straw and soil

Persistence of acetamiprid in paddy grain					**Persistence of acetamiprid in paddy straw**				**Persistence of Acetamiprid in Soil**			
Days Interval	Single dose (SD)		Double dose (DD)		Single dose (SD)		Double dose (DD)		Single dose (SD)		Double dose (D	
	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dis (%)
0	**0.36**	-	**0.75**	-	**0.31**	-	**0.71**	-	**0.29**	-	0.63	-
1	**0.2**	44.44	**0.43**	42.67	**0.23**	25.81	**0.55**	22.54	**0.26**	10.34	0.54	9.5
3	**0.11**	69.44	**0.27**	64.00	**0.12**	61.29	**0.28**	60.56	**0.19**	34.48	0.45	23.
5	**0.05**	86.11	**0.17**	77.33	**0.07**	77.42	**0.18**	74.65	**0.11**	62.07	0.31	42.
7	**0.04**	88.89	**0.09**	88.00	**0.06**	80.65	**0.1**	85.92	**0.06**	79.31	0.2	68.
10	**0.02**	94.44	**0.05**	93.33	**0.01**	96.77	**0.07**	90.14	**0.03**	89.66	0.09	85.
15	**BDL**	-	**0.04**	94.67	**BDL**	-	**0.05**	92.96	**BDL**	-	0.03	95.

In case of buprofezin, initially deposited residues were found to be 0.27 and 0.63 mg kg^{-1} in paddy grain, 0.23 and 0.61 mg kg^{-1} in paddy straw and 0.24 and 0.47 mg kg^{-1} in soil for single and double doses respectively (Table 4). Initially, buprofezin was degraded slowly in all the matrices. Growth dilution between the application of pesticides and sampling may be held prime responsible for dissipation and degradation of pesticide residues. Secondary causes possibly include volatilization occurring during the initial periods after application, decomposition by sunlight and heat, UV radiation, removal by weathering, or other complex conditions (Li et al. 2006).

Table 4
Buprofezin residue persistence in paddy grain, straw and soil

Persistence of buprofezin in paddy grain					Persistence of buprofezin in paddy straw				Persistence of buprofezin in Soil			
Days Interval	Single dose (SD)		Double dose (DD)		Single dose (SD)		Double dose (DD)		Single dose (SD)		Double dose (D	
	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dissipation (%)	Residue (mg kg^{-1})	Dis (%)
0	**0.27**	-	**0.63**	-	**0.23**	-	**0.61**	-	**0.24**	-	**0.47**	-
1	**0.23**	34.29	**0.56**	16.00	**0.21**	27.59	**0.57**	19.72	**0.23**	32.35	**0.35**	47.
3	**0.22**	37.14	**0.48**	24.00	**0.18**	37.93	**0.51**	28.17	**0.19**	44.12	**0.32**	52.
5	**0.19**	45.71	**0.41**	31.00	**0.11**	62.07	**0.39**	45.07	**0.12**	64.71	**0.19**	71.
7	**0.09**	74.29	**0.28**	44.00	**0.07**	75.86	**0.26**	63.38	**0.07**	79.41	**0.17**	74.
10	**0.05**	85.71	**0.12**	60.00	**0.05**	82.76	**0.14**	80.28	**0.04**	88.24	**0.14**	79.
15	**0.04**	88.57	**0.04**	68.00	**BDL**	-	**0.07**	90.14	**BDL**	-	**0.03**	95.

Dissipation kinetics and waiting periods

The dissipation behaviour of acetamiprid in paddy and soil are different. It was initially faster in paddy, however, in soil it was slowed down over time. This indicated an exponential degradation pattern following simple first-order kinetics that is sufficient to explain the dissipation dynamics of the insecticide residues. The similar pattern was observed for buprofezin with the R^2 value of more than 0.90 for both the pesticides in all the matrices (Figs. 3, 4, 5, 6, 7 and 8). Considering at the dataset of different sampling days (Tables 3 and 4), the PHIs estimated through first order kinetics were adequate in minimizing the residue level (i.e., < MRL), implying the appropriateness of this model to define the dissipation kinetics of acetamiprid and buprofezin residues in all the matrices. The PHIs for acetamiprid in grain and straw were 11.67 days and 11.82 days respectively for SD. Whereas PHI for buprofezin (SD) in case of paddy grain was 12.42 days and in case of straw was 9.69 days. One interesting point to note that the PHIs of both the pesticides at DD for straw matrices were beyond 15 days which signified that there would be much time needed to degrade the active ingredient and harvesting should be delayed after 15 days. In case of paddy grain matrix, buprofezin showed 13.93 days that was nearer to 15 days, which revealed that paddy grain was ready to harvest shortly, whereas straw required more time to be ready for further use after application of buprofezin pesticide.

In this kinetics model of acetamiprid for paddy matrix, one fraction of the applied pesticide went right away to the solution phase, where they degraded rapidly and the remaining portion possibly settled in a dynamic equilibrium while being adsorbed on cellular components. This happened owing to the rapid degradation of the insecticide residues in paddy at the double dose. As buprofezin has contact activity, so the presence of free (unabsorbed) molecules on paddy surfaces (exposed to the sunlight and other environmental factors resulting in degradation) might be higher for double dose that led to a comparably quicker rate of degradation. Almost 40 % of the initial deposits of acetamiprid dissipated within 24 hours (day 1) of application for both doses, with more than 95 % dissipation found by day 10 in case of paddy grain matrices, whereas in case of paddy straw almost 20 % dissipated within day 1 and almost 90 % dissipated by day 10 for both single and double dose. For the soil, the acetamiprid dissipation was around 10 % within day 1 and came to almost 86 % by day 10 for both the doses that indicated its slower degradation in the soil matrix. In the case of buprofezin, there was no similar behaviour observed for single and double dose in case of paddy grain matrix. It dissipated 89 % at 15 days for single dose, whereas 68 % for double dose. In the other two matrices, it followed the same pattern like acetamiprid. For paddy straw, it dissipated around 80 % by 10 days for both the doses, whereas in case of soil, more than 80% degraded by 10 days. It suggested that acetamiprid had a higher rate of degradation compared to buprofezin. The probable reason can be the functional group attached to the moieties present in both the compounds. Acetamiprid, due to the attachment of chlorine (Cl) as an electronegative group at pyridine moiety, was susceptible to release labile group as chloro-pyridine resulting in a faster dissipation compared to buprofezin, where no electronegative group was attached to pyrimidine moiety. The half-lives of acetamiprid in case of single dose for paddy grain, straw and soil were 2.47, 2.19 and 2.95 days respectively, whereas, in case of double dose for the same matrices were 1.37, 1.48 and 1.43 days respectively. The half-lives of buprofezin in case of single dose for paddy grain, straw and soil were 4.88, 4.23 and 3.67 days respectively, whereas, in case of double dose for the same matrices were 3.75, 4.56 and 4.17 days respectively.

Therefore, the present research evaluated the dynamics of acetamiprid and buprofezin residues in paddy and soil in a holistic way. The PHI data can be useful to paddy growing farmers of a particular location to ascertain the safe use of pesticides for management of rice insect pests, while the half-life values in the soil will help manage the residues of these insecticides in plant, soil and other matrices.

Food safety

The residues of acetamiprid and buprofezin were dissipated to below MRL with the almost same pattern in rice grain. There is hardly any reported data regarding the safety of acetamiprid and buprofezin in rice and therefore, the safety evaluation associated with these insecticides residues was very crucial. The MPI of acetamiprid and buprofezin was estimated as 0.4 and 0.16 mg $person^{-1}$ day^{-1} respectively. The dietary exposures of the residues were less than the MPI on all the sampling days for both the doses (Table 5). Therefore, acetamiprid and buprofezin are concluded to possess low toxicity risk when practiced for pest management in paddy.

Table 5
Safety evaluation of day wise residues of acetamiprid and buprofezin in paddy grain

Sampling days	Acetamiprid				Buprofezin			
	Recommended dose		Double dose		Recommended dose		Double dose	
	Residues (mg kg^{-1})	Dietary exposure (mg person^{-1} day^{-1})	Residues (mg kg^{-1})	Dietary exposure (mg person^{-1} day^{-1})	Residues (mg kg^{-1})	Dietary exposure (mg person^{-1} day^{-1})	Residues (mg kg^{-1})	Dietary exposure (mg person^{-1} day^{-1})
0	**0.36**	0.097	**0.75**	0.203	**0.27**	0.073	**0.63**	0.170
1	**0.2**	0.054	**0.43**	0.116	**0.23**	0.062	**0.56**	0.151
3	**0.11**	0.030	**0.27**	0.073	**0.22**	0.059	**0.48**	0.130
5	**0.05**	0.014	**0.17**	0.046	**0.19**	0.051	**0.41**	0.111
7	**0.04**	0.011	**0.09**	0.024	**0.09**	0.024	**0.28**	0.076
10	**0.02**	0.005	**0.05**	0.014	**0.05**	0.014	**0.12**	0.032
15	**BDL**	**-**	**0.04**	0.011	**0.04**	0.011	**0.04**	0.011

Conclusions

We investigated the residues and dissipation patterns of two insecticides (acetamiprid and buprofezin) under the open-field system for paddy cultivation. An easy and simple analytical method was developed, standardized and validated using liquid chromatographic technique (HPLC) for estimation of residue in soil and paddy matrices. The LOQ values were found to be 0.01 and 0.02 mg kg^{-1} for acetamiprid and buprofezin respectively in all of the matrices. The study indicated that both insecticides dissipated rapidly with an almost similar pattern in all the three matrices under field condition with acetamiprid having higher dissipation than buprofezin. The PHIs (days) of insecticides were also proposed afore harvest based upon the dissipation equations. Both the insecticides were deemed to maintain a safe toxicological profile in case of dietary exposures of the residues at both doses. It is highly anticipated that this research findings certainly furnish reliable data for apprehending the fate of buprofezin and acetamiprid residues and supply fruitful guidance towards successful residue management and robust assurance to safety of foods.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

This work was carried out in collaboration among all authors. PM, S_OM and S_UM designed the study and wrote the protocol. BM, S_OM and S_UM managed the analysis of the study. AP, TP and NS made data interpretation. S_UM and PM were major contributors in writing the manuscript. All authors thoroughly read and approved the final manuscript.

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Figures

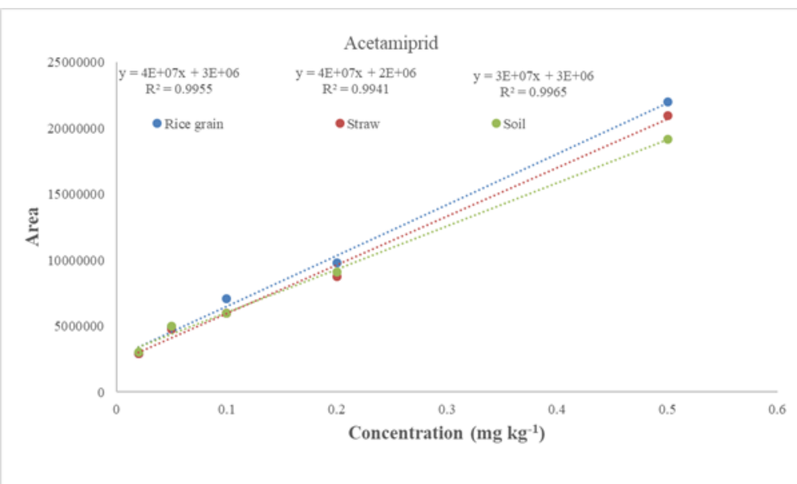

Figure 1

Linear graph of acetamiprid in different matrices

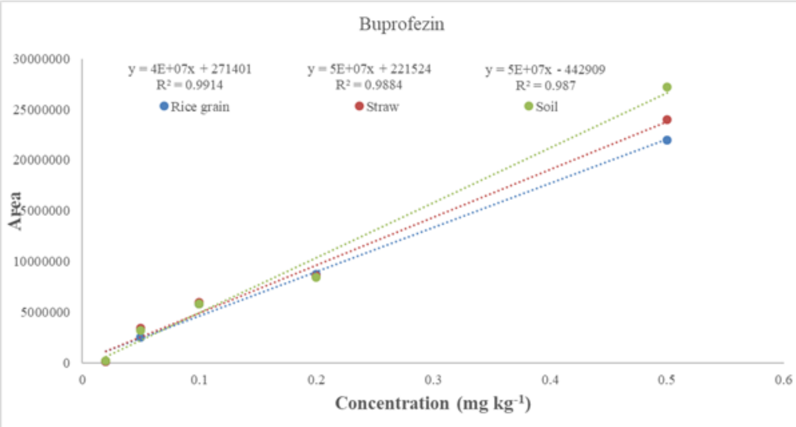

Figure 2

Linear graph of buprofezin in different matrices

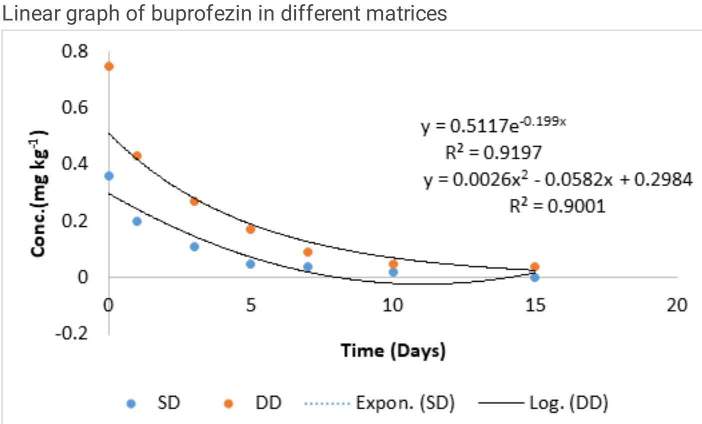

Figure 3

Acetamiprid dissipation in paddy grain

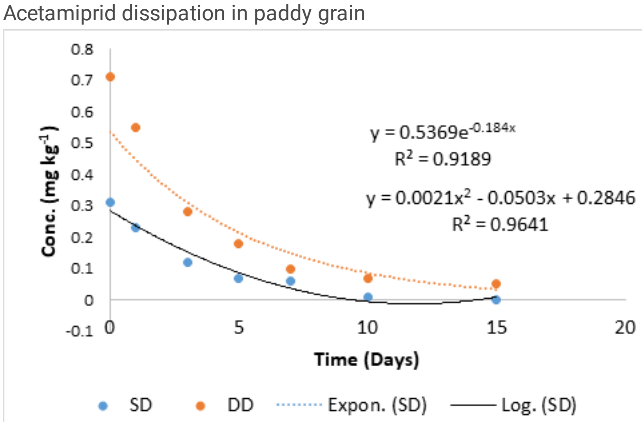

Figure 4

Acetamiprid dissipation in paddy straw

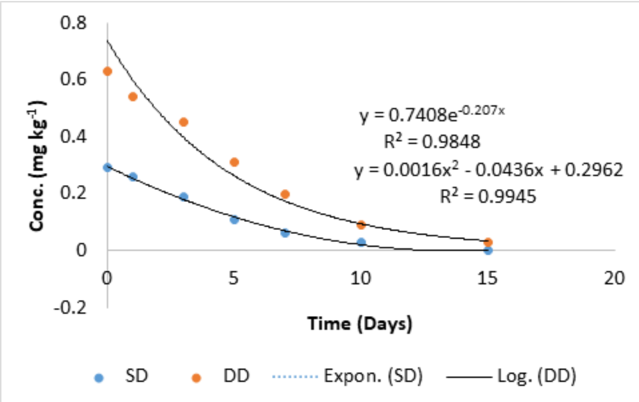

Figure 5

Acetamiprid dissipation in paddy soil

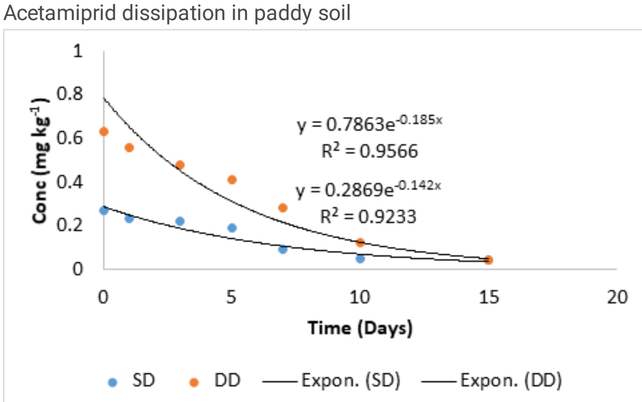

Figure 6

Buprofezin dissipation in paddy grain

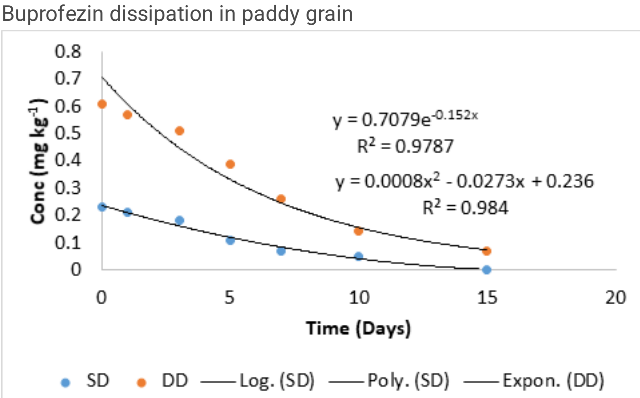

Figure 7

Buprofezin dissipation in paddy straw

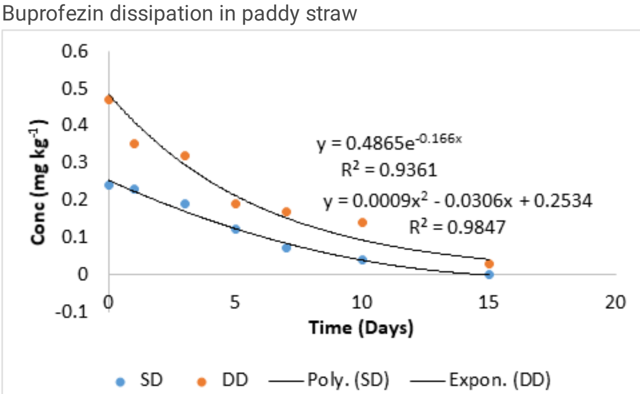

Figure 8

Buprofezin dissipation in paddy soil