



DEVELOPMENT OF A MULTI-RESIDUE METHOD FOR 11 MULTICLASS PESTICIDES IN A SWEET LIME ORCHARD SOIL NEAR PULIVENDULA USING GC-MS/MS WITH QUECHERS EXTRACTION

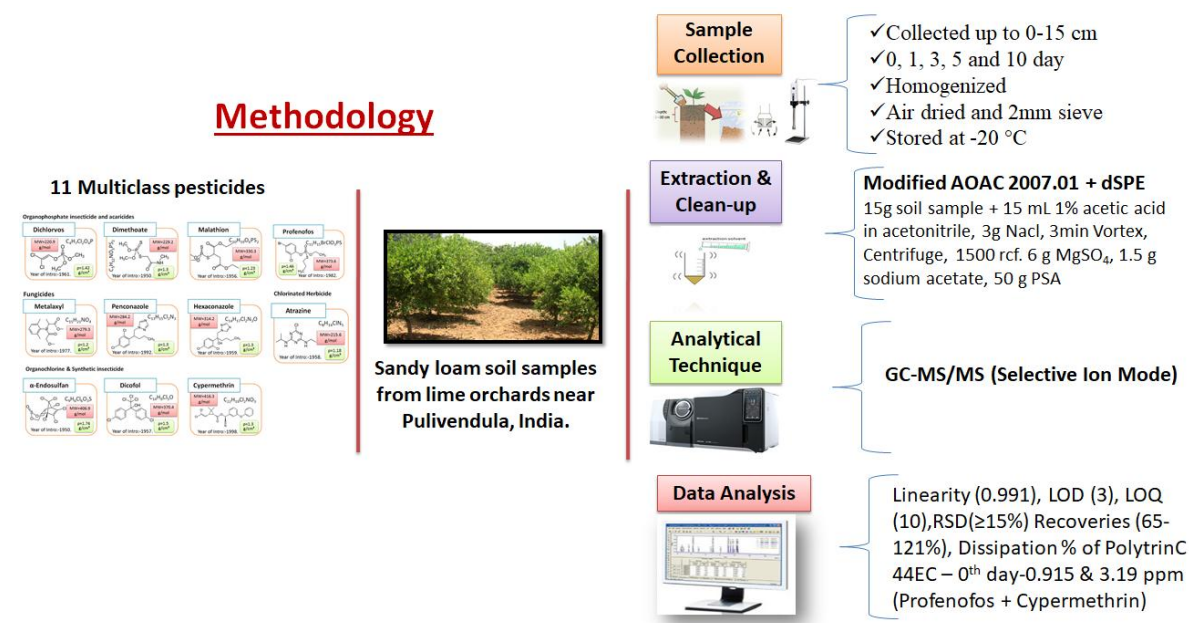
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Graphical Abstract



Abstract:

A modified AOAC (Association of Official Agricultural Chemists) 2007.01 (acetate buffered QuEChERS) method with d-SPE clean-up was developed for the detection of 11 multiclass pesticide residues. Gas chromatographic separation along with tandem mass spectrometry (GC-MS/MS) was used to look for pesticide residues in the soil samples. By spiking all soil samples, the validation experiments were carried out with 11 readily available pesticides. Studies on linearity, recovery, precision, and accuracy were used to validate the modified AOAC 2007.01 method. Except for dicofol and penconazole, all pesticides reached the required recovery range of 65–121% with RSD values under 15% and correlation (r^2) scores greater than 0.991. The kinetics of Polytrin-C 44 EC (400 g/l profenofos and 40 g/l

cypermethrin) pesticide degradation in soil from sweet lime orchards were also studied using the optimised multi-residue approach. After spraying the recommended dosage of Polytrin-C 44 EC pesticide on sweet lime trees, soil samples were taken from orchards in and around Pulivendula, India, at 0 (within an hour), 1, 3, 5, and 10 days later for analysis. The residues of profenofos and cypermethrin on the zeroth-day sample were 0.915 ppm \pm 0.016 and 3.19 ppm \pm 0.13, respectively. Finally, on the tenth day, both pesticide residues were found to be below the detection level (BDL). The correlation coefficients (R^2) for profenofos and cypermethrin were 0.92 and 0.94, respectively.

Key words:GC-MS/MS; AOAC 2007.01;Polytrin-C 44 EC, dissipation kinetics, multi-residues analysis, Sweet lime orchard soils.

1. Introduction

After mango and banana, citrus fruits are the third most produced fruit in India. Over 1.04 million acres of land scattered through 26 states, it is grown [1]. Citrus fruits are infested by a wide variety of fungus and insects, which results in permanent harm and lower crop production. Undoubtedly the production of agricultural goods like citrus oranges is increased by the application of pesticides. Long-distance movement of pesticides through the air, soil, and water increases the likelihood that they will contaminate crops even if they are not treated. As a result, pesticide residues are regularly found in agricultural goods, which have an impact on the safety of humans and the quality of their food. Additionally, they pose a number of health hazards and negatively impact consumers[2]. The World Health Organization (WHO) says that about 3 million people get sick every year from being exposed to pesticides. Several public and private organisations throughout the world have been analysing pesticide residues in food and environmental samples for about 40 years. Yet, it is anticipated that contemporary residue monitoring methods would adapt to establish a system given the most recent advancements in agriculture. For laboratories to increase overall analytical quality and laboratory efficiency, new, quicker, and more effective analytical procedures must be implemented [3]. As demonstrated by the extensive literature recently published for fruits, vegetables[2], [4]–[7]and soil[8]–[12], gas chromatography combined with mass spectrometry (GC-MS/MS) is a very potent method for identifying and quantifying a wide range of thermally stable and unstable pesticides in complicated environmental matrices. Herbicide and pesticide analysis at trace levels is possible with tandem mass spectrometry (MS/MS), which has exceptional sensitivity and selectivity even when

interfering substances may share the same parent mass. GC-MS/MS, usually in combination with an ion trap device, is the best method for identifying and measuring substances. Most of the time, soils with a lot of clay or organic matter have high pesticide adhesion. In sandy soils, they are not as thoroughly absorbed. Environmental factors, particularly in agricultural soils with crop residues and nutrients, can have a substantial impact on the sorption and behaviour of pesticides [13]. A sample preparation should ideally be quick, simple, inexpensive, environmentally friendly, and yield clean extracts. Soxhlet extraction, single-drop microextraction, pressurised liquid extraction, microwave-assisted extraction, or supercritical fluid extraction, ultrasonic solvent extractions are just a few of the common traditional cleanup techniques. In some cases, SPE or SPME (solid-phase microextraction) is used as the final step in the cleanup process. The quick, easy, cheap, efficient, robust, and safe (QuEChERS) approach, which is based on ACN extraction, has shown to be very successful and has eliminated or replaced numerous difficult analytical processes frequently used in conventional methods. Moreover, it offers high quality findings with high sample throughput, little labour, low solvent and glassware consumption, and a low cost per sample of analysis [13], [14].

The examined pesticides display a wide range of physical/chemical features, such as acid-base characteristics, which significantly affect their water-acetonitrile partition. Also, as soil is a complex matrix, careful sample preparation is necessary for a consistent and accurate analysis. Hence, the selection of the buffer, the kind of solvent, and the shaking time were examined in order to establish the ideal extraction step. In truth, the official AOAC and EN techniques' buffered systems may maintain a pH constant of about 5. This pH level prevents base-sensitive insecticides from degrading while achieving good recoveries for acid-sensitive ones. [15], [16]. The AOAC method, type "A" d-SPE tubes, and 0.1% formic acid solution in acetonitrile, which meet the recovery parameters defined for mandarin oranges and grapefruit, recover more pesticides. Moreover, the reports show that type A d-SPE results in average recoveries that are almost 100% [2].

11 pesticides listed in the literature as soil contaminants were chosen for the current study. Profenofos and cypermethrin were most frequently employed to get rid of the Bollworm Complex, Aphids, Jassies, Whiteflies, and Thrips during the growth of sweet lime orchards in Andhra Pradesh. With the modified AOAC 2007.01 QuEChERS method for the extraction and d-SPE cleanup of pesticides in sandy loam soil [17] in lime orchards in the villages around Pulivendula in the Indian state of Andhra Pradesh, the goal of this work was to evaluate a group of 11 selected multiclass pesticides in sweet lime orchard soils. The present

research was also driven by the desire to find the dissipation kinetics of a Syngenta PolytrinC 44 EC insecticide (400 g/l profenofos and 40 g/l cypermethrin) in selected soils.

2. Materials & Methods.

2.1 Chemicals & Reagents:

Technical-grade standards of profenofos (94.30%) and cypermethrin (97.63%) were purchased from M/S Chromatopak Analytical Instrumentation Pvt. Ltd. in Mumbai. Sigma Aldrich in Bengaluru, Karnataka, sells the rest of the pesticides, fungicides, and herbicides. These include dichlorvos, dimethoate, malathion, metalaxyl, penconazole, hexaconazole, endosulfan, and dicofol (having $\geq 98\%$ purity). The physico characteristics of the pesticides chosen for the present investigation are shown in Figure 1. Extraction- solvents such as acetic acid, acetonitrile, acetone, and hexane, as well as QuEChERS extraction salts like sodium acetate, $MgSO_4$, and primary secondary amine (PSA), were supplied by local vendors. For a field experiment, a Syngenta PolytrinC 44 EC insecticide (400 g/l profenofos and 40 g/l cypermethrin) was bought at a local agricultural pesticide store in Pulivendula, Kadapa district, A.P.

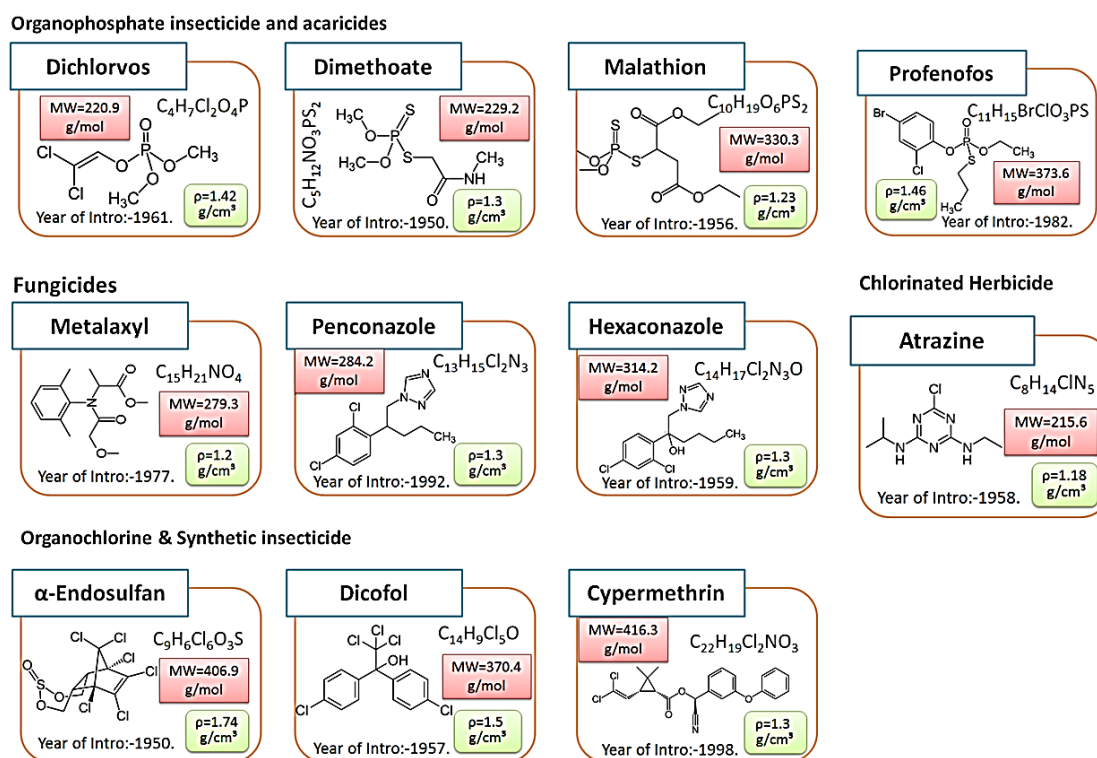


Figure 1. Physico Characteristics of pesticides used for the analysis.

2.2 Sampling & Sample Preparation:

Soil samples were collected from sandy loam soil in lime orchards in the villages around Pulivendula, in the Indian state of Andhra Pradesh. Syngenta PolytrinC 44 EC insecticide @ 2 ml/l was sprayed on sweet lime trees. About 3 kg of soil samples were taken from the same orchard at 0 day (within one hour), 1 day, 3 days, 5 days, and 10 days after spraying. These samples were placed in airtight containers and stored at -20 °C in a refrigerator for further analysis. During the sampling period, the ambient temperature ranged from 23 to 35 degrees Celsius, and the relative humidity ranged from 49 to 55 percent. Before the tenth-day sample collection, the orchards were watered once with drip irrigation. The research was conducted using standard agronomic practises advised by the regional agricultural office in Tirupati, Andhra Pradesh, during the hasta season (sweet lime blossoming season), which began in October 2022. Testing was done to figure out what kind of soil sample it was, and the results are reported in Table 1.

Table 1. Quality characteristics of collected soil samples

S.No	Parameter	Quantity
1	pH _{water}	8.2
2	Sand	520 g/Kg
3	Clay	282 g/Kg
4	Silt	90 g/Kg
5	Organic matter	108 g/Kg
6	Carbonate Ion(CO ₃ ²⁻)	0.20 meq/l
7	Bicarbonate Ion HCO ₃	5.72 meq/l
8	Chloride Ion Cl ⁻	35 meq/l
9	Na ⁺	70.28 meq/l
10	K ⁺	0.57 meq/l

2.3 Optimized conditions for GC-MS/MS analysis:

The GC-MS analyses were carried out using a GCMSTQ8040NX mass spectrometer from Shimadzu, Japan. And it is connected to a GC-2010 Plus outfitted with an AOC-20i autosampler and a 20S autoinjector. A 30-meter-long SX-Rxi-5 Sil MS capillary column with an internal diameter of 0.25 mm and a film thickness of 0.25 μm was used. Nitrogen served as the carrier gas at a constant pressure that was adjusted daily. A splitless GC glass liner with glass wool (Shimadzu, Japan) was placed in the inlet of the gas chromatograph. The electron energy of the EI for the mass spectrometer was 70 eV, and the injection port and transfer line were both 250 °C with a 1 ml/min column flow and a 3 ml/min purge flow. The GC oven was operated with the following temperature program: initial temperature of 60 °C hold for 1 min, ramped at 40 °C/min to 170 °C not hold, followed by a ramp of 10 °C/min to 310 °C hold for

3 min. The total run time was 20.75 min, the interface was kept at 250°C, the ion source at 230°C, and the M/Z (scan) range was between 50 and 500.

2.4 Preparation of standard solutions

Weighing 1000 ppm of each analyte in a volumetric flask (certified class "A") and dissolving it in a 15 mL mixture of acetone and hexane solvent produced the principal stock solutions for each specific pesticide standard. They were kept at -4 °C in the dark. The intermediate standard mixture was stored in the dark at -4 °C after being diluted to 100 ppm and 10 ppm. The stability of the standards was monitored throughout the entire investigation in accordance with SANTE recommendations. The calibration standards (10, 20, 50, 100, and 200 ppb) were produced via hexane serial dilution of the intermediate mixture. The appropriate volume of the pesticide-spiked combination was added to the BS (Blank Soil) matrix to extract and create the matrix-matched standard preparation.

2.5 Multiclass Residue extraction and clean-up

Extraction:

A modified QuEChERS AOAC 2007.01 acetate buffer technique was employed for multiclass pesticide residue analysis [3]. After air drying, soil samples were homogenised by passing them through a 2 mm sieve. After weighing 15 g of soil into a 50-mL Teflon centrifuge tube, it was extracted with a 15-mL mixture of acetonitrile containing 1% acetic acid and NaCl. The liquid mixture was shaken violently in a lab vortex for 1 minute after being shaken by hand for 15 seconds. Immediately after adding six grams of MgSO₄ and 1.5 grams of sodium acetate, the mixture was vortexed for 15 seconds. It was then centrifuged at 1500 rcf for 1 minute after being vigorously shaken for 1 minute in a lab vortex.

Clean-up–d-SPE

A 2mL d-SPE clean-up mini-tube containing 150 mg MgSO₄ and 50 mg PSA (primary secondary amine) per mL extract was filled with an aliquot of 1.8 mL from the top layer, which was then vortexed once more for 30 seconds before being centrifuged for 1 minute at 1500 rcf at room temperature. Utilize LVI (large-volume injection) to analyse and extract immediately from the prepared sample's top layer. The LVI has been solvent switched for toluene; it is not present in the extract. The residue was calculated using the equation 1 shown below:[18]

$$\text{Residue} \left(\frac{\mu\text{g}}{\text{gm}} \right) = \frac{\text{Area of sample}}{\text{Area of std}} \times \frac{\text{Conc. of std}}{\text{Weight of sample (g)}} \times \text{Dilution factor} \quad \text{-- Equ 1.}$$

3. Method development and validation

3.1 Method development:

Throughout the development of the method, linearity and recovery range, LOD, LOQ, accuracy, and precision were all validated. For an accurate analysis, the equipment needs to be calibrated. The capacity of an analytical process to generate test results that are directly proportional to the concentration of an analyte in the sample is known as "linearity." A standard regression analysis of the diagram of responses as a function of analyte concentration and a minimum of six linear concentrations are used to evaluate it. The minimal concentration was used to determine the LODs and LOQs for each pesticide, with a signal-to-noise (S/N) ratio of 3 and 10, respectively. Matrix-matched calibration standards were studied with four concentration matrix standards that had all 11 multiclass pesticide analytes at 10, 100, 150, and 200 ppb concentrations. Recovery studies with four spiked levels in three replicates were used to test the method's accuracy and precision. Generally speaking, acceptable pesticide recoveries have a relative standard deviation (RSD $n = 3$) of 15% and fall between 70 and 120%. The average retention periods of the calibration standards measured in the same analytical sequence matched the retention times of pesticides in sample extracts with a tolerance of ~0.1 min.

3.2 Dissipation kinetics of Profenofos & Cypermethrin residues in Soil samples

The calculation of the dissipation kinetics of pesticide residues was made possible by plotting the residue concentration v_s the number of days since spraying, and the curves of the best-fitting equations were then produced for the best coefficients of determination (R^2). It was discovered that the Profenofos and cypermithrin dissipation in soil followed an exponential relationship, which corresponded to the general first-order kinetic.[4]

$$R_t = R_0 e^{-kt} \text{ Equ. 2.}$$

Where R_0 is the initial residue concentration, R_t is the quantity of pesticide residues present at time t , and k denotes the pesticide's daily dissipation rate, which is constant.

3.3 Statistical analysis

The trend of Profenofos and cypermithrin dissipation over time in soils was described using the below logarithmic first order kinetics, a derivative of exponential decay. Also computed were the biological half-lives, or the amount of time needed for the original residue to degrade by one-half as shown in figure 4.

4. Results & Discussions:

4.1. Method development and validation

A modified AOAC 2007.01 (acetate buffered QuEChERS) method with d-SPE clean-up were developed for the detection of a group of four organophosphorus pesticides, including

Dichlorvos, Dimethoate, Malathion, and Profenofos; three triazole fungicides, including Metalaxyl, Penconazol, and Hexaconazol; two organochlorine pesticides, including Endosulfan and Dicofol; one synthetic pesticide, including Cypermethrin; and one chlorinated herbicide, including Atrazine. Tandem mass spectrometry with gas chromatographic separation (GC-MS/MS) was used to look for pesticide residues in the soil from Pulivendula sweet lime orchards. Figure 2 depicts the GC-MS/MS total ion chromatograms (TICs) of two standard mixture (all chemical) solutions at different concentrations: (a) 5 ppm and (b) 100 ppm. All pesticides were successfully isolated using the professional approach outlined above.

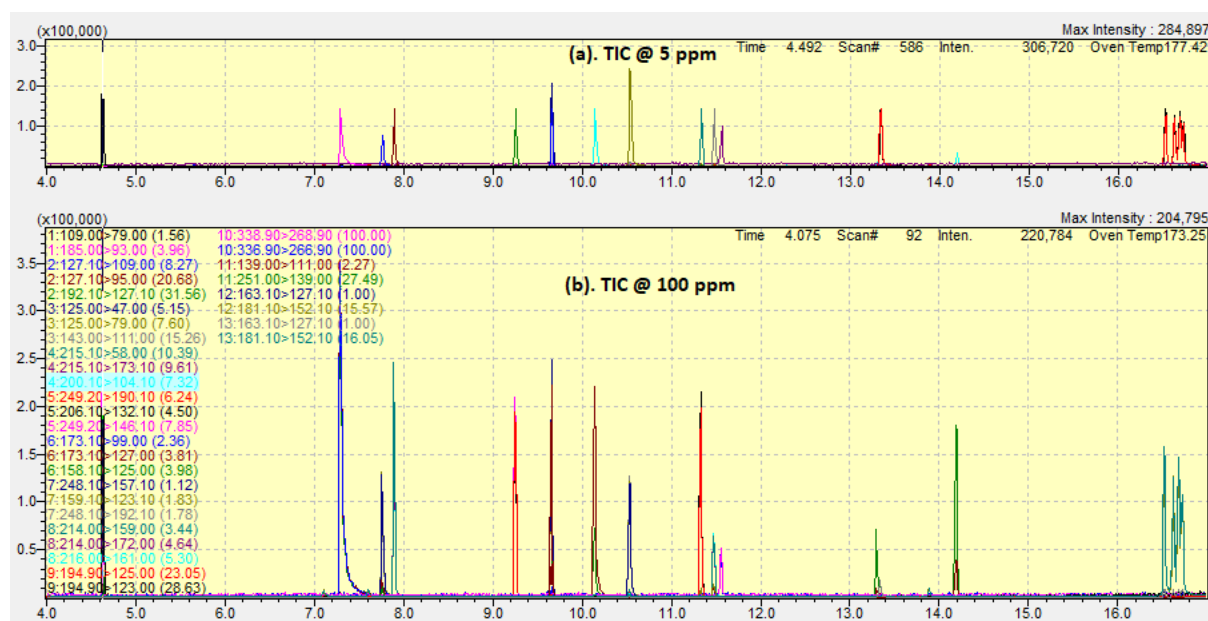


Figure 2. GC-MS/MS total ion chromatograms (TICs) of (a) a standard mixture (all compounds) solution at 5 ppm and (b) a standard mixture (all compounds) solution at 100 ppm.

The linearity of all pesticides was tested at 6 different concentrations of standard aliquot compounds at 10, 20, 50, 100, 150, and 200 ppb. All pesticides' MS responses were linear in the examined concentration range, with determination coefficients > 0.991. Tables 2 & 3 provide a summary of the calibration data for the pesticides under investigation.

The pesticides are listed in Table 2 along with information about their retention times, molecular weights (M/Z), regression equations, target and qualifier ions, and qualifier to target abundance ratios. The presence of pesticides was confirmed by finding the target and qualifier ions and figuring out the qualifier-to-target ratio. The suggested methods LOQ, LOD, R^2 , and RSD are listed in table 3.

Table 2: lists the retention time (R_i), mass (m/z), and reference ions (Ref. ions) of targeted compounds.

S. No	Name of the compound	R _t	m/z	Ref. ions
1	Dichlorvos	4.639	109.00>79.00	185.00>93.00
2	Dimethoate	7.799	125.00>47.00	125.00>79.00-143.00>111.00
3	Atrazine	7.934	215.10>58.00	215.10>173.10-200.10>104.10
4	Metalaxyl (Mefenoxam)	9.295	206.10>132.10	206.10>132.10-249.20>190.10
5	Malathion	9.703	173.10>99.00	173.10>127.00-158.10>125.00
6	Penconazole	10.513	248.10>157.10	159.10>123.10-248.10>192.10
7	alpha-Endosulfan	11.335	194.90>125.00	194.90>123.00
8	Hexaconazole	11.52	214.00>159.00	214.00>172.00-216.00>161.00
9	Profenofos	11.559	338.90>268.90	336.90>266.90
10	Dicofol	14.229	139.00>111.00	251.00>139.00
11	Cypermethrin-1	16.554	163.10>127.10	181.10>152.10
12	Cypermethrin-2	16.561	163.10>127.10	181.10>152.10
13	Cypermethrin-3	16.612	163.10>127.10	181.10>152.10
14	Cypermethrin-4	16.613	163.10>127.10	181.10>152.10

Table 3: List of Regression Equations, Linearity (R²), Relative Standard Deviations (RSD), Limit of Detection (LOD), and Limit of Quantification (LOQ) of Targeted Compounds

S. No	Name of the compound	Regression Equation	R ²	RSD %	LOD	LOQ
1	Dichlorvos	Y = (1028.42282)X + (-556.33162)	0.9924	6.897	3	10
2	Dimethoate	Y = (233.56501)X + (-653.21786)	0.992	13.66	3	10
3	Atrazine	Y = (185.76909)X + (-190.07597)	0.995	7.21	3	10
4	Metalaxyl (Mefenoxam)	Y = (369.76922)X + (-109.69743)	0.9956	5.46	3	10
5	Malathion	Y = (737.59667)X + (682.76508)	0.9804	11.47	3	10
6	Penconazole	Y = (1222.40273)X + (8892.75533)	0.97	24	3	10
7	alpha-Endosulfan	Y = (87.90080)X + (-64.08590)	0.998	4.58	3	10
8	Hexaconazole	Y = (636.46633)X + (251.65306)	0.97	11.45	3	10
9	Profenofos	Y = (442.988)X + (-198.1273)	0.9997	2.03	3	10
10	Dicofol	Y = (130.77484)X + (-376.09400)	0.98	20	3	10
11	Cypermethrin-1	Y = (40.95271)X + (162.13269)	0.991	14.67	3	10
12	Cypermethrin-2	Y = (40.95271)X + (162.13269)	0.991	14.67	3	10
13	Cypermethrin-3	Y = (40.95271)X + (162.13269)	0.991	14.67	3	10
14	Cypermethrin-4	Y = (40.95271)X + (162.13269)	0.991	14.67	3	10

Higher peak areas were achieved for the same pesticide dosage when standards were made by spiking blank soil samples with known concentrations of pesticides. This can be explained by the "matrix effect," which boosts the chromatographic response of some pesticides, especially organophosphorus chemicals, and enhances the transport of analytes from the injection port to the column. Several scholars have also noted this impact while analysing pesticides in other matrices [8], [12], [16], [19]. Hence, augmented blank samples were used in the assessment of pesticide residues. These pesticides, which belong to the most significant chemical pesticide families, are frequently applied to fruit crops. In fact,

all of these pesticides have been well studied in research that looks at how they work in different soils in India. [20].

By analysing a sample that had been spiked at 5 ppb, the reproducibility of our chromatographic procedure was assessed. An automated injector was used to administer the sample five times. The relative standard deviation (RSD) values for the peak areas, with the exception of dicofol and penconazole, ranged from 2.03% to 14.67% and are presented in Table 3.

The results of the pesticide mean recoveries are shown in Figure 3. Before extraction, the soil was fortified at 10, 100, 150, and 200 ppb by adding 2 mL of the corresponding working standard solution along with internal standards containing 150 mg of MgSO₄ and 50 mg of PSA (principal secondary amine). GC-MS/MS was used to analyse the extracts. Before extraction, the fortification solvent was allowed to evaporate from the fortified samples for 20 minutes. Three replicate samples were taken from each fortification level-spiked sample. With the exception of dicofol and penconazole, the majority of the target compounds satisfied the validation criteria, with mean recoveries ranging from 65 to 121% and RSDs ≤15%. The obtained recoveries of all pesticides are good when compared to other findings[8], [12], [16], [19].

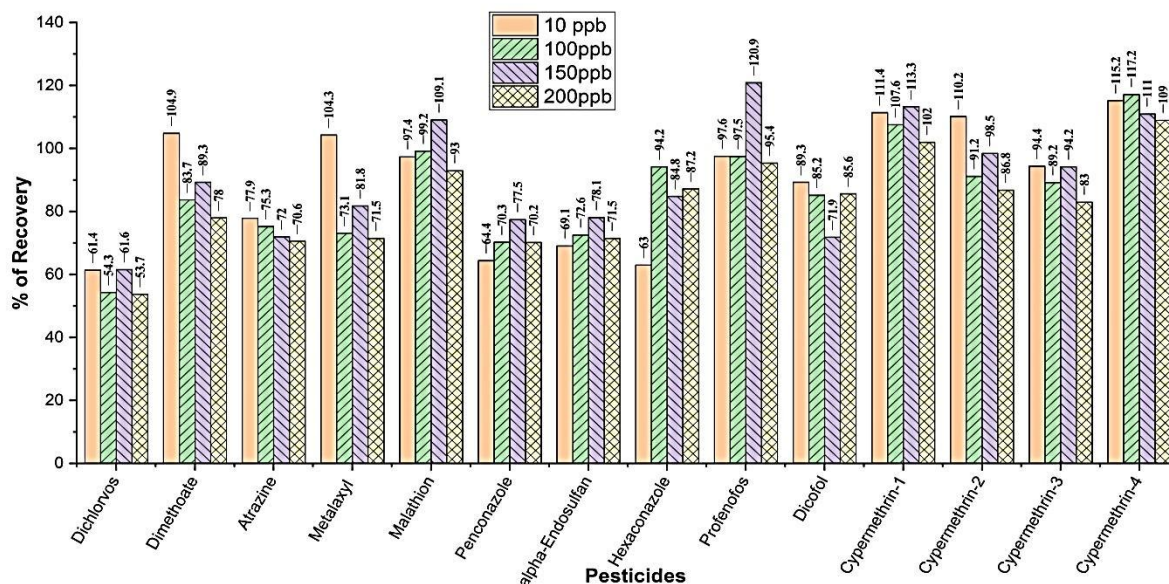


Figure 3, Recovery % at different concentrations of all pesticides

Real samples:- The developed method was applied to determine the dissipation rates of profenofos and cypermethrin in soil samples collected in a sweet lime orchard near

Pulivendula, India. The dissipation of profenofos and cypermethrin residues in soil followed first-order dissipation kinetics and is reported in Table 4. The residues of profenofos and cypermethrin on the zeroth-day sample were 0.915 ppm \pm 0.016 and 3.19 ppm \pm 0.13, respectively. Residues of profenofos dissipated to an extent of 78.25 percent after one day, showing residues of 0.199 ppm \pm 0.004. After one day, cypermethrin residues had dissipated to the extent of 48.74 percent, with residues of 1.67 ppm \pm 0.083. Finally, on the tenth day, both pesticide residues were found to be below the detection level (BDL). The correlation coefficients (R^2) for profenofos and cypermethrin were 0.92 and 0.94, respectively. Using equation 1 (SOP number: METH009.02), it was determined that the half-lives of profenofos and cypermethrin were 1.31 and 2.36 days, respectively. This insecticide's same behaviour was reported by (31). Depending on the formulation and the rate of application, the half-life values of cypermethrin ranged from 2.0 to 4.8 days. Similarly, depending on the rate of application, profenofos' half-life values ranged from 2.2 to 5.4 days. The earlier research that showed profenofos and cypermethrin rapidly degraded from hot pepper, sweet pepper, and eggplant, with half-lives of 1.84, 1.74, and 1.96 days, respectively, provide support for the current study. Using the pre-mix formulation of Polytrin-C, the half-life values on okra were 1.35 days [4]–[6], [21], [22]. Alkaline hydrolysis, which occurs when a pesticide's pH rises above 7, is a process that some pesticides can go through. At the approved amount of 400 g a.i./ha in the combi-mix formulation, profenofos residues of 0.220–0.27 mg/kg were found in soil; however, they stopped being detectable on the 10th day. At the suggested rate (40 g a.i./ha), cyclomethrin residues in soil were below the detection limit. Yet, the residues of individually applied cypermethrin were found in the soil on day 0 and disappeared from detection in 10 days [22].

Table 4. Dissipation studies of Profenofos and Cypermethrin

Interval	Profenofos Residue in ppm							Cypermethrin residue in ppm						
	R1	R2	R3	Mean	\pm SD	RSD%	Dissipation %	R1	R2	R3	Mean	\pm SD	RSD%	Dissipation %
0 day	0.916	0.930	0.898	0.915	0.016	1.74	00	3.32	3.06	3.18	3.19	0.130	4.08	00
1 day	0.194	0.199	0.203	0.199	0.004	2.01	78.25	1.62	1.76	1.63	1.67	0.083	4.67	48.74
3 day	0.178	0.181	0.173	0.177	0.004	2.25	80.65	1.42	1.39	1.33	1.38	0.048	3.32	56.73
5 day	0.052	0.050	0.054	0.052	0.002	3.84	94.31	0.35	0.37	0.37	0.37	0.014	3.17	88.36
10 day	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

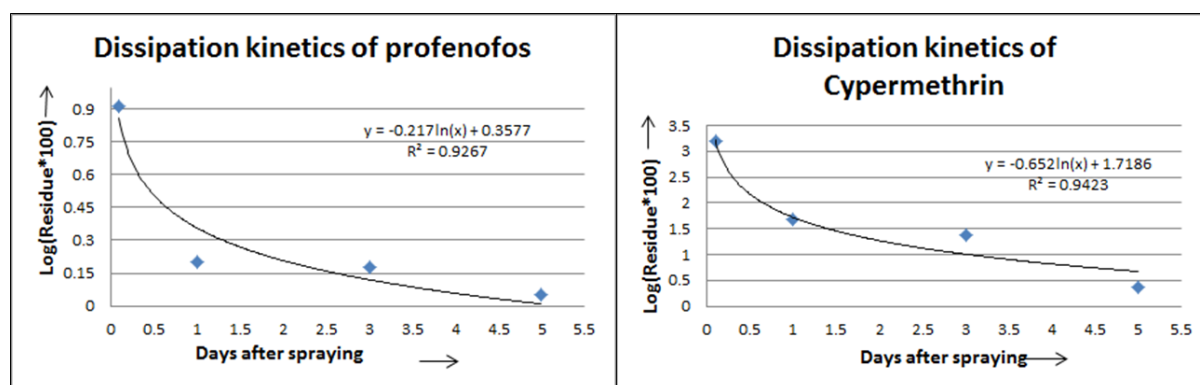


Figure 4. Dissipation kinetics of profenofos and cypermethrin in real soil samples

Conclusion:

In this study, 11 pesticides that are typically employed in agricultural operations have been extracted using a modified AOAC acetate buffer extraction and dSPE clean-up. Except for dicofol and penconazole, all pesticides reached the required recovery range of 65–121% with RSD values under 15% and correlation (r^2) scores greater than 0.991. The kinetics of Polytrin-C 44 EC (400 g/l profenofos and 40 g/l cypermethrin) pesticide degradation in soil from sweet lime orchards were also studied using the optimised multi-residue approach. The residues of profenofos and cypermethrin on the zeroth-day sample were 0.915 ppm \pm 0.016 and 3.19 ppm \pm 0.13, respectively. Finally, on the tenth day, both pesticide residues were found to be below the detection level (BDL). The correlation coefficients (R^2) for profenofos and cypermethrin were 0.92 and 0.94, respectively. The earlier research that showed profenofos and cypermethrin rapidly degraded from hot pepper, sweet pepper, and eggplant, with half-lives of 1.84, 1.74, and 1.96 days, respectively, provide support for the current study. Using the pre-mix formulation of Polytrin-C, the half-life values on okra were 1.35 days [4]–[6], [21], [22].

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