RESEARCH ARTICLE

A liquid chromatographic method for determination of acetamiprid and buprofezin residues and their dissipation kinetics in paddy matrices and soil

Sujan Majumder[1] · Somnath Mandal[2] · Biswajit Majumder[3] · Anindita Paul[4] · Tarun Paul[5] · Nandita Sahana[2] · Prithusayak Mondal[6]

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 procedure 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-performance liquid chromatography (HPLC) with ultraviolet (UV) detector and confirmed by ultra-performance liquid chromatography (UPLC) coupled with mass spectrometry (UPLC-MS/MS). 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.

Keywords Acetamiprid · Buprofezin · Insecticide residues · LC-MS/MS · Method validation · Persistence · Paddy · Soil · Consumer safety

Sujan Majumder and Somnath Mandal contributed equally to this work.

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✉ Prithusayak Mondal
   prithusayak@gmail.com

1   ICAR-Indian Institute of Vegetable Research, Varanasi, Uttar Pradesh, India

2   Department of Biochemistry, Uttar Banga Krishi Viswavidyalaya, Pundibari, Cooch Behar, West Bengal, India

3   Quality Control Laboratory, Uttar Banga Krishi Viswavidyalaya, Pundibari, Cooch Behar, West Bengal, India

4   ICAR-Central Tobacco Research Institute, Rajahmundry, Andhra Pradesh, India

5   Department of Agronomy, Uttar Banga Krishi Viswavidyalaya, Pundibari, Cooch Behar, West Bengal, India

6   Regional Research Station (Terai Zone), Uttar Banga Krishi Viswavidyalaya, Pundibari, Cooch Behar, West Bengal, India

Introduction

Rice (*Oryza sativa*) is one of the prime staples for people in low- and lower-middle-income countries that feed 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 (International Rice Research institute) 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 defense strategies. Acetamiprid (IUPAC name: N-[(6-chloro-3-pyridyl)methyl]-N'-cyano-N-methyl-acetamidine) is a systemic, odorless, 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, chili, okra, and cabbage in India (DPPQS (Directorate of Plant Protection, Quarantine, and Storage) 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, is an insect growth regulator which is recommended for solo use in rice, cotton, chili, okra, mango, and grape in India (DPPQS (Directorate of Plant Protection, Quarantine, and Storage) 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. For detection of pesticidal or drug residues from diverse environmental matrices, different standardized chromatographic methods such as, GC/ GC-MS/ LC/ LC-MS have been followed (Pascale et al. 2020; Shinde et al. 2021; Wartono et al. 2018). The residues in acetamiprid and buprofezin were reported to be analyzed using sophisticated liquid chromatographic techniques (Wu et al. 2012; Sanyal et al. 2008; Lee and Jang 2010). Analysis of buprofezin residues was practiced 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), and grapes (Oulkar et al. 2009). 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) and water (HPLC grade) were purchased from Sigma-Aldrich, India. 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 μl), 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 (stored in refrigerator at −20°C) 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 0.01, 0.025, 0.05, 0.1, 0.25, and 0.5 μg 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 (longitude: 89.386° E, latitude: 26.402° N) trial was conducted on Swarna variety of autumn (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.

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 active ingredient (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 zigzag fashion) in each plot at 0 (2 hours after spraying), 1, 3, 5, 7, 10, and 15 days after spraying following a modified sampling plan (Oulkar et al. 2009). The soil was randomly sampled to a depth of 0–15 cm in each plot using a soil-sampling apparatus (soil auger). All samples were stored in a deep freezer (−20 °C) until 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 min 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 min, 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 min on a vortexer and then again centrifuged for 3 min at 10000 rpm. The supernatant was passed through a

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 gage method (WMO (World Meteorological Organization) 2009)
4	Av. rainfall (min) (mm)	1.75	Rain gage method (WMO (World Meteorological Organization) 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 (Williams 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 (United States Department of Agriculture) 1999)

0.22 μm polypropylene filter and collected into an autosampler vial for HPLC analysis.

Quantification by HPLC-UV

Analytical determinations were attained using high performance liquid chromatography (HPLC, Model No. Shimadzu LC-2010CHT) having Perfectsil C18 stainless steel column (250 × 4.6 mm i.d., 5 μm particle size) coupled with ultraviolet (UV) detector. The standardized mobile phase was an isocratic elution of solvent mixtures comprising of equal (1:1, v/v) quantity of acetonitrile (Sigma-Aldrich, HPLC grade) and water (Sigma-Aldrich, HPLC grade) containing 0.1% orthophosphoric acid. The injection volume was 20 μl. The column temperature was maintained at 35 °C and the flow rate was 0.8 mL min^{-1} with the run time of 20 min. The wavelength (λ_{max} value) for analysis was 254 nm with retention times of 4.7 min and 10.7 min for acetamiprid and buprofezin, respectively. The data were processed utilizing system software Empower 2 (version 5.1).

Confirmation by UPLC-MS/MS

The results of LC-UV were confirmed by injecting 10 μL analytes to an API-3200 LC–MS/MS system (AB Sciex, Vaughan, Canada) bridged to a Waters UPLC (USA) controlled by Analyst 1.5 software for data acquisition and processing. Analytes were separated onto a reverse phase Zorbax SB-C18 (150 × 4.6 mm i.d., 5 μm particle size) column (Agilent Technologies, USA) maintained at 35 °C temperature. The mobile phase was prepared using (A) 5 mM ammonium formate in methanol and (B) 5 mM ammonium formate in water. The gradient elution program was as follows: A (95%) B (5%) at the initial time (0 min), A (95%) B (5%) (at 1.70 min), A (50%) B (50%) (at 4.90 min), A (10%) B (90%) (at 9.90 min), A (10%) B (90%) (at 11.50 min), A (95%) B (5%) (at 13.21 min), A (95%) B (5%) (at 14 min). The mobile phase flow rate was 0.35 ml min^{-1} with total run time of 14 min. The mass spectrometric (MS/MS) analysis of both the insecticides were carried out and determined in positive electrospray ionization mode (ESI$^+$) with dwell time of 30 ms using multiple reactions monitoring (MRM) method. The MS source parameters used were as follows: ion source temperature of 500 °C, ion spray voltage of 5.5 kV in positive mode, curtain gas of 30 psi, collision-activated dissociation (CAD) gas of 5 psi, nebulizer gas (GS1) of 40 psi, heater gas of (GS2) 40 psi. The mass spectrometer was monitored for the quantification and for confirmation from the precursor and product ions.

Method validation

Analytical method validation was performed following standardized guidelines issued by the European Commission (SANTE 2017; EURACHEM 2021).

Calibration curves and linearity

The calibration curve was prepared by establishing six concentration points with calibration standards in the range of 0.01–0.50 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, and 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 (ME) 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.

$$ME\ (\%) = \frac{(Peak\ area\ of\ matrix\ matched\ standard - Peak\ area\ of\ solvent\ Standard)}{Peak\ area\ of\ matrix\ matched\ standard} \times 100$$

Dissipation kinetics and waiting periods

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

$$A_t = A_0 e^{-kt} \tag{1}$$

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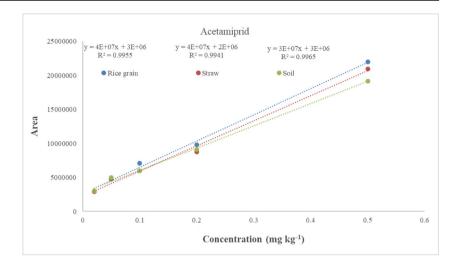
Calculation of half–life ($t_{1/2}$) was required to an analysis by the following equation:

$$t_{1/2} = \ln 2/k \tag{2}$$

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

Fig. 1 Linear graph of acetamiprid in different matrices

Acetamiprid

$y = 4E+07x + 3E+06$
$R^2 = 0.9955$

$y = 4E+07x + 2E+06$
$R^2 = 0.9941$

$y = 3E+07x + 3E+06$
$R^2 = 0.9965$

● Rice grain   ● Straw   ● Soil

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:

$$PHI = [\log(intercept) - \log(MRL)]/slope \qquad (3)$$

The residue data, after plotting against time (days) were fitted to TableCurve 2D, where $(1+1)^{st}$ 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 intakes (MPIs) were estimated by multiplying the acceptable daily intake (ADI) by the average body weight of child (approx. 16 kg). The ADIs of acetamiprid and buprofezin were 0.025 and 0.01 mg kg^{-1} body weight day, respectively, (EU (European Union) 2020). Dietary exposures were calculated via multiplication of 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 (Indian Council of Medical Research—National Institute of Nutrition) 2020).

Results and discussion

Method performance

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 (SANTE 2017) validation system. MS/MS method was applied to study the optimal two ion transitions (primary and secondary transitions of a precursor to product ions) from which the identification of
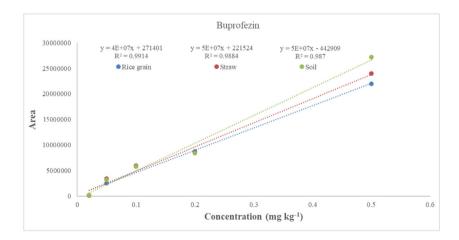
Fig. 2 Linear graph of buprofezin in different matrices

Buprofezin

$y = 4E+07x + 271401$
$R^2 = 0.9914$

$y = 5E+07x + 221524$
$R^2 = 0.9884$

$y = 5E+07x - 442909$
$R^2 = 0.987$

● Rice grain   ● Straw   ● Soil

Table 2 Retention time, mass spectrometric parameters for insecticides analyzed in MS/MS

Insecticides	RT	Precursor ion (m/z)	First transition quantification		
			Product ion (m/z)	DP(V)	CE(V)
Acetamiprid	4.88	223	126	60	27
		223	56	60	35
Buprofezin	13.51	306.15	200.9	68	11
		306.15	116.1	68	30
		306.15	57.15	68	16

D.P.; Declustering potential, *C.E.*; Collision energy

both insecticides in samples was confirmed through optimization of instrument acquisition parameters (Table 2). 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 3). The coefficient of determination (R^2) was 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 SANTE 2017 guidelines for the determination of acetamiprid and buprofezin residue in the matrices of paddy grain, straw, and soil.

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 4). 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.

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 5). Initially, buprofezin was degraded slowly in all the matrices. Growth

Table 3 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

Table 4 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 | | | |
| | Single dose (SD) | | Double dose (DD) | | Single dose (SD) | | Double dose (DD) | | Single dose (SD) | | Double dose (DD) | |
Days Interval	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})	Dissipation (%)
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	9.52
3	0.11	69.44	0.27	64.00	0.12	61.29	0.28	60.56	0.19	34.48	0.45	23.81
5	0.05	86.11	0.17	77.33	0.07	77.42	0.18	74.65	0.11	62.07	0.31	42.86
7	0.04	88.89	0.09	88.00	0.06	80.65	0.1	85.92	0.06	79.31	0.2	68.25
10	0.02	94.44	0.05	93.33	0.01	96.77	0.07	90.14	0.03	89.66	0.09	85.71
15	BDL	-	0.04	94.67	BDL	-	0.05	92.96	BDL	-	0.03	95.24

Table 5 Buprofezin residue persistence in paddy grain, straw, and soil

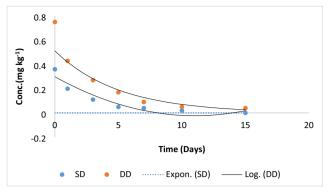| | Persistence of buprofezin in paddy grain | | | | Persistence of buprofezin in paddy straw | | | | Persistence of buprofezin in Soil | | | |
| | Single dose (SD) | | Double dose (DD) | | Single dose (SD) | | Double dose (DD) | | Single dose (SD) | | Double dose (DD) | |
Days Interval	Residue (mg kg^{-1})	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})	Dissipation (%)
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	47.76
3	0.22	37.14	0.48	24.00	0.18	37.93	0.51	28.17	0.19	44.12	0.32	52.24
5	0.19	45.71	0.41	31.00	0.11	62.07	0.39	45.07	0.12	64.71	0.19	71.64
7	0.09	74.29	0.28	44.00	0.07	75.86	0.26	63.38	0.07	79.41	0.17	74.63
10	0.05	85.71	0.12	60.00	0.05	82.76	0.14	80.28	0.04	88.24	0.14	79.10
15	0.04	88.57	0.04	68.00	BDL	-	0.07	90.14	BDL	-	0.03	95.52

Fig. 3 Acetamiprid dissipation in paddy grain

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).

Dissipation kinetics and waiting periods

The dissipation behavior of acetamiprid in paddy and soil were 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 4 and 5), 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
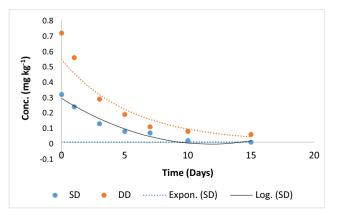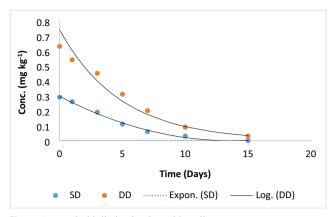

Fig. 5 Acetamiprid dissipation in paddy soil

PHIs of both the insecticides at DD for straw matrices were prolonged (beyond 15 days), which signified that there would be much time needed to degrade the active ingredient. In case of paddy grain matrix, buprofezin showed comparatively shorter (13.93 days) PHI, 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 h (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
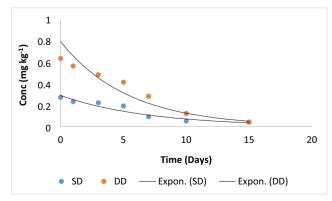

Fig. 4 Acetamiprid dissipation in paddy straw
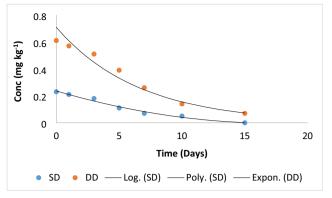

Fig. 6 Buprofezin dissipation in paddy grain

Fig. 7 Buprofezin dissipation in paddy straw

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 behavior 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 SD for paddy grain, straw, and soil were 4.88, 4.23, and 3.67 days, respectively, whereas, in case of DD for the same matrices were 3.75, 4.56, and 4.17 days, respectively. Previous
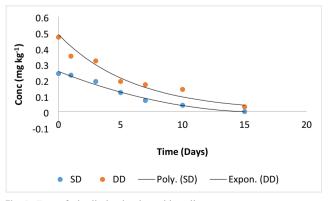
experiments reported half-lives of acetamiprid in the range of 1–2 days for plant matrices like rice (Saha et al. 2017), okra (Singh and Kulshrestha 2005), mustard (Pramanik et al. 2006), and tea (Gupta and Shanker 2008); however, comparatively higher half-lives (2–5 days) were reported in some literature for watermelon (Wu et al. 2012), cowpea (Fu et al. 2020), and chili (Sanyal et al. 2008). For soil matrices, half-lives ranging from 5 to 10 days were generally found (Yu et al. 2011) and in some cases, half-lives of more than 10 days were also observed (Fu et al. 2020; Wu et al. 2012). For buprofezin, the studies on plants and soil were limited and its persistence behavior was found varying with various crops (Mohapatra et al. 2020). In a study, the half-lives of buprofezin in cabbage were estimated as 1.73 and 1.85 days for SD and DD, respectively; and for cauliflower, these values were 2.1 and 2.36 days for SD and DD, respectively (Abdallah et al. 2019). In our case, the half-lives were slightly lower than those earlier reports. These might be due to the differences in environmental matrices, agro-climatic conditions, application techniques. and other associated factors.

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 MPIs of acetamiprid and buprofezin were 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 6). Therefore, acetamiprid and buprofezin were concluded to possess low toxicity risk when practiced for pest management in paddy.

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

Fig. 8 Buprofezin dissipation in paddy soil

Table 6 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

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 toward successful residue management and robust assurance to safety of foods. From this study, a package of practices can be recommended regarding the application schedule of acetamiprid and buprofezin, with dose, number of sprays, inter-spray interval etc. Thus, this work is of high practical significance to the domestic and export purposes to ensure safety compliance in respect of residues, keeping in view of the requirements of international trade.

Abbreviations *a.i.,* Active Ingredient; *ADI,* Acceptable Daily Intake; *BDL,* Below Detectable Limit; *CAD,* Collision-activated Dissociation; *CE,* Collision Energy; *CIB,* Central Insecticide Board; *CRM,* Certified Reference Material; *DD,* Double Dose; *DP,* Declustering Potential; *ESI,* Electrospray Ionization; *FSSAI,* Food Safety and Standard Authority of India; *GC-MS,* Gas Chromatography – Mass Spectrometry; *HPLC,* High Performance Liquid Chromatography; *LC-MS,* Liquid Chromatography – Mass Spectrometry; *LOD,* Limit of Detection; *LOQ,* Limit of Quantification; *ME,* Matrix Effect; *MPI,* Maximum Permissible Intake; *MRL,* Maximum Residue Limit; *MRM,* Multiple Reaction Monitoring; *nAChR,* Nicotinic Acetylcholine Receptor; *PHI,* Pre-harvest Interval; *PSA,* Primary Secondary Amine; *RBD,* Randomized Block Design; *RC,* Registration Committee; *RT,* Retention Time; *SD,* Single Dose; *UPLC,* Ultra Performance Liquid Chromatography; *UV,* Ultraviolet

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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