

## RESIDUE KINETICS OF INSECTICIDE PYMETROZINE IN RICE FIELD SOIL

### KEYWORDS

Pymetrozine,  
Residue,  
Alluvial, Red  
lateritic, Rice  
field, Soil,  
Dissipation

### ABSTRACT

Soils are the most diverse and complex ecosystem in the world. In addition to providing humanity with 98.8% of its food, soils provide a broad range of other services, from carbon storage and greenhouse gas regulation, to flood mitigation and providing support for our sprawling cities. Therefore, protection of soil health from various pollutants including pesticides is important for its future sustenance. The pesticide Pymetrozine widely used in rice fields for the control of aphids and whiteflies is also registered in India for crop protection in Paddy. This study aimed to examine how long the pesticide Pymetrozine persists and how it breaks down in different types of soil in West Bengal. This research was conducted through laboratory experiments using LC-MS/MS at Bidhan Chandra Krishi Viswavidyalaya, Nadia. Applied two doses of Pymetrozine and analyzed soil samples over 30 days. Pymetrozine levels decreased by 95-97% after 15 days and fell below detectable levels after 30 days. Dissipation followed first-order kinetics, with a faster rate in new alluvial soil compared to red lateritic soil. This difference could be due to variations in soil properties, like organic carbon content and water retention.

### 1. Introduction

The planet's most complex and varied ecosystem is found in the soil (Alrahman *et al.*, 2020). In addition to producing almost all of humanity's food, soils perform a multitude of vital tasks such as storing carbon, controlling greenhouse gas emissions, preventing flooding, and delivering the structural basis for urban growth (Kopittke *et al.*, 2019). But soil is a limited resource, and as the world's population grows at an accelerated rate and its consumption rises, soils are under unprecedented strain from intensifying agricultural methods meant to increase crop yields per unit of land (Adhikari *et al.*, 2019). Delivering a variety of

ecosystem services necessary for human well-being is a critical function of soils (Jia *et al.*, 2019). These include regulating services like flood control, nutrient and contaminant filtration, carbon storage, greenhouse gas regulation, detoxification, waste recycling, and pest and disease control; provisioning services like food, timber, fiber, raw materials, and physical infrastructure support; and cultural services like recreational opportunities, aesthetic value, cultural heritage, and identity (Wanget *al.*, 2020). The need for food and fiber is increasing quickly, which puts a lot of strain on soils (Maienfisch *et al.*, 2019). In addition, the production of biofuels requires a lot of land which, 32 million hectares, according to current studies (Lang *et al.*, 2007). Pesticides are used all around

the world to protect crops, textiles, people's health, and convenience (Nollet *et al.*, 2016). However, their volatility and long-range movement combined with misuse or incorrect application, especially in poor countries lead to widespread environmental damage over time (Pasalu *et al.*, 2006). Furthermore, poor nations use a large number of antiquated, non-patented, very hazardous, environmentally persistent, and low-cost chemicals widely, which has a negative impact on the environment both locally and globally and causes serious health problems right away (Boquelet *et al.*, 2015).

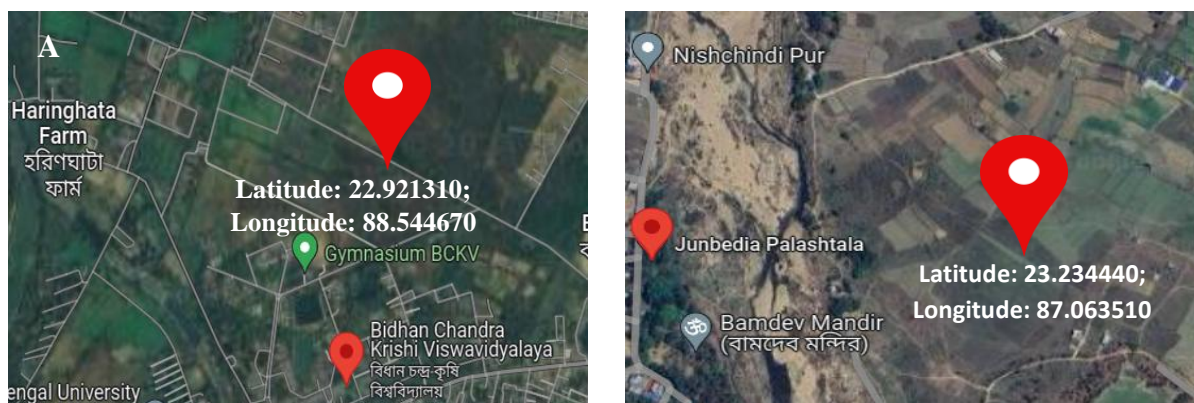
Pymetrozine residue and dissipation in soil were investigated using a new and trustworthy analytical technique (Sen *et al.*, 2020). In a previous study dissipation of pymetrozine was analyzed, Li *et al.*, in 2011, studied and analyzed

Pymetrozine in alluvial and red lateritic soils, as well as to analyze residues of the insecticide Pymetrozine in soils using LC-MS/MS. Pymetrozine's maximum residual limit in soil was established with the help of the suggested dosage, which was confirmed to be safe for both humans and animals.

## 2. Materials and Methods

### 2.1. Materials Used

The experiment was conducted under laboratory conditions in the Testing and Training Center for Food and Water Quality, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya (BCKV), Mohanpur, Nadia, West Bengal in 2022 to study the "Residue Kinetics of Insecticide Pymetrozine in Rice Field Soil". Materials used in this research are listed below.



**Fig. 1. Map showing the location of the study sites, A) BCKV, West Bengal; B) Bankura, West Bengal.**

the dissipation rate of pymetrozine in rice field ecosystems. But in new alluvial and red lateritic soil, no research was done by scientists. Pymetrozine residues were extracted with acetonitrile, cleaned, and then ultra-performance liquid chromatography-electrospray ionization tandem mass spectrometry (LC-MS/MS) was used to determine the dissipation rate. Pymetrozine dissipated according to first-order kinetics in soil, where half-lives varied from 2.85 to 3.47 days. The goals of this study are to compare the persistence of

#### 2.1.1. Certified Reference Material

The Certified Reference Material (CRM) of Pymetrozine (PESTANAL, Analytical Standard) was procured from Sigma-Aldrich International GmbH [Purity: 99.9%; Quality release date: 24 April 2019; and Expiry date: March 2024].

#### 2.1.2. Solvents And Reagents

- a. Millipore water

- b. Acetonitrile (HPLC grade, J.T.Baker)
- c. Methanol (HPLC grade, J.T.Baker)
- d. Magnesium sulfate- MgSO<sub>4</sub> (anhydrous) [Merck life science Pvt. Ltd.]
- e. Sodium Chloride- NaCl (Merck life science Pvt. Ltd.)
- f. Primary secondary amine, PSA (Agilent Bondesil)
- g. C18 sorbent (Agilent Technologies)
- h. Florisil (Merck life science Pvt. Ltd.)

### 2.1.3. Glassware and Equipment

- a. Beaker (50 mL, 100 mL, 250 mL, 1000 mL, Borosil Glass)
- b. Glass rod
- c. Measuring cylinder (10 mL, 20 mL, Borosil Glass)
- d. Calibrated graduated tube (25 mL, 50 mL, Borosil Glass)
- e. Nitrogen tube (Borosil)
- f. Calibrated micropipette and Microtip (200 µl and 1000 µl, Eppendorf Research, Accupipet, Tarsons microtip)
- g. Refrigerator (Bluestar, Whirlpool)
- h. Micro-Centrifuge (2 mL, Eppendorf, Centrifuge 5804 R)
- i. Centrifuge (50 mL, Eppendorf, Centrifuge 5804 R)
- j. Polypropylene Centrifuge Tubes with cap (2 mL & 50 mL, Tarsons)
- k. Electrical Balance, (Measure Techno Lab Wensar)
- l. Analytical balance (Mettler Toledo, Model No. ME204)
- m. Vortex mixer (Tarsons Spinix)
- n. Nitrogen turbo-vap evaporator
- o. BOD Incubator
- p. Sonicator
- q. Funnel
- r. Spatula

- s. Disposable petriplate
- t. Mortar & pestle
- u. Hot air oven
- v. Millipore water purification system (Elix<sup>®</sup> Essential Water Purification System)
- w. Hamilton<sup>®</sup> clean-up syringe
- x. 0.2µ filter papers (Pall Life Science Corporation)
- y. Autosampler vials (0.5-2 mL, Agilent Technologies)

LC-MS/MS (Waters, TQ-S Micro)

## 2.2. Method

### 2.2.1. Collection and Processing of Soil

Two types of soil were collected from cultivated land with no previous history of Pymetrozine application from the New Alluvial and Red Laterite zones in West Bengal during March 2022.

### 2.2.2. Location and Date of Collection

The New Alluvial soil was collected from the Teaching Farm located at Jaguli in the main campus of Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, Nadia (Latitude: 22.921310; Longitude: 88.544670) on 10/03/2022 and the Red Lateritic soil was collected from Palashtala, Bankura Town, Bankura (Latitude: 23.234440; Longitude: 87.063510) on 04/03/2022 (Figure 1). The soil sample was collected from the cultivated layer (from the surface to about 15 cm depth) using soil augur from 5-6 sites in the selected field. The collected soil from the field was mixed together and a representative sample (about 5.0 kg) was taken in a Polyethylene bag and transported to the laboratory for the experiment.

### 2.2.3. Processing of Soil

Both the new alluvial and red lateritic soil were air dried under shade, grounded with the help of

Mortar-pestle, mixed well, and screened through a 20 mm mesh sieve.

#### 2.2.4. Physico-Chemical Properties of Soil

Physico-chemical properties of soil like pH which measured using potentiometer using electrode, Electrical Conductivity (EC) by saturation extraction method, Organic Carbon (OC) by walkley-Black chromic acid wet oxidation method, Phosphorus by Olsen method and Bray & Kurtz method, Potassium (K) and  $K_2O$  by Inductivity Coupled Plasma-Optical Emission Spectrometry method, and Water Holding Capacity (WHC) by using percolation method. These properties were determined using the methods as listed in Table 1.

### 2.3. Application of Pymetrozine in Soil

#### 2.3.1. Preparation of Standard Solution of Pymetrozine

A stock standard solution of Certified Reference Material (CRM) of pymetrozine ( $129.9 \mu\text{g}/\text{mL}$ ) was prepared by dissolving 13 mg analytical standard (purity: 99.9%) in a 100 mL volumetric flask using methanol. Solvents used in this experiment were analytical grade and freshly distilled before use. The concentration of the primary stock solution was determined using the formula:

$$\text{Concentration (mg/L)} = \text{Wt. of CRM (mg)} \times \text{Purity of CRM (\%)} \times 1000 / \text{Final Volume (mL)} \times 100 = 129.87 \text{ mg/L (ppm)}$$

#### 2.3.2. Preparation of Working Standard Solution of Pymetrozine

Stock standard solutions of pymetrozine ( $129.9 \mu\text{g}/\text{mL}$ ) were serially diluted to 100, 50, and 20

$\mu\text{g}/\text{mL}$  using methanol. The working standard solutions of  $12 \mu\text{g}/\text{mL}$  and  $6 \mu\text{g}/\text{mL}$  were prepared from  $20 \mu\text{g}/\text{mL}$  using methanol for spiking in soil.

#### 2.3.3. Spiking in Soil

Soil (400g) taken in a beaker (1000 mL) was added with 50 mL pymetrozine working standard solution ( $6 \mu\text{g}/\text{mL}$  in methanol) to prepare the spiking level of  $0.75 \mu\text{g}/\text{gm}$  in each soil. Similarly, a double dose of pymetrozine @  $1.50 \mu\text{g}/\text{gm}$  of soil was prepared by adding 50 mL of pymetrozine working standard ( $12 \mu\text{g}/\text{mL}$ ) solution in 400 g of each soil. The standard solution of pymetrozine (50 mL) was added dropwise to the soil followed by stirring for uniform mixing. The mixture was allowed to stay for about 2 hours. Then 10 g soil was taken in petriplates and placed in a BOD incubator maintained at  $30^\circ\text{C}$ .

#### 2.3.4. Sampling for Residue Analysis

Three Petri plates each containing 10 g of spiked soil were taken for residue analysis of pymetrozine at 0, 1, 3, 5, 7, 10, 15, and 30 days intervals.

### 2.4. Method of Residue Analysis

#### 2.4.1. Principle

Pymetrozine residue was determined by LC-MS/MS. Soil samples were extracted with acetonitrile and subjected to clean-up using PSA,  $C_{18}$  and Florisil. Then cleaned-up aliquot containing acetonitrile was filtered, evaporated, made up the volume with methanol, and analyzed in LC-MS/MS for Pymetrozine residue.

#### 2.4.2. Instrumental parameters of LC-MS/MS

**Table 1 Method adopted for analysis of soil physicochemical properties**

Soil Parameters	Method Used
pH	Potentiometer using Electrode
Electrical Conductivity (EC)	Saturation extraction method
Organic Carbon (OC)	Walkley-Black chromic acid wet oxidation method
Phosphorus	1. Olsen Method (for pH >6.5) 2. Bray & Kurtz (for pH <6.5)
Potassium (K)	Inductivity Coupled Plasma-Optical Emission Spectrometry (ICP-OES)
K <sub>2</sub> O	Inductivity Coupled Plasma-Optical Emission Spectrometry (ICP-OES)
Water Holding Capacity (WHC)	Percolation Method

**Table 2: Instrumental parameters of the Ultra-Performance Liquid Chromatograph (UPLC)**

<b>UPLC System</b>	Waters Acquity H-class UPLC plus system with a Quaternary solvent manager				
<b>Column</b>	Waters Acquity UPLC BEH C18 column (2.1 mm× 100 mm, 1.7 μm particle size)				
<b>Mobile Phase</b>	A mixture of solvents A (0.5% Formic acid + 10 mM Ammonium formate buffer in water) and B (100% MeOH)				
<b>Elution</b>	Gradient				
	<b>Time (minute)</b>	<b>%A</b>	<b>%B</b>	<b>%C</b>	<b>%D</b>
<b>Gradient programming for Pymetrozine</b>	0.00	80.0	20.0	0.0	0.0
	0.25	80.0	20.0	0.0	0.0
	1.50	10.0	90.0	0.0	0.0
	2.50	10.0	90.0	0.0	0.0
	3.10	80.0	20.0	0.0	0.0
	5.00	80.0	20.0	0.0	0.0
Flowrate(mL/min)	0.300				
Max.PressureLimit (bar)	15000psi or 1034.2136 bar				
Injectionvolume	1μL				
Needlewash	9:1 MeOH: H <sub>2</sub> O				
Sealwash	9:1 MeOH: H <sub>2</sub> O				
TotalRun time	5.00 min				
RetentionTime ofPymetrozine	0.77 Minute				

**Table 3: Operating conditions of the Mass Spectrometer**

Instrument	Waters Xevo TQ-S micro (with ESI/APPI/APCI/ESCI)
Ionization mode (ESI)	(+) Ve Ion
Scan type (Method)	MRM
Dwell Time (secs)	0.164 secs
Desolvation gas Flow	800 L/hour
Source temperature	150°C
Gas temperature	350 °C
Nebulizer Gas	99.95% Nitrogen
Collision Gas	99.999% Argon
Capillary voltage (kV)	2.2 kV
Cone voltage (V)	30 V
Collision cell lenses	Entrance: 30 V
	Exit: 30 V
Software used	Mass Lynx
Molecular ion	218.20
MRM	Pymetrozine:
	218.2 > 105 (Quantifier)
	218.2 > 78 (Qualifier)

Operating details of MRM	Precursor ion	Product ion	Retention Time (min)	Collision Energy, C.E. (Volt)	Polarity
		218.2	105	0.77	24
	218.2	78	0.77	48	+Ve

Liquid Chromatography with Tandem Mass Spectrometry (LC-MS/MS, Waters, TQ-S Micro) was used for residue analysis of Pymetrozine. The operating conditions of the Ultra Performance Liquid Chromatography (UPLC) and Mass Spectrometry are presented in Table 2 and Table 3 respectively.

#### 2.4.3. Preparation of mobile phase for LC-MS/MS

**Mobile phase A:** Approximately 500 mL of Millipore water was taken in a 1000 mL measuring cylinder. After that 5 mL of formic acid and 630.559 mg ammonium formate salt were added to it. Finally, the volume was made up to 1000 mL with millipore water which produced 0.5% (v/v) formic acid containing 10 mM ammonium formate

buffer solution. The mixture was filtered using a vacuum pressure pump fitted with 0.45 µm multiple N<sub>66</sub> nylon 6,6 membrane. The solvent mixture was sonicated for 30 minutes to remove the air bubbles. **Mobile phase B:** 100% methanol was taken in a 1000 mL measuring cylinder. Then the methanol was sonicated for 15 minutes to remove the air bubbles present in it.

#### 2.4.4 Linearity

The intermediate working standard solutions of different concentrations (1, 0.5, 0.25, 0.1, 0.05, 0.02, 0.01, and 0.005 mg/L) were prepared and injected for checking the linearity in LC-MS/MS

under the operating conditions as mentioned in Tables 2 and 3. The linearity of the detector response was determined from the 8-point calibration graph by plotting the area of Pymetrozine standard versus concentration using the Mass Lynx software.

#### **2.4.5. Extraction and Clean-up for Pymetrozine Residues**

##### **2.4.5.1. Extraction**

Spiked soil samples (10 g) in a Petri plate in three replicate numbers were taken from the BOD incubator for extraction at each day interval. The soil from the Petri plate was transferred to a centrifuge tube (50 mL) and water (10 mL) was added to it followed by the addition of acetonitrile (10 mL). The mixture was subjected to vortex for 1 minute followed by the addition of anhydrous MgSO<sub>4</sub> (4 g) and NaCl (1g) and vortexed for 1 minute. Then the sample was centrifuged for 6 minutes at 5000 rpm for the new alluvial soil and 10 minutes at 10,000 rpm for red lateritic soil. The supernatant aliquot (5 mL) was taken for cleanup.

##### **2.4.5.2 Clean-up Process**

The acetonitrile extract (2 mL) was evaporated using a nitrogen evaporator and transferred to a polypropylene microcentrifuge tube using 1.5 mL methanol. Afterward, 50 mg PSA, 25 mg C<sub>18</sub>, 150 mg MgSO<sub>4</sub>, and 25 mg florisil were added to it and vortex for 2 minutes. The sample was again centrifuged for 6 minutes at 8000 rpm. After centrifugation 1 mL supernatant was collected by micropipette and filtered through a 0.2 µ nylon membrane filter with a Hamilton clean-up syringe and finally cleaned extract was analyzed by LC-MS/MS to estimate pymetrozine content present in soil samples.

#### **2.5 Recovery Experiment**

A recovery experiment was carried out to establish the reliability of the stated analytical method and to know the efficiency of extraction and clean-up steps for the present study by fortifying Pymetrozine standard in the soil at the level of 0.01, 0.05, and 0.1 mg/kg in triplicate along with untreated control samples. Fortified samples were left to stand for 30 minutes before extraction to allow the pesticide absorption into the matrix.

##### **2.5.1 Preparation of Blank Matrix Matched Standard Calibration Curve**

The selected residue analytical method of Pymetrozine in the present study was carried out with the control samples of soil. During the final volume makeup, the desired concentration of pymetrozine was added to the control samples to get 0.001, 0.0025, 0.005, 0.01, 0.02, 0.05 0.10, 0.25, 0.5, and 1.0 µg/gm for each substrate. Thus, the ten levels of Blank Matrix Matched Standard solution for soil were prepared and injected into LC-MS/MS. The Blank Matrix Matched Standard calibration curve was generated using Mass Lynx Software.

#### **3. Result**

##### **3.1. Physico-chemical Properties of Soil**

The physicochemical properties of the New Alluvial and Red Lateritic soils are presented in Table 4. The physicochemical properties significantly varied between the two soils. The New Alluvial soil was characterized by neutral pH (7.25), medium OC content (0.65 %), and higher electrical conductivity (255.6 µs/cm), P (26.88 kg/ha), K (324.69 kg/ha) and K<sub>2</sub>O (389.63 kg/ha) content. Whereas the Red Lateritic soils were acidic in pH (5.95), OC content (0.40 %) was significantly low with lower electrical conductivity (164.90 µs/cm), P (21.53 kg/ha), K (135.41 kg/ha)

and K<sub>2</sub>O (162.49 kg/ha) content compared to the New Alluvial soil.

### 3.3. Detection of Pymetrozine by LC-MS/MS

The solution of Pymetrozine analytical standard in methanol (1  $\mu\text{g/gm}$ ) was injected into LCMS/MS maintained with the operational parameters as mentioned in Tables 1 and 2 under the Materials and Method section. The retention time of pymetrozine recorded in LC-MS/MS was 0.77 minutes (Figure 2).

#### 3.2.1 Linearity and Limit of Detection (LOD)

The 8-point calibration graph (Figure 3) indicated an excellent linear correlation between the injected amount of pymetrozine and the detector response of LC-MS/MS. The regression coefficient ( $R^2$ ) of the calibration curve was  $>0.9989$  for pymetrozine which is in good agreement with the findings of Li *et al.*, 2011, thereby establishing the linearity. The limit of detection (LOD) was found to be 0.001  $\mu\text{g/gm}$  considering a signal-to-noise ratio of  $> 3 < 10$  concerning the background noise (Zhang *et al.*, 2015).

#### 3.2.2 Results of Recovery Experiment

The reliability of the method was evaluated by a recovery study of Pymetrozine at three concentration levels (0.01, 0.05, and 0.10  $\mu\text{g/gm}$ ) in new alluvial and red lateritic soils. The results are presented in Table 5. The results indicated overall recovery in the range of 91.1% to 104.13%. The lowest recovery 91.1% was obtained in red lateritic soil fortified @ 0.02  $\mu\text{g/gm}$  and the highest recovery (104.13%) was obtained in new alluvial soil fortified at 0.05  $\mu\text{g/gm}$ . Wang *et al.* (2015) also reported the recovery percentages of Pymetrozine in the range from 75.2% to 115.9% with the relative standard deviation (RSD) from 2.6% to

19.1% using UPLC-ESI-MS/MS combined with the external standard method.

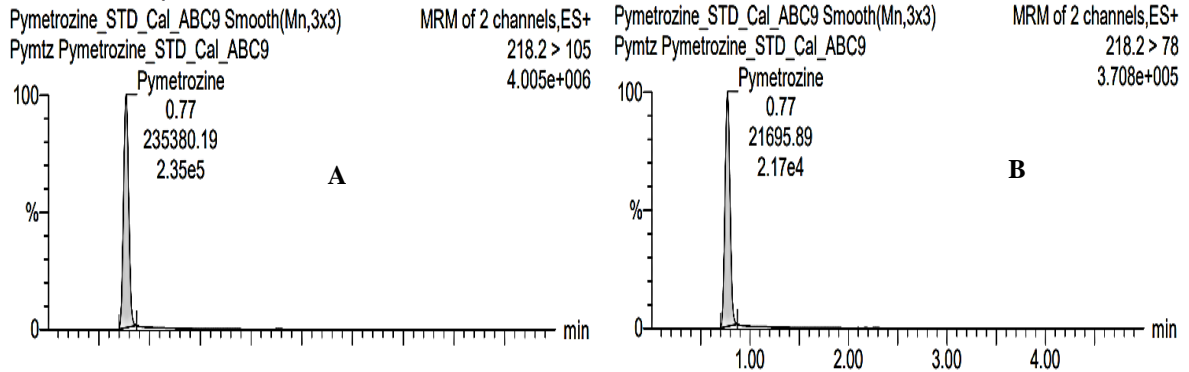
#### 3.2.3 Limit of Quantification (LOQ)

From the above result, the lowest level of Pymetrozine which could be detected with confidence from both new alluvial and red lateritic soil, i.e. the Limit of Quantification (LOQ) of Pymetrozine was considered as 0.02  $\mu\text{g/gm}$ . The recovery values (90% or more) along with the RSD ( $\leq 10\%$ ) and signal-to-noise ratio ( $>10$ ) at 0.02  $\mu\text{g/gm}$  were in the acceptable range according to the document of DG-SANTE (2019). Thus, from the recovery study, the limit of quantification for soil samples was considered as 0.02  $\mu\text{g/gm}$  and the method appeared to be appropriate for the present investigation.

#### 3.2.4 Matrix Matched Standard Calibration

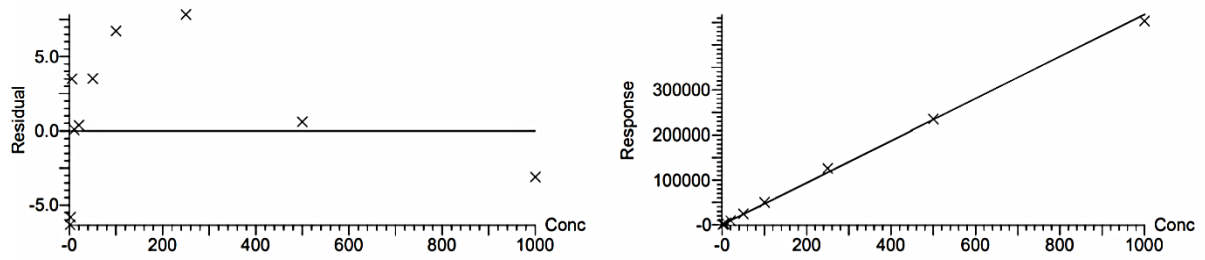
The selected residue analytical method of Pymetrozine in the present study as described above was carried out with the control samples of new alluvial and red lateritic soil. Then the calculated volume of Pymetrozine analytical standard solution was added to the control samples which were extracted and cleaned up following the method described above to get the desired concentration of 0.02, 0.05, 0.10, 0.25, and 0.5  $\mu\text{g/gm}$  for each soil. Thus, the five levels of Matrix matrix-matched standard solutions for soil were prepared and injected into the LCMS/MS along with the respective blank matrix solutions. The Matrix Matched Standard calibration curves were generated for each substrate using Mass Lynx Software which was used for quantification of Pymetrozine residues in the soil samples.

**Sample Name: Pymetrozine\_STD\_Cal\_ABC9**



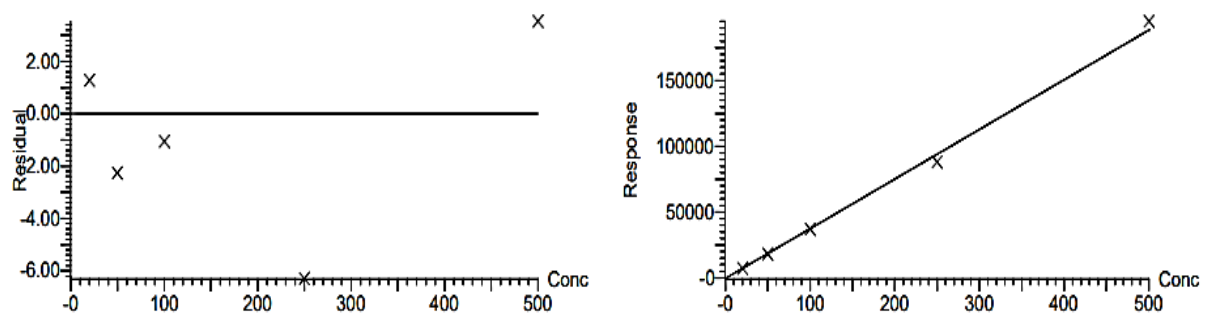
**Figure 2: LC-MS/MS Chromatogram of Pymetrozine (1  $\mu\text{g/gm}$ ) under MRM mode for (A): Quantifier (218.2 > 105) and (B): Qualifier (218.2 > 78) ions**

Compound name: Pymetrozine  
 Correlation coefficient:  $r = 0.999197$ ,  $r^2 = 0.998395$   
 Calibration curve:  $467.937 * x + 34.3586$   
 Response type: External Std, Area  
 Curve type: Linear, Origin: Include, Weighting: 1/x, Axis trans: None



**Figure 3: Detector linearity of Pymetrozine in solvent-only calibration**

Compound name: Pymetrozine  
 Correlation coefficient:  $r = 0.998848$ ,  $r^2 = 0.997697$   
 Calibration curve:  $377.518 * x + -362.797$   
 Response type: External Std, Area  
 Curve type: Linear, Origin: Include, Weighting: 1/x, Axis trans: None



**Figure 4: Matrix-matched standard calibration of Pymetrozine in new alluvial soil**

Compound name: Pymetrozine  
 Correlation coefficient:  $r = 0.998748$ ,  $r^2 = 0.997498$   
 Calibration curve:  $665.335 * x + -481.956$   
 Response type: External Std, Area  
 Curve type: Linear, Origin: Include, Weighting: 1/x, Axis trans: None

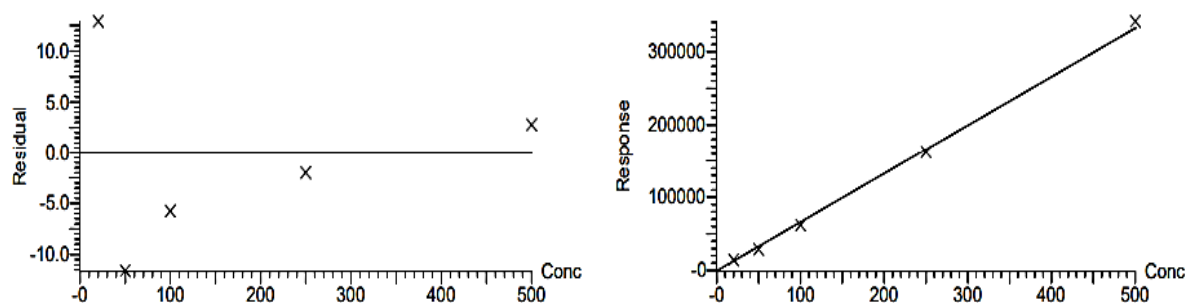


Figure 5: Matrix-matched standard calibration of Pymetrozine in red lateritic soil

Table 4: Physico-chemical properties of the soils under study

Parameters	New Alluvial Soil	Red Lateritic Soil
pH	7.25	5.95
Electrical Conductivity (EC)	255.6 $\mu\text{s/cm}$	164.90 $\mu\text{s/cm}$
Organic Carbon (OC)	0.65 % (Medium)	0.40 % (Low)
Phosphorus (P)	26.88 kg/ha	21.53 kg/ha
Potassium (K)	324.69 kg/ha	135.41 kg/ha
K <sub>2</sub> O	389.63 kg/ha	162.49 kg/ha
Water Holding Capacity (WHC)	92%	48%

Table 5: Recovery of Pymetrozine from Soil by LC-MS/MS

Soil Type	Fortification level ( $\mu\text{g/gm}$ )	Amount Recovered ( $\mu\text{g/gm}$ )			Mean Amount Recovered ( $\mu\text{g/gm}$ ) ( $\pm\text{SD}$ )	RSD (%)	Mean Recovery (%)	Overall Mean Recovery (%)
		R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>				
New Alluvial	0.02	0.0182	0.020	0.0198	0.0193 (0.0009)	5.10	97.0	100.61
	0.05	0.052	0.055	0.048	0.0516 (0.003)	6.80	104.1	
	0.10	0.099	0.102	0.100	0.1003 (0.0015)	1.52	100.7	
Red Laterite	0.02	0.017	0.017	0.019	0.0176 (0.0011)	6.54	91.1	98.12
	0.05	0.050	0.050	0.049	0.0496 (0.0005)	1.16	100.0	
	0.10	0.105	0.100	0.103	0.1026 (0.0025)	2.45	103.3	

**Table 6: Persistence of Pymetrozine in New Alluvial Soil**

Days Interval	Residues of Pymetrozine occurring in soil ( $\mu\text{g/gm}$ ) following application @									
	$T_1 = 0.75 \mu\text{g/gm}$					$T_2 = 1.50 \mu\text{g/gm}$				
	$R_1$	$R_2$	$R_3$	Mean ( $\pm\text{SD}$ )	RSD (%)	$R_1$	$R_2$	$R_3$	Mean ( $\pm\text{SD}$ )	RSD (%)
0	0.61	0.60	0.62	0.610 (0.01)	1.64	1.25	1.32	1.17	1.250 (0.07)	6.02
1	0.54	0.51	0.49	0.510 (0.025)	4.90	1.03	1.21	0.88	1.040 (0.16)	15.89
3	0.27	0.29	0.27	0.280 (0.011)	4.17	0.42	0.45	0.50	0.463 (0.040)	8.85
5	0.18	0.20	0.19	0.194 (0.01)	5.26	0.32	0.28	0.26	0.293 (0.03)	10.66
7	0.09	0.08	0.08	0.086 (0.005)	6.93	0.17	0.22	0.18	0.194 (0.026)	13.93
10	0.032	0.043	0.029	0.034 (0.0073)	21.26	0.099	0.101	0.088	0.096 (0.007)	7.29
15	ND	0.021	ND	-	-	0.039	0.041	0.027	0.035 (0.007)	21.23
30	ND	ND	ND	-	-	ND	ND	ND	-	-

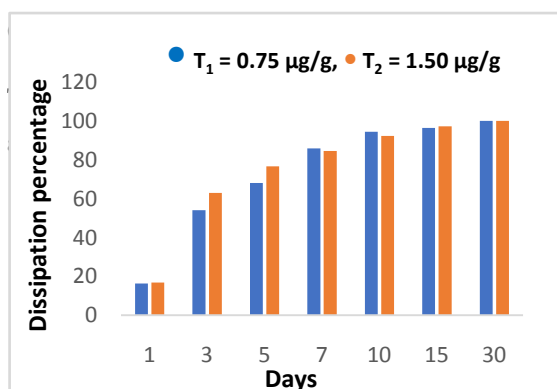
**Table 7: Persistence of Pymetrozine in Red Lateritic Soil**

Days Interval	Residues of Pymetrozine occurring in soil ( $\mu\text{g/gm}$ ) following application @									
	$T_1 = 0.75 \mu\text{g/gm}$					$T_2 = 1.50 \mu\text{g/gm}$				
	$R_1$	$R_2$	$R_3$	Mean ( $\pm\text{SD}$ )	RSD (%)	$R_1$	$R_2$	$R_3$	Mean ( $\pm\text{SD}$ )	RSD (%)
0	0.68	0.70	0.73	0.71 (0.025)	3.58	1.40	1.43	1.44	1.427 (0.020)	1.46
1	0.52	0.46	0.42	0.472 (0.050)	10.79	1.239	1.259	1.111	1.203 (0.080)	6.67
3	0.404	0.389	0.345	0.38 (0.030)	8.08	1.184	1.161	1.217	1.187 (0.028)	2.37
5	0.322	0.335	0.283	0.314 (0.027)	8.64	0.795	0.764	0.555	0.705 (0.130)	18.52
7	0.239	0.234	0.246	0.24 (0.006)	2.52	0.440	0.425	0.453	0.439 (0.014)	3.19
10	0.113	0.097	0.087	0.099 (0.013)	13.25	0.310	0.289	0.277	0.292 (0.016)	5.72
15	0.025	0.035	ND	0.02 (0.018)	90.14	0.068	0.072	0.065	0.0687 (0.003)	5.14
30	ND	ND	ND	-	-	ND	ND	ND	-	-

### 3.3 Residues of pymetrozine in soil

The residues of pymetrozine on different days occurring in New Alluvial soil following application at different doses are presented in Table

progressively to 0.194  $\mu\text{g/gm}$  on day 5, 0.034  $\mu\text{g/gm}$  on day 10 and 0.021  $\mu\text{g/gm}$  on 15 days after application in  $T_1$ . The residue of pymetrozine was not detectable 30 days after application (Table 6).



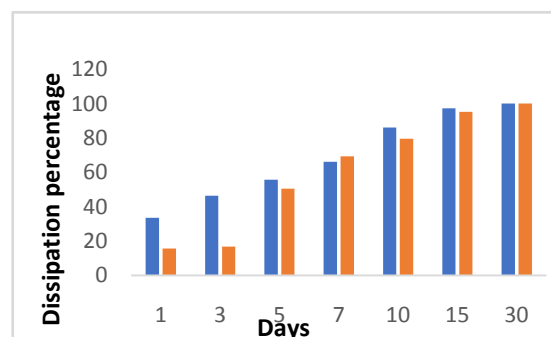
**Figure 6: Dissipation behavior of pymetrozine in new alluvial soil**

In the case of  $T_2$ , the initial concentration of pymetrozine in new alluvial soil (1.250  $\mu\text{g/gm}$ ) was reduced progressively to 0.293  $\mu\text{g/gm}$  on day 5, 0.096  $\mu\text{g/gm}$  on day 10 and 0.035  $\mu\text{g/gm}$  on 15 days after application (Table 6). The residue of pymetrozine was not detectable 30 days after application. The initial concentration of pymetrozine in red lateritic soil (0.71  $\mu\text{g/gm}$ ) was reduced progressively to 0.314  $\mu\text{g/gm}$  on day 5, 0.099  $\mu\text{g/gm}$  on day 10 and 0.0202  $\mu\text{g/gm}$  on 15 days after application in  $T_1$ . The residue of pymetrozine was not detectable 30 days after application (Table 7). In the case of  $T_2$ , the initial concentration of pymetrozine in red lateritic soil (1.427  $\mu\text{g/gm}$ ) was reduced progressively to 0.705  $\mu\text{g/gm}$  on day 5, 0.292  $\mu\text{g/gm}$  on day 10 and 0.0687  $\mu\text{g/gm}$  on 15 days after application (Table 7). The residues of pymetrozine were not detectable 30 days after application.

**3.4 Dissipation of pymetrozine in soil**

In new alluvial soil following application @ 0.75  $\mu\text{g/gm}$  ( $T_1$ ), the initial residue of pymetrozine (0.61  $\mu\text{g/gm}$ ) was dissipated by 16.3% on day 1 which further increased to 54%, 68%, 85.9%, 94.4% and 96.5% on 3, 5, 7, 10 and 15 days respectively (Figure 6) and reached below LOQ of 0.02  $\mu\text{g/gm}$  after 30 days. In the case of  $T_2$  (1.50  $\mu\text{g/gm}$ ), the initial residue of pymetrozine (1.25  $\mu\text{g/gm}$ ) was dissipated by 16.8% on day 1, which further increased to 63%, 76.6%, 84.5%, 92.3%, 97.2% on 3, 5, 7, 10 and 15 days respectively and reached below LOQ of 0.02  $\mu\text{g/gm}$  after 30 days.

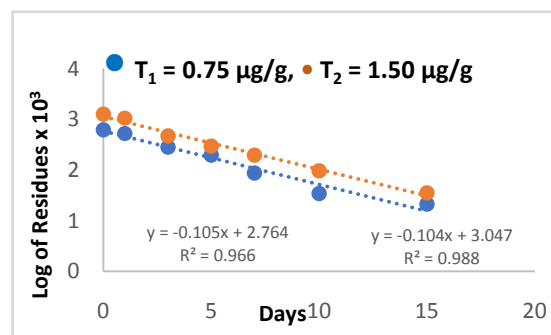
In red lateritic soil following application @ 0.75  $\mu\text{g/gm}$  ( $T_1$ ), the initial residue of pymetrozine (0.710  $\mu\text{g/gm}$ ) was dissipated by 33.50% on day 1 which further increased to 46.47%, 55.77%, 66.19%, 86.05% and 97.18% on 3, 5, 7, 10 and 15 days respectively (Figure 7) and reached below LOQ of 0.02  $\mu\text{g/gm}$  after 30 days. In case of  $T_2$  (1.50  $\mu\text{g/gm}$ ), the initial residue of pymetrozine (1.427  $\mu\text{g/gm}$ ) was dissipated by 15.69% on day 1, which further increased to 16.81%, 50.59%, 69.23%, 79.53%, 95.18% on 3, 5, 7, 10 and 15 days respectively and reached below LOQ of 0.02  $\mu\text{g/gm}$  after 30 days.



**Figure 7: Dissipation behavior of pymetrozine in red lateritic soil**  
 •  $T_1 = 0.75 \mu\text{g/g}$ , •  $T_2 = 1.50 \mu\text{g/g}$

**3.5 Residue kinetics of pymetrozine in soil**

The residual data of pymetrozine was converted to log values and plotted against day intervals to understand the kinetics of pymetrozine dissipation. The formation of the straight line by plotting the log residues vs. time indicated the first-



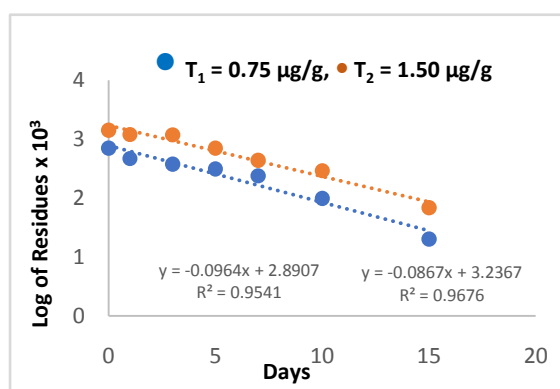
order reaction kinetics of the pymetrozine residues and presented in Figure 8 for new alluvial soil, and Figure 9 for red lateritic soil.

The regression equation and residual half-life of pymetrozine in new alluvial and red laterite soil are presented in Table 8. The dissipation rate was higher in new alluvial soil (0.1042 to 0.1056) as indicated by the slope of the first-order reaction curve (Figure 8 & Table 8) compared to the red lateritic soil (0.0867 to 0.0964; Figure 9 & Table 8).

**Figure 8: 1<sup>st</sup> Order reaction kinetics of Pymetrozine residues in new alluvial soil**

Consequently, the calculated half-life value was lower in new alluvial soil (2.85 to 2.88 days) compared to red lateritic soil (3.12 to 3.47 days) (Table 8).

**Table 8: Dissipation kinetics and half-life of pymetrozine in soil**



**Figure 9: 1<sup>st</sup> Order reaction kinetics of pymetrozine residues in red lateritic soil**

The difference in the persistence behavior of Pymetrozine in two soils may be due to the variation in the physico-chemical properties of the

selected soils under study (Table 4). The variations in degradation rates of pesticides in soil depend on the soil-pesticide combination (Liu et al., 2018). The observed higher dissipation rate in new alluvial soil than in red lateritic soil might be due to significant variations in the soil physicochemical parameters (Table 4). New alluvial soils under the present investigation contain more organic carbon and water-holding capacity than red lateritic soil (Table 4).

The degradation rates of pymetrozine were positively influenced by soil OC content and negatively influenced by soil pH. A positive relationship linked their sorption and degradation parameters, probably as a consequence of a catalyzed hydrolysis after sorption onto soil organic matter (Kleber *et al.*, 2021). The pH (5.95) of Red lateritic soil was lower than new alluvial soil (7.25). pH is a factor that influences the dissipation rate of pymetrozine in soil and also influences the half-life of pymetrozine (Tudi *et al.*, 2022).

Type of soil	Applicati on dose	Regression equation	Regressi on Co-efficient (R <sup>2</sup> )	Half-life (Days)
New Alluvial	T <sub>1</sub> (0.75 µg/gm)	y = -0.1056x + 2.7647	0.9661	2.85
	T <sub>2</sub> (1.50 µg/gm)	y = -0.1042x + 3.0475	0.9884	2.88
Red Laterite	T <sub>1</sub> (0.75 µg/gm)	y = -0.0964x + 2.8907	0.9541	3.12
	T <sub>2</sub> (1.50 µg/gm)	y = -0.0867x + 3.2367	0.9676	3.47

Therefore, the present study revealed the significant effect of the soil parameters on the dissipation kinetics of Pymetrozine residues in soil.

#### 4. Conclusion

In previous study, I saw that the half-lives of the pymetrozine were 7.0 days, 0.7 days, and 0.89 days, respectively. Pymetrozine degraded slightly faster in water compared to its degradation rate in rice straw (Li *et al.*, 2011). In another study, Zhang and his co-workers have find that After 7 days, the remaining amounts of pymetrozine in rice

(including rice straw, brown rice, and rice husk) were below the Maximum Residue Limits (MRLs) set by the EU at 0.02 mg kg<sup>-1</sup>. This indicates that it is safe for both human consumption and the environment, with a safe interval of 7 days (Zhang *et al.*, 2015). In this study, I conclude that the observed differences in dissipation rates between new alluvial soil and red lateritic soil can be attributed to significant variations in soil physicochemical parameters. Specifically, the higher dissipation rate in new alluvial soil is likely due to its higher organic carbon content and water-holding capacity compared to red lateritic soil. The study also revealed that soil organic carbon content and pH play important roles in influencing the degradation rate of pymetrozine residues in soil. These findings underscore the importance of considering soil parameters in understanding pesticide dissipation kinetics and highlight the need for tailored soil management practices in pesticide applications to optimize efficacy and minimize environmental impact. This research would help provide direction on the safe and appropriate usage of the pesticide.

## References

- Adhikari, B., Padhi, J., & Dohling, P. N. K. (2019). Pymetrozine: An effective insecticide for management of planthoppers in rice. *J Entomol Zool Stud*, 7, 528-531.
- Boquel, S., Zhang, J., Goyer, C., Giguère, M. A., Clark, C., & Pelletier, Y. (2015). Effect of insecticide- treated potato plants on aphid behavior and potato virus Y acquisition. *Pest Management Science*, 71(8), 1106-1112. <https://doi.org/10.1002/ps.3892>
- Deekshita, K., & Ramarao, C. V. (2018). Pymetrozine: A Pyridine Azomethine insecticide for management of rice brown planthopper in Indi. *Chemical Science Review and Letters*, 7(25), 335-339.
- DG-SANTE (Directorate-General for Health and Food Safety, European Commission) (2019). Analytical Quality Control and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed, No. SANTE/12682/2019. Available at [https://www.eurlpesticides.eu/userfiles/file/EurlALL/AqcGuidance\\_SANTE\\_2019\\_12682.pdf](https://www.eurlpesticides.eu/userfiles/file/EurlALL/AqcGuidance_SANTE_2019_12682.pdf) (Accessed on 17.08.2021).
- Gong, J., Zheng, K., Yang, G., Zhao, S., Zhang, K., & Hu, D. (2019). Determination, residue analysis, risk assessment and processing factor of pymetrozine and its metabolites in Chinese kale under field conditions. *Food Additives & Contaminants: Part a*, 36(1), 141-151. (<https://doi.org/10.1080/19440049.2018.1562237>)
- HU, X., SHEN, G. Q., LU, Y. T., & YAO, L. F. (2008). Determination of Pymetrozine Residues in Cabbage with HPLC [J]. *Agrochemicals*, 3.
- Jia, G., Zeng, L., Zhao, S., Ge, S., Long, X., Zhang, Y., & Hu, D. (2019). Monitoring residue levels and dietary risk assessment of pymetrozine for Chinese consumption of cauliflower. *Biomedical Chromatography*, 33(4), e4455 (<https://doi.org/10.1002/bmc.4455>)
- Kleber, M., Bourg, I. C., Coward, E. K., Hansel, C. M., Myneni, S. C., & Nunan, N. (2021). Dynamic interactions at the mineral-organic matter interface. *Nature Reviews Earth & Environment*, 2(6), 402-

- 421.(<https://doi.org/10.1038/s43017-021-00162-y>)
- Kopittke, P. M., Menzies, N. W., Wang, P., McKenna, B. A., & Lombi, E. (2019). Soil and the intensification of agriculture for global food security. *Environment international*, 132, 105078.(<https://doi.org/10.1016/j.envint.2019.105078>)
- Lang, Y. C., Ni, J. P., & Diao, Y. M. (2007). Progress of pymetrozine biological activity and application. *Pesticides-Shenyang*, 46(8), 513.
- Li, C., Yang, T., Huangfu, W., & Wu, Y. (2011). Residues and dynamics of pymetrozine in rice field ecosystem. *Chemosphere*, 82(6), 901-904.(<https://doi.org/10.1016/j.chemosphere.2010.10.053>)
- Liu, Y., Lonappan, L., Brar, S. K., & Yang, S. (2018). Impact of biochar amendment in agricultural soils on the sorption, desorption, and degradation of pesticides: a review. *Science of the total environment*, 645, 60-70.(<https://doi.org/10.1016/j.scitotenv.2018.07.099>)
- Maienfish, P. (2019). Selective feeding blockers: pymetrozine, flonicamid, and pyrifluquinazon. *Modern Crop Protection Compounds*, 3, 1501-1526. (<https://doi.org/10.1002/9783527699261.ch34>)
- Nollet, L. M., & Rathore, H. S. (2016). Handbook of pesticides: methods of pesticide residues analysis. CRC press.2016 Apr 19.
- Pasalu, I.C., Katti, G., 2006. Advances in ecofriendly approaches in rice IPM. *J. of Rice Research* 1(1), 83–90.
- Sen, S., Chakraborty, R., & Kalita, P. (2020). Rice- not just a staple food: a comprehensive review on its phytochemicals and therapeutic potential. *Trends in FoodScience & Technology*, 97, 265-285. (<https://doi.org/10.1016/j.tifs.2020.01.022>)
- Tudi, M., Atabila, A., Ruan, H. D., Wang, L., Lyu, J., Tong, S., ... & Connell, D. (2022). Natural dynamics and residues of pymetrozine for typical rice-growing areas of China. *Ecotoxicology and Environmental Safety*, 232, 113230. (<https://doi.org/10.1016/j.ecoenv.2022.113230>)
- Wang, L. X., Zhang, Y. C., Tao, S., Guo, D., Zhang, Y., Jia, Y. L., ... & Wu, S. F. (2020). Pymetrozine inhibits reproductive behavior of brown planthopper Nilaparvata lugens and fruit fly Drosophila melanogaster. *Pesticide biochemistry and physiology*, 165, 104548. (<https://doi.org/10.1016/j.pestbp.2020.02.014>)
- Wang, Q., Cao, M., Liu, Y., Wei, P., Zhu, G. N., & Wang, M. C. (2015). Analysis of residual profiles of pymetrozine and isoprocarb SC in paddy field by QuEChERS combined with UPLC-ESI-MS/MS. *J Agro-Environ Sci*, 34(3), 431-437.
- Zhang, Y., Zhang, L., Xu, P., Li, J., & Wang, H. (2015). Dissipation and residue of pymetrozine in rice field ecosystem. *Environmental Monitoring and Assessment*, 187(3), 1-6. (

<https://doi.org/10.1007/s10661-014-4256->

[x](#))