Review Article

Ultimate fate and determination of Pyriproxyfen and Fenpropathrin in the environment: A critical Review

Abstract

Since the 1990s, the insect growth regulator pyriproxyfen and pyrethroids such as fenpropathrin have been widely used to reduce pest populations in agriculture. The widespread use of these insecticides makes it essential for researchers to understand how they behave in terrestrial ecosystems and how they can be detected. This work reviewed the most effective analytical techniques used to detect pyriproxyfen and fenpropathrin in various samples. The degradation of pyriproxyfen and fenpropathrin in soil takes time, but in aerobic environments, pyriproxyfen and fenpropathrin are degraded rapidly following first-order kinetics or pseudo-first-order kinetics. Both insecticides tend to adsorb on soils and are not susceptible to leaching into groundwater. Based on greenhouse or field conditions, both insecticides degrade differently by following first-order kinetics, and their half-lives in plants range from one to three weeks. Since both insecticide residues are soluble in acetone, hexane, ethyl acetate, and acetonitrile, they can be extracted in those solvents. They can also be processed in a variety of ways discussed in this paper. Ultimately, the review explains how fate profiles of pyriproxyfen and fenpropathrin in soil and plants affect these molecules' adverse effects on non-target organisms.

Keywords: Metabolic pathways, pyriproxyfen, Fenpropathrin, Analytical techniques, Dissipation,and Persistance.

UNDER PEER REVIEW

Introduction

Today, the agriculture industry can benefit from current science and technology in addition to the significant expertise of earlier generations of farmers to ensure food security (Meenambigai *et al.*, 2017). Agricultural scientists are currently working to devise a set of practices to boost food production sustainably. Among the various ways and procedures created by scientists to achieve high crop yields, safeguarding them from diseases, insects, and pests is essential, as their appearance can have a deleterious impact on the amount and quality of food produced (Kumar Ghosh et al. 2015). That is why, since the Green Revolution, pests have been one of the significant constraints to agricultural productivity (Alam et al. 2016). Farmers are combating this problem by using a wide range of management strategies, from the most sophisticated chemical approaches to the simplest biological ones. However, with the demand for better and faster pest management, biological is no longer a viable option for farmers. As a result, our farmers are rapidly adopting low-cost agrochemicals for limiting the negative impacts of pests and weeds on crop yield. In addition to this, these agrochemicals also simplify harvesting and provide consistent harvests year after year (Cooper and Dobson, 2007). Thus, by reducing crop losses, and improving the production and quality of the crops, agrochemicals contribute to global food security.

Since a significant amount of pesticides is sprayed on crops regularly, they ultimately end up accumulating in the soil, air, water, and food supply chains. Pyriproxyfen 2-[1-methyl-2-(4-phenoxyphenoxy)ethoxy]pyridine is a juvenile hormone analogue that disrupts the growth of insects by mimicking a natural hormone (Schenck et al. 2008). It's an insect growth regulator that is used to control houseflies, mosquitoes, and cockroaches for public health purposes by affecting young insects and eggs. It is permitted for the control of whitefly (*Bemisia tabaci*), bollworm, jassids, aphids, and cutworms in agriculture (Chang *et al.,* 2012). Sumitomo Chemical Co. Ltd. developed Fenpropathrin as a powerful pyrethroid pesticide for agricultural application. Fenpropathrin [(RS)-a-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate] is a racemic mixture of two optical isomers (R, S) because of the asymmetric nature of the benzyl a-carbon atom (Nasiri et al. 2016). It has a strong insecticidal action against whiteflies and has low mammalian toxicity. As a result, it's utilized to control a wide range of mites and insects (Romeh and Hendawi, 2014). Pests can be controlled with these chemicals as long as they comply with country regulations in the country where they are used. It is therefore possible to detect pesticide residues in apples, almonds, apricots, bananas, beans, cabbage, carrots, citrus, cotton, cucumber, grape wine, mango, melon, olive, papaya, pear, pepper, soybean, strawberry, tomato, watermelon, and zucchini ((Navickiene *et al.,* (1999), Farouk *et al*., (2014), Hepsağ, (2019), Payá *et al.,* (2007), Cervera *et al.,* (2010)). Detection of Pyriproxyfen and Fenpropathrin in soils Song *et al*., (2021) and water resources is also possible (Schaefer and Miura, 1990). Therefore, it is essential to study how pyriproxyfen and fenpropathrin behave in a specific growing environment in order to determine whether pre-harvest residue levels remain below the maximum residue level (MRL).

Consumers throughout the world demand low residue levels of pesticides in agricultural goods. Therefore, residue levels must be monitored and controlled to ensure safe food production. This requires careful consideration of the use of pesticides and the application of integrated pest management strategies (Ahmed and Mohammed, 2014). Therefore, considering the growing concern of the world about environmental pollution by pesticides, it becomes logical to investigate the state and residue levels of pesticides in the environment (Qin and Hu, 2022). Moreover, the detection of these chemicals also reduces the potential risk of contamination of food items, soil, and water sources (Dong *et al*., 2018). It is difficult to determine the persistence of pyriproxyfen or

UNDER PEER REVIEW

fenpropathrin in various commodities. This is due to a lack of information about the analytical methods used to detect residuals of either pesticide. Therefore, this review paper attempts to provide a comprehensive overview of analytical methods used for detecting residues of pyriproxyfen and fenpropathrin. This paper will provide valuable insight into the persistence and detection methods of both pyriproxyfen and fenpropathrin. This will allow for better management of pest control and an improved understanding of the impact of these pesticides.

Residues of Pyriproxyfen and Fenpropathrin in various crops, soils, and water

Residues of Pyriproxyfen and Fenpropathrin in various crops grown in different conditions

In recent years, pesticide residues in fruits and vegetables have become a source of concern for consumers as well as environmentalists. There are a wide variety of pesticides available on the market that are used to control or eliminate pests that damage crops and reduce agricultural yields. Despite their importance to modern agriculture, their presence on food crops raises health and environmental questions. Therefore, Dong *et al.*, (2018) carried out an experiment to investigate the kinetic behavior of four pesticides, including Pyriproxyfen, on citrus fruits. The initial Pyriproxyfen residues were 0.14 mg/kg at an application dosage of 80 mg/L, with 92.3 % dissipation after 45 days. According to reports, the half-life was 13.3 days. Albadri *et al.*, (2012) evaluated the dissipation of Fenpropathrin, lambda-cyhalothrin, and deltamethrin in tomato fruit grown in Khartoum, Sudan. Fenpropathrin residues on tomatoes were initially 40.58 mg/kg. The disappearance of Fenpropathrin under examination was found to reflect a Pseudo first order kinetics pattern, with correlation values $r^2 = 0.972$. The decrease in Fenpropathrin concentrations over 16 days suggests a half-life ($t_{1/2}$) of 7.53 days. Deposits were found to be different from the above findings this may be due to different substrates, climatic conditions, etc.

The persistence of pesticides on the crop depends upon various factors including temperature, humidity, wind rate, spray pattern and climatic zones etc. To understand the fate of pesticides in the environment, the dissipation of pesticides in different climatic conditions must be studied. Therefore, Singh *et al.*, (2019) conducted a field trial in Village Kesali, Dist. Navsari to evaluate the dissipation behavior of fipronil, lambda-cyhalothrin, ethion, cypermethrin, Fenpropathrin, and fenazaquin in chilli crop. When Fenpropathrin (30% EC) was sprayed at a rate of 150 mL a.i./ha, the initial deposits of Fenpropathrin observed on 0 day were 1.58 µg/g. On the 15th day, the initial deposit of the required dosage had been dissipated to the extent of 77.33 %. Fenpropathrin's dissipation first order kinetics reflects the half lifetime of 8.14 days. Ahmed and Mohammed, (2014) studied the dissipation kinetics of Fenpropathrin in squash fruits intercropped with garden rockets under field conditions. The residual data indicated that the half-life values of Fenpropathrin in squash fruit and garden rocket were 1.78 and 1.85 days, respectively. Fenpropathrin residues

UNDER PEER REVIEW

were significantly more concentrated in the squash fruit shell than in the squash fruit pulp. The initial Fenpropathrin concentration in squash fruit (1.52 mg/kg) was lower than in garden rocket plants (1.76 mg/kg). Fenpropathrin levels in squash fruit or garden rocket were found to be less than the MRL value (1.0 mg/kg) three days after spraying, and no residues were found on the tenth day.

Both the pesticides dissipates differently in green house conditions as compared to the field conditions. Therefore, the dissipation kinetics of Pyriproxyfen, fenitrothion, and spinosad on tomatoes and green peppers cultivated in greenhouses is investigated by Kmel, (2008). The results demonstrated that Pyriproxyfen dissipation followed Pseudo first order kinetics, with initial deposits of 2.89 and 6.71 mg/kg on tomatoes and green peppers, respectively. After 14 days, the percentage of disappearance on tomatoes was 84.14 % and 88.08 % on peppers. On both tomatoes and peppers, the half-life time ($t_{1/2}$) of Pyriproxyfen was found to be 5.41 days. A research was also conducted in a greenhouse by Fenoll *et al.*, (2009) to study the dissipation of three insecticides (pirimicarb, Pyriproxyfen, and buprofezin) and three fungicides (cyprodinil, fludioxonil, and tebuconazole) on peppers. Pepper samples were collected over a six-week period during which these pesticides were applied twice in succession. Pyriproxyfen had a relatively low residue (0.12 mg/kg) after the first treatment. Pyriproxyfen's decay rate displays Pseudo first order kinetics ($r = -0.953$) and a half-life ($t_{1/2}$) of 21.47 days. The residue level on peppers after the second treatment was 0.24 mg/kg. With Pseudo first order kinetics ($r = -0.959$), the $t_{1/2}$ was 18.57 days. This diference in the half-life values may be due to the different climatic conditions and the spray pattern. Albadri *et al.*, (2012) also evaluated the dissipation of Fenpropathrin, in tomato fruit in greenhouse conditions with initial deposits of 40.58 mg/kg, and the dissipation kinetics of Fenpropathrin under examination was found to reflect a pseudo first order kinetics pattern, with a half-life ($t_{1/2}$) of 7.53 days. This difference in results can be due to the different climatic conditions, different country, and different doses of the Fenpropathrin used.

Residues of Pyriproxyfen and Fenpropathrin in different soil

The degradation of pyriproxyfen and Fenpropathrin (pyrethroid) is affected by the catabolic activity of soil microbes as well as by the different properties of soil, i.e., soil texture, organic matter content, moisture, pH, temperature and type of fertilizers.

Effect of Soil texture

Soil texture can significantly affect the degradation of pesticides. Soil texture refers to the relative proportions of sand, silt, and clay particles in the soil, which influence various soil properties. In an study, Liu *et al.*, (2017) investigated Pyriproxyfen dissipation in soil having different soil textures from six different locations: Beijing (sandy clay loam), Heilongjiang (clay loam), Hunan (loam), Hainan (sandy loam), Human (clay loam), and Quingdao (sand).

UNDER PEER REVIEW

Pyriproxyfen disappeared at a faster rate in Heilongjiang and Hainan soils, but at a significantly slower rate in the other soils. Enantioselective degradation was observed in Hainan soil and Quingdao sand, and it was discovered that while Pyriproxyfen alone showed minimal persistence in soil, moisture content, soil type, combination formulation, and second spray treatment all played key roles in Pyriproxyfen dissipation. Thus, it can be concluded that found that pyriproxyfen dissipated at faster rate in clay loam (OC 36.76%) and sandy loam (OC 28.68) soil while at a much slower speed in rest of the soils. Liu et al. (2017) also observed the effect of moisture content, use of mixture formulation on dissipation behaviour of pyriproxyfen. It was concluded that moderate moisture content (25%) enhance pyriproxyfen dissipation in soil and residues dissipation rate was slower with Ai Qiu (pyriproxyfen mixed with emamectinbenzoate) application while Shi dringkang (pyriproxyfen mixed with imidacloprid) application showed a small accelerated effect. These results were highly supported by Liu *et al.,* (2019a) who examined the dissipation behaviour of pyriproxyfen and its metabolites in five differently textured soil. They also found that pyriproxyfen degraded at fastest in loamy sand and clay soil with half-life ranging from 2.11 days to 9.69 days than other soils.

Zhang *et al.,* (2017) conducted an experiment to study the enantioselective breakdown of Fenpropathrin enantiomers in non-sterile soil, sterile soil, and artificial soil having different soil tectures. After 28 days, over 80% of the initially spiked Fenpropathrin had been dissipated. S-Fenpropathrin concentrations were higher than R-Fenpropathrin concentrations at all time frames. Furthermore, the kinetic data demonstrate that the degradation of S-Fenpropathrin and R-Fenpropathrin followed the first order kinetic equation. The degradation half-lives of S-Fenpropathrin and R-Fenpropathrin were 17.8 and 12.6 days, respectively. Li *et al.,* (2009) examined the degradation of Fenpropathrin and fenvalerate in soil which is alkaline using enantioselective high-performance liquid chromatography (HPLC). Fenpropathrin decomposed rapidly in alkaline soil, with almost 90% of the initially spiked Fenpropathrin disappearing within 55 days of the incubation period. The degradation of Fenpropathrin in alkaline soil was modestly enantioselective. S-Fenpropathrin and R-Fenpropathrin rate constants were 0.0478 and 0.0453 day^{-1} for Fenpropathrin, with half-lives of 15.3 and 16.2 days, respectively. In alkaline soil, Fenpropathrin was found to be configurationally unstable, and significant racemization at the chiral α-C site occurred concurrently with the degradation process. Thus, it's important to consider the interplay between soil texture and pesticide properties when assessing degradation rates. Pesticides with higher water solubility may be more prone to leaching in sandy soils, while those with stronger adsorption tendencies might have reduced availability for degradation in clay soils. Understanding the specific characteristics of the pesticide and the soil texture can help in determining the potential fate and persistence of pesticides in different soil types.

UNDER PEER REVIEW

Effect of Temperature

The temperature of the soil can indeed affect the degradation of pesticides. Temperature is one of the key factors influencing the rate of chemical reactions, including the breakdown or degradation of pesticides in the soil. Temperature can affect the degradation rates of pesticides, microbial activity of soil, volatilization and photodegradation of pesticides. in an study, Chang *et al.*, (2012) studied the dissipation behaviour of pyriproxyfen in soil with respect to the temperature of the soil and concentration of pyriproxyfen in the soil. It was observed that the lower concentrations (1 mg/kg and 5 mg/kg) and higher incubation temperatures (30 ºC and 40 ºC) showed increased rate of degradation with half- lives varied from 48.27 to 4.80 days, respectively. Thus, higher the temperature higher will be the degradation. Cycoń *et al.*, (2014) also reported that the high temperatures and high moisture content lead to the faster degradation of pyrethroid molecules like fenproptahrin in the soil. Different pesticides have different chemical properties and degradation pathways, which can be influenced by temperature to varying degrees. Additionally, extreme temperatures, either extremely high or low, may have negative effects on microbial populations and enzyme activity, potentially slowing down degradation processes. It is always important to consider the recommended application and environmental conditions specified on the pesticide label, as they often provide guidance on optimal temperature ranges for effective and safe use of the pesticide.

Effect of Fertilizers

The presence of fertilizers in soil can have both positive and negative effects on the degradation of pesticides. Thus, Akhtar *et al.*, (2004) designed a research to assess the persistence of chlorpyrifos (an organophosphate) and Fenpropathrin (pyrethroid) pesticides alone and in conjunction with synthetic fertilizers such as urea, DAP, SOP, and foliar fertilizer polydol in tap/hard water. All fertilizers were applied at 1% to soil obtained from the vegetable-producing region of Memon Goth in Karachi, and pesticide fortification was done at 100 ppm and 1000 ppm. After two months, both pesticides recovered up to 100 % of their active components from the parent insecticide in all four treatments as well as in the untreated soil. As a result, it is possible to conclude that the Fenpropathrin persists for a long period in soils, and the addition of fertilizers did not influence the persistence of OP and pyrethroid pesticides. Liu *et al.*, (2019a) investigated the effects of urea, potassium dihydrogen phosphate, organic fertilizer, and compound fertilizer on the dissipation kinetics of two enantiomers of Pyriproxyfen in soil. The half-life of (-)-Pyriproxyfen and (+)-Pyriproxyfen in blank soil was reported to be 16.67 and 16.91 days, respectively. After applying compound fertilizer to blank soil, the half-lives of (-)-Pyriproxyfen and (+)-Pyriproxyfen dropped to 9.88 and 9.58 days, respectively. While potassium dihydrogen phosphate and organic fertilizer enhanced the half-lives of both enantiomers to 20.29 and 18.76 days, 20.07 and 20.46 days, respectively. When urea was applied to soil no substantial dissipation was detected until 42

UNDER PEER REVIEW

days. It can be concluded that compound fertilizer might accelerate Pyriproxyfen dissipation in soil, but the other three fertilizers hindered Pyriproxyfen dissipation.

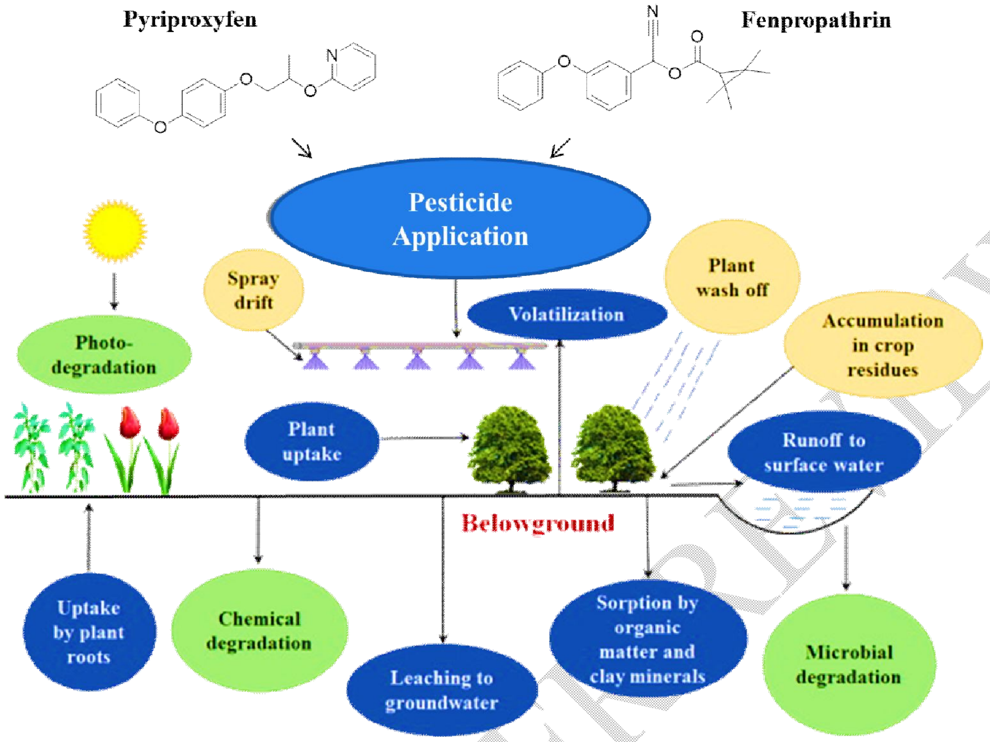

Fig.1 : Fate of pyriproxyfen and fenpropathrinin the environment

Leaching potential of pyriproxyfen and fenpropathrin

Leaching is the vertical displacement of contaminants, such as water-soluble pesticides or fertilizers, carried by water downward through the soil profiles to the groundwater (Devillers et al. 2005), (Pérez-Lucas et al. 2019). Soil texture and structure, organic matter and water content affect the leaching of pesticides in soil (Xiao et al. 2021). The physicochemical properties of the pesticides also influence the leaching behavior of pesticides (Bintein and Devillers 1996), . K_{oc}, which is defined from the distribution coefficient (K_d) and the organic carbon fraction of the soil, is the key parameter for measuring the relative mobility of pesticides in soils. The parameter has been related to the 1-octanol/water partition coefficient ($\log K_{oc} = f(\log K_{ow})$) (Cycon and Piotrowska-Seget, 2016). Pesticides with high K_{oc} values are prone to a lower mobility in soils than those with low K_{oc} values. Thus, the lower water solubility values for Pyriproxyfen and Fenpropathrin (0.367 mg/L, 0.33mg/L), high partition coefficient ($\log K_{ow} = 5.37$, $\log K_{ow} = 6.0$) support that that they don't leach down and don't contaminate the growndwater. This was supported by Fenoll et al. (2010) who conducted an experiment to determine the leaching potential of five insecticides namely pyridaben, pyriproxyfen, tebufenpyrad, buprofezin, pirimicarb and six fungicides by use of disturbed soil columns. For the study, 100 µg of each pesticide was added to column that

UNDER PEER REVIEW

contained 150 g of clay loam soil and leached with 600 mL of 0.01M $CaCl_2$ for 10 days. Leachates and soil fractions were analysed for residues. Primicarb (insecticide) was detected (48% of initial amount) in leachates and 55% was recovered from the soil layers, other insecticides were not detected in leachates and almost all applied amount remained in top soil fraction thus showing non-leaching behaviour. Thus, pyriproxyfen doest not leach down in the soil. In another leaching study with fine sandy loam, loamy sand, clay, and loam soils, Schaefer et al. (Schaefer, Dupras Jr, and Mulligan III 1991) showed that over 50% of the pyriproxyfen applied remained in the upper 6 cm of the 30-cm soil columns, demonstrating that pyriproxyfen did not have capacity for downward migration.

Fenpropathrin is nonpolar and therefore has low water solubility. This property causes it to sorb strongly to soils and organic matter to avoid contact with water for thermodynamic reasons. Consequently, the insecticide have a low potential for leaching through soils to groundwater. Its Henry's law constant (18.2 Pa m^3 mol^{-1}at 25 °C) indicates that volatilization from wet soil is possible but is unlikely due to its strong sorption capacity. Additionally, volatilization from dry soil is limited by its moderate vapour pressure (0.76 mPa) at 20 °C (Kanawi, Budd, and Tjeerdema 2013). Fenpropathrin's potential for leaching has been examined in light clay, sandy clay loam, clay loam, and sand by Sakata et al. (1992) (Sakata et al. 1992). Soils were treated and labeled with ^{14}C and used either immediately or aged for 4 weeks under dark, aerobic conditions. Under both treatments of the pyrethroid was detected in the eluates from the light clay, sandy clay loam, and clay loam soils. However, 21–47% of the applied ^{14} C was detected in the eluate of the sandy soil. While fenpropathrin has a high soil sorption coefficient, this study highlights the influence of soil type on its potential for leaching. Its low sorption to sand is likely due to a low organic matter content (less than 0.1%); being nonpolar, fenpropathrin will sorb best to soils of high organic matter content (Xiao et al. 2021). Thus, in the absence of organic matter, the pesticide is slightly more likely to percolate into groundwater. In California, 88 sediment samples analysed had no detectable concentration of fenpropathrin (Kanawi et al. 2013).

Residues of Pyriproxyfen and Fenpropathrin in water

The persistence of Pyriproxyfen (EC, 10%) in experimental rice plots filled with water was investigated by Schaefer and Miura, (1990). Three plots were treated with 0.05 kg a.i./ha Pyriproxyfen and the other three with 0.11 kg a.i./ha Pyriproxyfen. Three plots were utilised as controls. Two samples (1 L each) were obtained from every pond for extraction and residue analysis. After one day, no measurable residues were identified in plots treated with Pyriproxyfen at 0.05 kg a.i./ha, and no residues were found after two days at the higher dose of 0.11 kg a.i./ha. Takahashi *et al.*, (1985) investigated the photodegradation of Fenpropathrin [(RS)-a-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate] in distilled water, humic acid

UNDER PEER REVIEW

solution, river water, sea water and aqueous acetone using ^{14}C-preparations labelled independently at the cyano group, cyclopropyl-C_1, or in the benzyl ring. The rate of Fenpropathrin photodegradation in water by direct sun decreased in the following order: aqueous acetone>sea water>river water>aqueous solution of humic acid>distilled water. Fenpropathrin degraded to half of its initial concentrations in >6 weeks in distilled water, 6.0 weeks in humic acid aqueous solution, 2.7 weeks in river water, 1.6 weeks in sea water, and half day in aqueous acetone.

Metabolic pathway of Pyriproxyfen

In plants

The metabolism of radio labeled [^{14}C] Pyriproxyfen in tomato fruits was studied by Fukushima *et al.*, (2005) using topical applications of acetonitrile solution and emulsifiable concentration (EC) formulation at 35, 21, and 7 days before harvest. In the instance of the EC application, I went deeper into plant tissues than in the case of the acetonitrile solution application. This is because the EC formulation contains a surfactant, which is known to promote pesticide penetration from the plant surface to the tissues. As a result, discrepancies in radiocarbon distribution between the two applications arise. However, the metabolic processes in these applications are nearly identical. The metabolic routes of I in tomato fruit are postulated in Fig. 1 based on the recovered radioactivity of the metabolites from the rinse, juice, and pomace. I experienced hydroxylation at the 4′-position of the terminal phenoxyphenyl ring to generate III, cleavage of the propylpyridyl ether and propyl phenyl ether bond takes place by following the dephenylation to produce IV, XI, and V, respectively. Fukushima, Fujisawa, and Katagi (2005b) investigated the metabolism of radiolabelled pyriproxyfen in tomato. They observed mainly five metabolites in tomato namely: 4-(4-hydroxyphenoxy) phenyl (RS)2-(2-pyridyloxy) propylether (4-OH-PYR), 4-hydroxyphenoxy (RS)2-(2- pyridyloxy) propylether (DPH-PYR), (RS)-2-hydroxyphenoxy 4- phenoxyphenylether (POPA), 4-(4-hydroxyphenoxy) phenyl(RS)-2-hydroxyphenoxy4-phenoxyphenylether (4-OH-POPA), (RS)-2-(2- pyridyloxy)propanol (PYPA).

UNDER PEER REVIEW

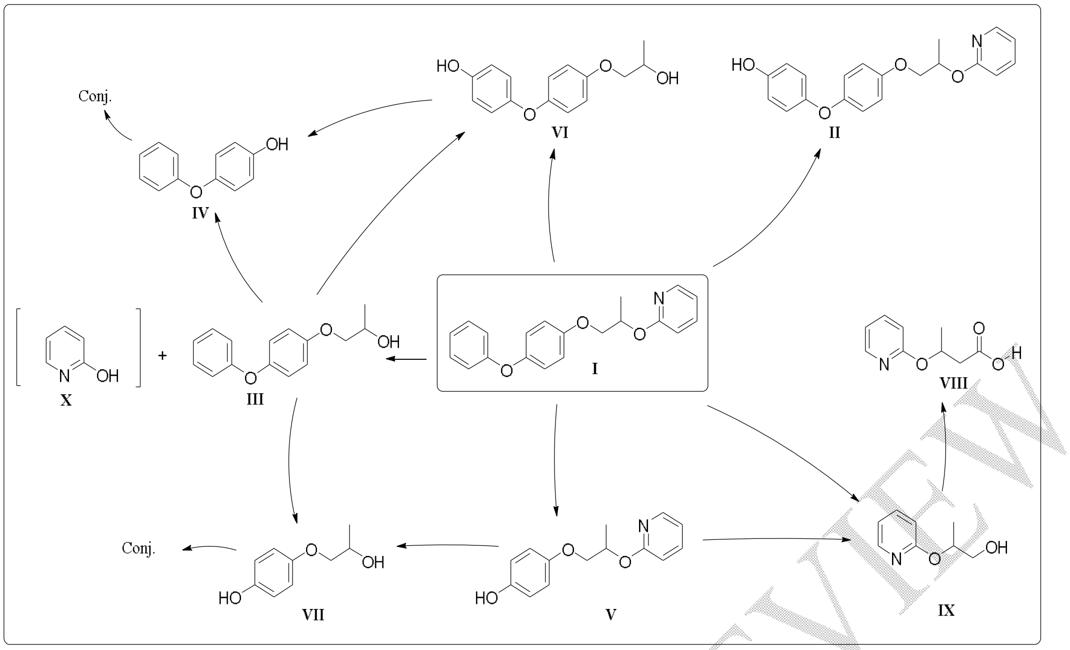

Fig. 2: Metabolic pathway of Pyriproxyfen in plants

In soils

In 1996, the FAO/WHO joint meeting on pesticide residues identified PYPAC and 4-OH-pyr as the predominant and minor soil degradation products, respectively. Liu *et al.*, (2017) identified the formation of 4-OH-Pyr and DPH-Pyr metabolites from the degradation of Pyriproxyfen in soil. Metabolism of PYR in soil and the formation of 4-OH-PYR, POP, POPA, DPH-PYR, and 4-OH-POPA metabolites was studied by Sullivan and Goh (2008). The chemical structure for all the metabolites of Pyriproxyfen in the soil is shown in Fig. 2. Kumari and her co-workers observed that the degradation of Pyriproxyfen takes place through its hydroxylation, photodegradation, and microbial degradation. Fig.3 depicts the degradation of PYR into six metabolites in the subtropical agroclimatic condition in sandy loam soil provided by Kumari *et al.*, (2021).

UNDER PEER REVIEW

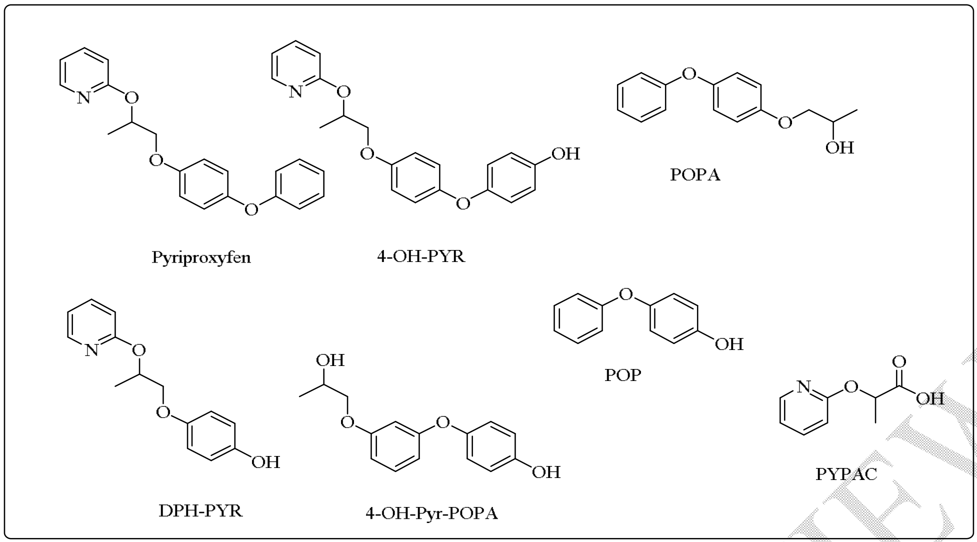

Fig. 3: Pyriproxyfen and its main degradation products in soil

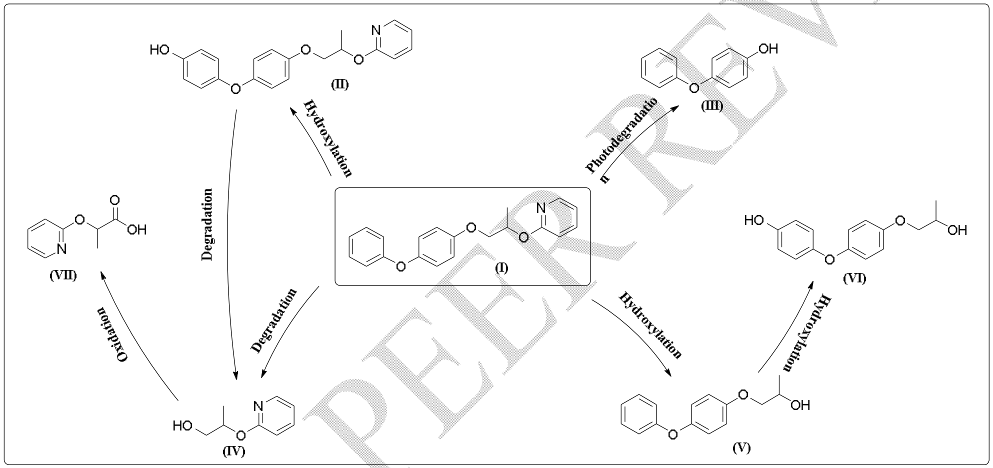

Fig. 4: Metabolic pathway of Pyriproxyfen in soil

UNDER PEER REVIEW

Fathulla (1995) studied soil metabolism of pyriproxyfen in California sandy loam soil by fortifying with ^{14}C- pyriproxyfen at a concentration of 0.60 mg/kg. The fortified soil samples kept in glass chamber in dark at 25±2°C for 189 days. Humid aerobic environment was maintained by passing humid air through the system continuously. Biological catalysis of pyriproxyfen was found as the major metabolic pathway in which insecticide itself serving as a carbon source for soil microorganisms. Three degradation products, were identified as 4-OH-PYR, PYPAC, DPH-PYR.

Metabolic pathway of Fenpropathrin

In plants

The metabolic fate of Fenpropathrin in cabbages was studied by Mikami *et al.*, (1985) using ^{14}C preparations labeled separately at the cyano group and the benzyl and cyclopropyl rings. Under greenhouse conditions, Fenpropathrin disappeared from the treated leaves of cabbages with a half-life of around 11-12 days. The possible metabolic pathway for Fenpropathrin degradation in cabbages is depicted in Fig. 4. Mikami and his colleagues discovered that the insecticide experienced ester bond cleavage, hydrolysis of the CN group to produce $CONH_2$ and COOH groups, hydroxylation at both of the gem-dimethyl groups followed by oxidation to form carboxylic acid. It was observed that the resultant carboxylic acids and alcohols were present in conjugation with sugars.

UNDER PEER REVIEW

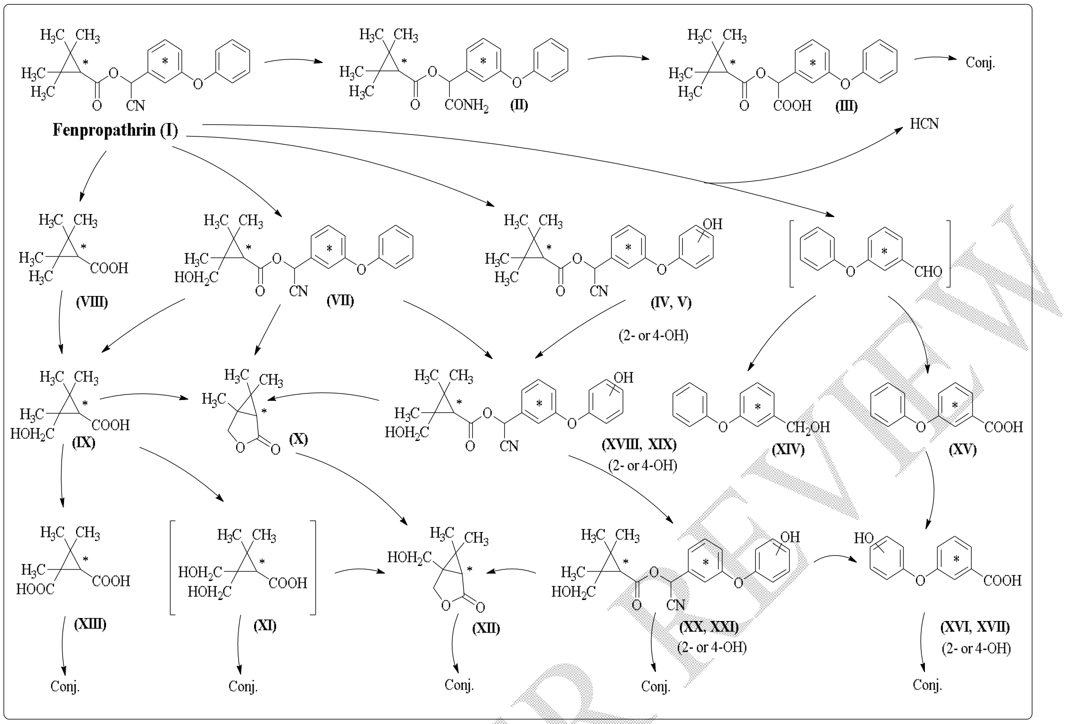

Fig. 5: Metabolic pathway of Fenpropathrin in plants

In soils

Under an aerobic environment, Fenpropathrin decomposed rapidly, but it deteriorated slowly under anaerobic conditions and barely degraded in sterile soils. Based on these findings, it appears that aerobic bacteria in soil are mostly responsible for Fenpropathrin degradation. The half-life of Fenpropathrin in soils ranged from 11 to 17 days in aerobic soil. Fig. 5 depicts the predicted Fenpropathrin degradation routes described by Sakata *et al.*, (1990). The insecticide undergoes diphenyl ether bond cleavage, ring hydroxylation, and hydrolysis of the CN group to $CONH_2$ and COOH groups, followed by easter bond cleavage. The ester bond was hydrolyzed, resulting in the synthesis of VI from the cyclopropyl-label and 3-phenoxy mandelonitrile from the benzyl-label.

UNDER PEER REVIEW

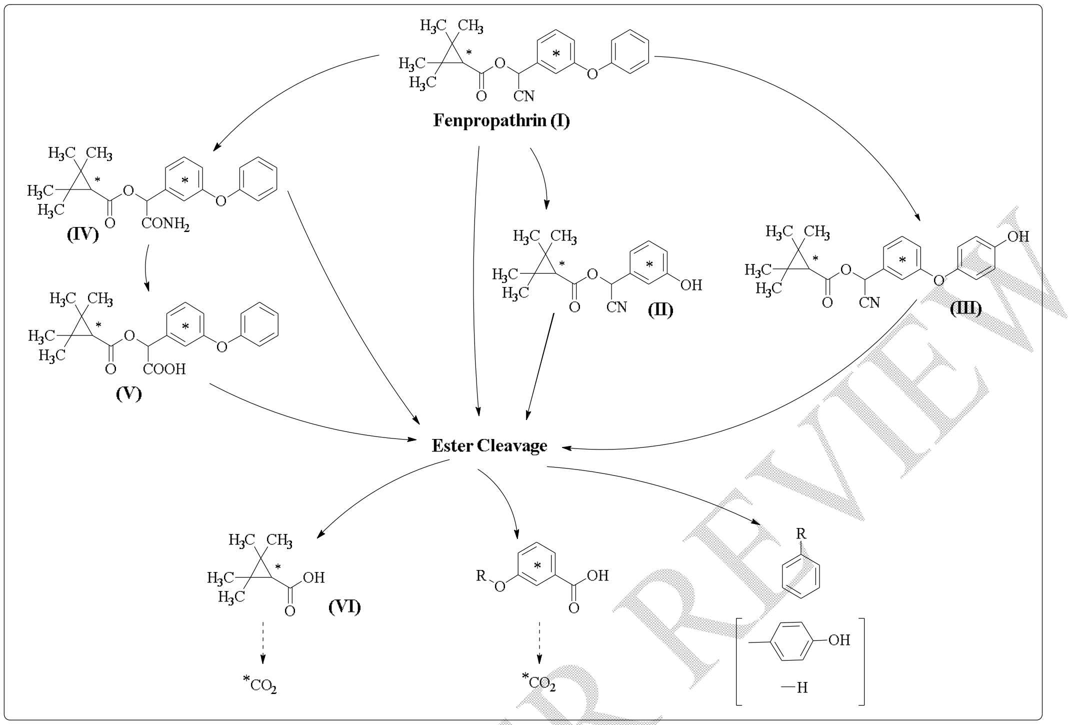

Fig. 6: Metabolic pathway of Fenpropathrin in soil

Analysis techniques involved in the estimation of the persistence of Pyriproxyfen and Fenpropathrin residues

The residue analysis of various plant-derived samples involves three primary steps: extraction, cleanup, and final residue evaluation using highly sophisticated chromatography equipment. The first step includes the extraction of pesticides along with waxes, plant pigments, and lipids into the appropriate solvent. The second step comprises the elimination of co-extractives with the aid of cleanup to avoid interference before the final estimation. The amount of cleanup required is entirely defined by the scope of testing, sample heterogeneity, and sensitivity of available detection techniques for the chemical in question. Finally, by using sophisticated detection instruments (GC-ECD/NPD/FID, HPLC-UV/DAD, LC-MS/MS, etc) the residue of the pesticide in concern is estimated (Handa *et al.*, 1999).

Extraction and cleanup

UNDER PEER REVIEW

Farouk *et al.*, (2014) carried out a study for the determination of Pyriproxyfen and pyridalyl residues in Egyptian tomatoes. The representative samples were first homogenized with ethyl acetate (for Pyriproxyfen) or acetone (for pyridalyl) in a blender with sodium sulphate for about 2 minutes. The supernatant was filtered and dried and the residues were redissolved in 2 mL of petroleum ether. Then, the cleanup was achieved through chromatographic separation using gradient elution with petroleum ether (Solvent A) and diethyl ether (Solvent B) from 5% to 50% (Solvent B). The eluate was concentrated to dryness and the residue was dissolved in 2 mL methanol:acetonitrile (4:1, v/v) for HPLC analysis. The recoveries ranged from 86.03 to 94.55 % for Pyriproxyfen and 95.08 to 99.38% for pyridalyl. The LOD of the method was 0.217 ppm for Pyriproxyfen and 0.186 ppm for pyridalyl.

Schenck *et al.*, (2008) validated a modified QuEChERS method for the multi-residue analysis including Pyriproxyfen and Fenpropathrin in pears. Extraction was carried in acetic acid + acetonitrile (1 + 99) followed by a salting out step. The cleanup was achieved by passing the acetonitrile extract down a single solid-phase extraction (SPE) column, which provided a cleaner extract than the dispersive SPE cleanup employed in the original QuEChERS method and later analysed by GC-MS/MS.

Navickiene *et al.,* (1999) developed a simple and efficient method for the determination of Fenpropathrin in oranges, pears, apples, and strawberries. The approach begins with the extraction of the homogenised samples with hexane:acetone (1:1, v/v) mixture, followed by a cleanup procedure based on a pre-packed column of florosil using a hexane : ethyl ether (7:3, v/v) mixture. The eluate was dried, the final volume was adjusted to 10 mL and an aliquot was analysed by GC-ECD. The average recoveries of fortified fruit samples varied from 83 % to 98 %, with coefficients of variation ranging from 1.4 to 13.5 and limits of detection from 0.1 to 0.2 mg/kg.

Ngolo *et al.*, (2019) developed an easy and efficient cleanup procedure for LC-MS/MS analysis of Fenpropathrin in soils, kales, and tomatoes. Soil, kale, and tomatoes were separately weighed into clean falcon tubes, and each tube received 10 mL of water and 10 mL of acetonitrile. To facilitate phase separation, a QuEChERS salt pouch comprising citrate buffer salts was introduced to the tubes following vigorous shaking. The upper organic layers

UNDER PEER REVIEW

(acetonitrile extract) were then transferred into clean tubes containing 900 mg magnesium sulphate + 150 mg PSA. To remove the highly pigmented chlorophyll from tomatoes and kale, graphitized carbon black (GCB) was also added and centrifuged at 3500 rpm for 3 minutes. One milliliter of the supernatant layer was transferred to vials for LC-MS/MS analysis. The percent recovery ranged from 83.5-97.5 (soil), 75.4-89.1 (kales), and 75-92% (tomatoes) and the %RSD varied between 0.69%-10.81%.

In a study, Rahmiani *et al.*, (2018) validated a method for the determination of the pesticides Fenpropathrin, lambda-cyhalothrin, and chlorothalonil in potatoes and tomatoes. First of all, the acetone-based extraction was performed. Then, the organic layer was partitioned with, 8 mL of petroleum ether and 4 mL of dichloromethane. The 3 mL of upper layers were then collected and concentrated until the residues were dry. Finally, residues were dissolved in 0.9 mL of isooctane : toluene (9:1) and evaluated using a GC fitted with an ECD detector. Recoveries ranged from 93% to 102% for analytes in the two samples with a relative standard deviation of 7%. LOD and LOQ values for Fenpropathrin, chlorothalonil, and lambda-cyhalothrin were 1.36 and 4.58, 1.45 and 4.85, and 1.12 and 3.73 ppb, respectively.

Hepsağ, (2019) describes a quick, easy, cheap, effective, rugged, and safe method for the determination of 233 pesticide residues including Pyriproxyfen and Fenpropathrin in cucumber and grapefruits. The samples were extracted in methanol:acetic acid (99:1, v/v), and salting out is done by adding 6 g $MgSO_4$ and 1.5 g sodium acetate. The supernatant was subjected to cleanup by using PSA as d-SPE sorbent and evaporated to dryness. The residues were reconstituted in n-hexane for the injection into GS-MS/MS for qualitative as well as quantitative analysis. The average recoveries for Pyriproxyfen range from 93.2 to 96 % in cucumber, whereas in grapefruit, recovery varies from 82.9 to 87.8% at two different fortification levels. In cucumber, LOD and LOQ values were 4.57, 15.24 µg/kg, respectively, but in grapefruit, LOD and LOQ values were 3.46, 9.12 µg/kg, respectively.

Galera *et al.*, (1997) established a method for the quantitative analysis of Fenpropathrin in tomatoes and green beans. The representative sample was shaken mechanically with acetone (100 mL) for 2 h and filtered into a 1L separating funnel. The filtrate was subjected to liquid-liquid partitioning by vigorously shaking it for 2 minutes in

UNDER PEER REVIEW

the presence of saturated sodium chloride solution (10 mL), n-hexane (60 mL), and dichloromethane (60 mL). This partitioning procedure was performed twice with n-hexane (60 mL). The organic layers were obtained by passing them through anhydrous sodium sulfate, then concentrated to dryness and reconstituted in 10 mL of hexane. This solution was injected into the GC-ECD and the average recoveries were found >90% in tomatoes and >87% in green beans with relative standard deviation lower than 5%. The values of LOD and LOQ are 0.010 and 0.035 kg/mL, respectively.

Song *et al.*, (2021) performed an experiment to study the dissipation rates of 10 pyrethroids including Fenpropathrin in different soil layers of the open fields and greenhouse soils of Shenyang, China. The soil samples were air-dried, grounded, and passed through 60 mesh sieve. Then, the soil samples were marinated in a mixture of petroleum ether:acetone (v/v, 2:1) overnight followed by ultrasonic extraction for 20 min. The ultrasonic extraction was repeated twice and the supernatants were combined with 50 mL 2 % Na_2SO_4 solution as a phase-transferring agent followed by shaking. The upper organic phase was collected, dried, concentrated to 1 mL by rotary evaporator, and purified by using wet packing columns. The chromatographic column was loaded four times with a 1 mL concentration and an 8mL combination of petroleum ether and ethyl acetate (v/v, 9:1). The eluent was collected and evaporated at room temperature, and dissolved in 1mL of n-hexane for GC-MS/MS analysis.

A study was conducted by Payá *et al.*, (2007) to analyse the residues of fenoxycarb and Pyriproxyfen in fresh and canned peaches using HPLC-DAD. The extraction was performed with acetone-dichloromethane:petroleum ether (50:50) and for cleanup procedure aminopropyl cartridges were used. The average recoveries of Pyriproxyfen from the fortified samples were 83.52-89.62% at two different spiking levels of 0.05 ppm and 1.0 ppm. The limit of detection (LOD) and limit of quantification (LOQ) values were 0.01 mg/kg and 0.05 mg/kg, respectively.

Cervera *et al.*, (2010) validated a method for the simultaneous determination of 130 pesticides including Pyriproxyfen in oranges, spinach, and nectarine. The extraction of the pesticide residues was carried out by using accelerated solvent extraction (ASE) with ethyl acetate. There is no need for cleanup in the case of orange and nectarine samples. However, due to the high levels of fats and lipids in spinach, the gel filtration chromatography (GPC)

UNDER PEER REVIEW

cleanup step was mandatory. The eluate from GPC was collected, evaporated, redissolved in ethylacetate, and injected in GC-MS/MS equipped with a triple quadrupole mass analyser. Recoveries for most of the pesticides were found in the range of 70-120% with RSD below 20% at 0.01 and 0.05 mg/kg fortification levels. The LOD of Pyriproxyfen for this method was 0.003 mg/kg.

Analytical methods/Recoveries

Different instrumental methods have been developed to determine Pyriproxyfen and Fenpropathrin residues in vegetables, fruits, and soils using gas chromatography, high-performance liquid chromatography, and spectroscopic methods. Du *et al.*, (2013) used ultra-performance liquid chromatography associated with tandem mass spectrometry (UPLC-MS/MS) to evaluate the residues of Pyriproxyfen, diflubenzuron, and avermectin in mushrooms. The samples were extracted in acetone and their purification was done by using PSA. Gradient elution with acetonitrile and water containing 0.2 percent formic acid mobile phase was used to produce chromatographic separation. The target compounds were detected in less than 3.0 minutes utilising an electrospray ionisation source in positive mode (ESI+). For all the analytes, average recoveries were in the range of 78.1–112.5% with the RSD values below 11.8%. The limits of detection varied from 0.016 to 1.5 mg/kg, and the limits of quantification ranged from 0.052 to 5 mg/kg.

UNDER PEER REVIEW

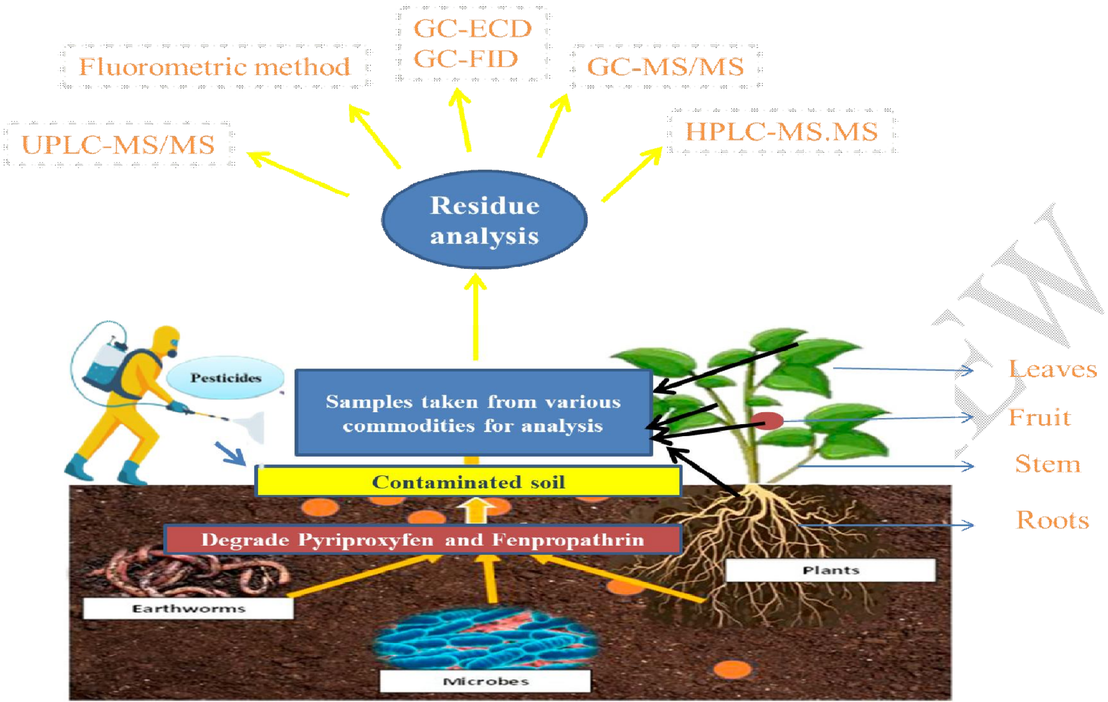

Fig.7 : Different Analytical techniques used fot the estimation of residues of pyriproxyfen and fenpropathrin in plants and soil

Farouk *et al.*, (2014) designed a fluorometric method for the determination of pyridalyl and Pyriproxyfen residues in Egyptian tomatoes. This method relies on the direct fluorometric measurement of Pyriproxyfen and pyridalyl residues in acetic and sulfuric acid at excitation and emission wavelengths of 320 and 646 nm, respectively. The fuorometric method has a distinct benefit over chromatographic methods in that it does not necessitate a cleaup procedure. The recoveries of Pyriproxyfen and pyridalyl in tomato samples ranged from 88 to 98% and 86 to 93%, respectively. The LOD of the method was 0.146 ppm for Pyriproxyfen and 0.078 ppm for pyridalyl.

Elbashir *et al.*, (2013) carried out a study to analyze the residues of Fenpropathrin, λ-cyhalothrin, and deltamethrin on tomato fruits grown in an open field by using gas chromatography equipped with electron capture detector. For the chromatographic separation, a C_{18} Capillary column was employed. The highest resolution was obtained using an injection port temperature of 280°C, column temperature of 240°C, ECD temperature of 300°C, and a flow rate of 1.5 mL/min of carrier gas (N_2). Recoveries were obtained in the

UNDER PEER REVIEW

range 85.77-95.61%, 91.77-98.59%, and 92.61-98.04% for Fenpropathrin, deltamethrin, and λ-cyhalothrin in tomatoes respectively.

A quick and efficient multi-residue method for the analysis of 12 pesticides including Fenpropathrin in cucumbers grown in garden and green house conditions was developed by Nasiri *et al.,* (2016). The representative samples of cucumber were processed by the QuChERS method. The confirmation and quantification of pesticide residues were achieved by GC/MS in SIM mode. At a constant flow rate of 1 mL/min, helium was employed as the carrier gas in the GC/MS. The injection port was set to 250 °C, and the splitless injection mode was employed. The oven temperature began at 75 °C and remained there for 3 minutes, climbed to 120 °C at a 25 °C/min ramp rate and then to 300 °C at a 5 °C/min ramp rate, holding there for 11 minutes. The average recoveries for Fenpropathrin are found to in the range of 76-101% at different fortification levels. The LOD and LOQ values for all the analytes were ≤10 ng/g and ≤25 ng/g respectively. Zhang *et al.,* (2017) performed an experiment to study the enantioselective degradation of Fenpropathrin in soil by using reverse-phase high-performance liquid chromatography (RP-HPLC). The separation of enantiomers of Fenpropathrin was achieved on Lux Cellulose-1, Lux Cellulose-3, and Chiralpak IC chiral columns. Fenpropathrin enantiomers obtain a baseline separation (Rs = 2.30) on the Lux Cellulose-3 column with methanol:water (85:15) mobile phase. On Lux Cellulose-1 and Chiralpak IC columns, partial separations were accomplished with maximum Rs = 1.01 and Rs = 0.64, respectively. In each run, 10 µL of the sample was injected into the column and the flow rate was 0.8 mL/min with the detection wavelength at 230 nm. For both the enantiomers of Fenpropathrin and 3-PBA, recoveries varied from 76-96%. Based on an acceptable RSD of 20%, the LODs for both enantiomers and 3-PBA in soil were 0.015 and 0.01 mg/g, respectively, while the corresponding LOQs were 0.05 and 0.03 mg/g.

Efficacy of the pesticide against soil bacterial community

Pesticides can have various effects on soil bacterial communities, depending on the specific pesticide, its concentration, application frequency, exposure duration, and the sensitivity of the bacterial species present. Ching S Chang et al. 2012) studied the effect of pyriproxyfen on soil microbial community. They concluded that lower concentrations showed less toxicity toward the microbial community and also found that the soil bacterial community changed

UNDER PEER REVIEW

(with less than 50 % similarity in cluster analysis) after pyriproxyfen application. Liu et al. (2019a) also studied the toxicological effect of pyriproxyfen and its metabolites on earthworm and soil enzymatic activity. They found that the toxicity of pyriproxyfen metabolites was far greater than pyriproxyfen. During the study on soil enzymatic activity they observed that pyriproxyfen inhibited sucrase, dehydrogenase activity and promoted catalase, urease activity. Akhtar et al. (2004) studied the effect of fenpropathrin on microbial growth showed that 100 ppm fortification had no adverse effect whereas at 1000-ppm suppressed the count of some of the bacterial colonies. Thus, high concentration of the pyriproxyfen and fenpropathrin molecule in the soil leads to more adverse effect on the soil bacterial community.

Efficacy of the pesticide against honey bees

Bees play a crucial role in pollinating a wide variety of plants, including many crops that are important for human food production. The use of pesticides can have detrimental effects on honey bees. Thus, to assess the impact of pyriproxyfen on honey bees Fourrier et al. (2015) conducted an experiment at two application doses of 23 and 57 ng per larva. They found that the higher dose was significantly more detrimental leading to high rate of malformed adults (atrophied wings) and pyriproxyfen treated bees showed shorter life span and fewer social behaviuor including brood care, ventillation, contacts with nestmates and food stocks. Chen et al. (2016) also evaluated the impact of pyriproxyfen on the development of honey bee (*Apis mellifera* L.) colony in field condition and found the impact of pyriproxyfen on larva, adult honey bee and the influence on royal jelly production. In vivo pyriproxyfen feeding showed that the highest concentration of pyriproxyfen treatment caused pupal death and deformed winged bees. Liao et al. (2017) explored the effect of fenpropathrin on survival and homing ability of honeybees *Apis mellifera* L. They found that the lifespan and homing rates were significantly decreased with the increase of fenpropathrin dose ($P < 0.05$). Tong et al. (2018) quantified the risk associated with fenpropathrin to honey bees by using the flower hazard quotient (FHQ) value. According to the data, they found that fenpropathrin posed an unacceptable risk to honeybees after spraying in fields.

UNDER PEER REVIEW

Table 1: Analytical techniques used for the qualitative and quantitative assessment of pyriproxyfen in different samples

Sample	**Solvent used for extraction**	**Clean up**	**Detection**	**Recoveries (%)**	**References**
Egyptian tomatoes	Ethyl acetate	Chromatographic separation using gradient elution with petroleum ether and diethyl ether	HPLC-DAD	86.03-94.55	Farouk *et al.*, (2014)
Pears	Acetic acid + Acetonitrile	SPE (Solid Phase Extraction) column	GC-MS/MS	98.5	Schenck *et al.*, (2008)
Cucumber and grapefruits	Methanol:Acetic Acid (99:1, v/v)	Primary Secondary Amine (PSA) as d-SPE	GS-MS/MS	82.9-96	Hepsağ, (2019)
Fresh and canned peaches	Dichloromethane:Petroleum ether (1:1, v/v)	Aminopropyl cartridges	HPLC-DAD	83.52-89.62	Payá *et al.*, (2007)
Oranges, spinach, and nectarine	Accelerated Solvent Extraction (ASE) with ethyl acetate	Gel Filtration Chromatography (GPC)	GS-MS/MS	70-120	Cervera *et al.*, (2010)
Mushrooms	Acetone	Primary Secondary Amine (PSA)	UPLC-MS/MS	78.1–112.5	Du *et al.*, (2013)
Egyptian tomatoes	Acetic acid	-	Fluorometer at excitation and emission wavelengths of 320 and 646 nm	88-98	Farouk *et al.*, (2014)

UNDER PEER REVIEW

Table 2: Analytical techniques used for the qualitative and quantitative assessment of fenpropathrin in different samples

Sample	**Solvent used for extraction**	**Clean up**	**Detection**	**Recoveries (%)**	**References**
Oranges, pears, apples, and strawberries	Hexane:Acetone (1:1, V/V)	Florosil column using hexane : ethyl ether (7:3, v/v)	GC-ECD	83-98	Navickiene *et al.*, (1999)
Soils, kales, and tomatoes	Acetonitrile	900 mg magnesium sulphate ($MgSO_4$) + 150 mg PSA for soil and, graphitized carbon black kales, tomatoes samples	LC-MS/MS	83.5-97.5 (soil), 75.4-89.1 (kales), and 75-92 (tomatoes)	Ngolo *et al.*, (2019)
Pears	Acetic Acid + Acetonitrile	SPE column	GC-MS/MS	99.5	Schenck *et al.*, (2008)
Potatoes and Tomatoes	Acetone	liquid-liquid partitioning with, 8 mL of petroleum ether and 4 mL of dichloromethane	GC-ECD	93 -102	Rahmiani *et al.*, (2018)
Cucumber and grapefruits	Methanol:Acetic Acid (99:1, V/V)	PSA as d-SPE	GS-MS/MS	87.7-93.1	Hepsağ, (2019)
Tomatoes and green beans	Acetone	Liquid-liquid partitioning with sodium chloride solution (10 mL), n-	GC-ECD	>90 in tomatoes and >87 in green beans	Galera *et al.*, (1997)

UNDER PEER REVIEW

		hexane (60 mL), and dichloromethane (60 mL)			
Soil	Ultrasonic Extraction with Petroleum Ether:Acetone (V/V, 2:1)	Chromatographic separation with petroleum ether and ethyl acetate (9:1, v/v)	GC-MS/MS	94.2-98.7	Song *et al.*, (2021)
Tomato	Acetonitrile	Florosil	GC-ECD	85.77-95.61	Elbashir *et al.*, (2013)
Cucumbers	Acetonilrile	$MgSO_4$ + PSA	GC/MS in SIM mode	76-101	Nasiri *et al.,* (2016)
Soil	Acetonirile	3 times partitioning with Dichloromethane	HPLC with Lux Cellulose-1, Lux Cellulose-3, and Chiralpak IC chiral columns	76-96	Zhang *et al.*, (2017)

UNDER PEER REVIEW

Conclusion

Whatever the type of soil, aerobic degradation of pyriproxyfen is fast. It is done in two steps, the former being quicker than the latter. A rather high variability can be found between the results of different studies even if the types of soils and the abiotic conditions are rather similar. Moisture, content in organic matter, presence of other pesticides or fertilizers, applied dose, and number of treatments also highly influence the degradation behaviour of pyriproxyfen. With low water solubility and high log K_{ow} values, pyriproxyfen is adsorbed onto the soil surfaces and it is not a leacher. In fruits and vegetables, the pyriproxyfen and fenpropathrin moelcules persisted from few days to weeks depending upon field and green house conditions having variable temperatures, humilities, wind rates and different type of crops. The analytical techniques discussed in this paper to detect both the pesticides resulted into better recoveries for the pesticides and the hyphenated techniques like UPLC-MS/MS, GC-MS/MS resulted into the lowest LOD values. In last this review conculeds that high concentrations of pyriproxyfen and fenpropathrin causes adverse effects in the non-target organisms from honey bees to the soil micro-organisms.

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UNDER PEER REVIEW

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UNDER PEER REVIEW

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