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Detoxification of Triazophos Pesticide Residues in Foxtail Millets (*Setaria Italica*) Using Mid-Infrared Rays

Umakanthan Thangaraju
Veterinary Surgeon, Gokulam Annadhan Temple Complex,
Plot no.: 1684, Meenavilakku-Meenakshipuram Road,
Anaikaraipatty Post, Bodinayakanur Taluk, Theni Dt,
Tamil Nadu, India - 625582

Madhu Mathi
Veterinary claims expert, Allianz Services Private Limited,
Technopark, Trivandrum, Kerala – 695581, India

ABSTRACT

Pesticide residues in agricultural products are currently inevitable and pose severe risks to human health and the environment. Present detoxification technologies for residues are less effective, not eco-friendly, reduce sensory attributes and nutrients of the agro products, and are uneconomical. To overcome this challenge to a certain extent, we developed a 2-6 µm mid-infrared generating atomizer, the mid-infrared was tried in the detoxification of pesticide viz. Triazophos. MIRGA accommodates water-based imbalance ionic solution. MIRGA spraying was performed externally over packaged (polythene >50 microns) foxtail millet (Setaria italica) mixed with different concentrations (5 to 10,000 ppm - 13 batches) of the commonly used pesticide Triazophos. The foraging behavior of fire ants was used as an indicator to evaluate triazophos toxicity. The foraging property was more significant in MIRGA-irradiated millet samples containing 5, 10, 50, and 100 ppm needed with 1-3 sprayings, 500-1000 ppm needed 2-5 sprayings, 2000 ppm needed 3 sprayings, 3000 ppm needed 2-4 sprayings, and 6000 ppm needed 4 or 5 sprayings than in non-irradiated (control) samples. As a result, we demonstrated the efficacy of 2–6 µm mid-IR detoxification. The 2-6 µm mid-infrared radiation generated by MIRGA was able to pass through the packaging material and interacted with the interior of foxtail millet. It was noted that foxtail millets sprayed with MIRGA containing 5 to 3000 ppm and 6000 ppm triazophos were eagerly consumed by ants. However, samples with 4000-5000 ppm and 7000-10,000 ppm were refused by the ants, while the blank control samples were consumed. The process of detoxification was studied by a variety of instrumentations and analytical investigations. The appearance of small peaks in the chromatogram data indicated a change in the components of the sample, resulting in the creation of new molecules that attracted ants more effectively. Two specific compounds identified post-spraying were 9,12-octadecadienoic acid (Z, Z) and 1-nonadecene, which explains the increased attractiveness of ants. The mid-IR radiation emitted during spraying led to the breakdown of some carbohydrates, releasing simpler sugars that are sweeter and naturally appealing to ants. The sprayed sample showed a fivefold increase in oleic acid content compared to the control sample, which may account for the reduced preference by ants. Furthermore, spraying induced alterations in various components such as

aliphatic protons, methyl groups, olefinic protons, and aromatic protons within the samples. The application of MIRGA on foxtail millet containing triazophos induced structural changes at the micron level, as evidenced by particle agglomeration and the disappearance of elongated structures. The MIRGA technology proves to be a safe, cost-efficient, and environmentally friendly method. This outcome also hints at the potential of MIRGA in detoxifying residues of other agricultural chemicals.

Keywords: MIRGA, 2-6 μm mid-IR, Foxtail millet, Pesticide residues, Triazophos, Degradation, Economy, Ecofriendly, Safe.

INTRODUCTION

Global crop losses due to pests, including insects, pathogens, and weeds, are estimated to be significant, with arthropods alone destroying 18-26% of annual crop production worldwide, valued at over $470 billion [1, 2, 3]. In developing countries, where future population growth is expected to be concentrated, losses are even higher, emphasizing the urgent need for precise estimation of food loss and waste to develop sustainable pest management strategies [2]. Crop pest infestations can have significant implications for food safety and security. Insect pests in stored grains can lead to reductions in protein and lipid content, affecting the quality of raw materials [4]. Thus, pesticides use plays a crucial role in combating pests to prevent significant crop losses, despite the widespread concern over pesticide residues in food and their potential adverse effects on human health.

Excessive use of pesticides, which remain as residues in agricultural products carries a health risk. The residues cause nausea, headaches, chronic neuro and respiratory symptoms, as well as cancer [5]. Children are more susceptible to such diseases [6, 7, 8]. Globally estimated maximum residue levels (MRLs) in agro harvest are now high, especially in developing countries where pesticides are used indiscriminately [9]. Pesticide contamination of surface and groundwater can be substantial even in organic agriculture areas. Prime importance should be given to the degradation/detoxification of residues. Traditionally washing, peeling, drying, cooking, salting, and addition of chemicals were practiced. However, it is well known that pesticide residues have a higher likelihood of persisting down the food chain, affecting the environment and consumer health. Also, even during food processing, residual pesticides are converted to more hazardous metabolic products than residues [10].

The impact of pesticides on human health is particularly concerning for vulnerable populations like children, pregnant women, and the elderly, who are more sensitive to the effects of these toxic substance. Therefore, while pesticides are essential for protecting crops from pests, it is crucial to prioritize human health by promoting safer alternatives and proper handling practices to minimize exposure and associated health risks. Currently, the scientific methods used for pesticide detoxification are chlorine dioxide solution, chlorine dioxide gas [11], electrical current and ultrasonication [12], electrolyzed water, chlorine dioxide, photocatalyst [13], and photochemical methods [14]. Recently ozone treatment has been relatively more advantageous than the other methods [10]. All these methods are not without associated limitations which include loss of sensory attributes and nutrition [15, 16] and risk [17]. As a result, there is an urgent need for more effective sustainable methods to degrade/detoxify pesticide residues to protect human health. As far as photodegradation is concerned, irradiation with gamma rays, ultraviolet, pulsed electric field, and ultrasound are used to degrade pesticide residues, but the ionizing nature poses a risk [10].

Although these methodologies offer a broad array of choices for the management of pesticide residues, they possess inherent constraints in terms of sophistication, application at the field level, operational intricacy, and cost implications. This necessitates a quest for more efficient and secure alternatives to maintain the intricate balance between pest control methodologies and the well-being of ecosystems. Hence, a balance approach that considers both the food safety and ecosystem services is crucial for ensuring sustainable pest management in the realm of agriculture. Consequently, we have opted for the utilization of the non-ionizing infrared spectrum, a technique commonly employed in both traditional and contemporary food processing practices. This type of radiation, constituting 66% of the solar radiation [18], presents a safer avenue for exploration.

Mid-infrared is a specific wavelength in the infrared spectrum. The frequency of all living entities, including humans, animals, and plants is in the mid-infrared range. The magnetic frequency of all living entities, including agro products, humans, animals, and plants, is in the mid-infrared spectrum. Mid-infrared radiation is biologically safe and can penetrate most intervening media. To be short, the majority of earthly molecules' vibrational frequencies are in the mid-infrared region [19]. And also, pesticides observe mid-infrared and cause changes in the chemical bond.

The Foxtail millets were contaminated with varying concentrations of Triazophos ranging from 5 to 10000 ppm. The MIRGA generated mid-infrared ray was applied over the pesticide (Triazophos) contaminated foxtail millet for detoxification. The most common foraging preference of trained ants was used as an indicator of pesticide residue detoxification. MIRGA technology in found to be more advantageous than the existing methods (detailed in Result and Discussion section).

Therefore, this study aimed to detoxify the pesticide residues present in agricultural products by using mid-infrared radiation. The irradiation caused the chemical compound transformation, was analyzed by liquid chromatography-mass spectrometry (LC-MS) and Gas chromatography-mass spectrometry (GC–MS). The chemical bond changes were determined by Fourier transform infrared spectroscopy (FTIR), and Proton nuclear magnetic resonance (NMR). The structural changes were analyzed by Powder X-ray diffraction (PXRD). The particle configuration changes were detected by Transmission electron microscopy (TEM). Overall, MIRGA technology, due to its effective, noninvasive nature and easy application, showcases its broad applicability in industrial settings to detoxify pesticides residues in tons and tons of agroproducts ensuring the consumers health and acceptance.

MATERIALS AND METHODS

Preparation of Samples

Triazophos (40% EC; Crop Chemical India Ltd.) was purchased from a local market. Triazophos (O, O-diethyl-O-1-phenyl-1H-1,2,4-triazol-3-yl phosphorothioate) is a broad-spectrum systemic insecticide and acaricide organophosphate compound that is extensively used in agricultural practices throughout the world [20]. Different concentrations of triazophos solution were prepared by adding distilled water. The concentrations tested ranged from 5 ppm to 10,000 ppm.

Foxtail millets were purchased from a local market and packed in virgin polythene (>50 microns) bags weighing 50 g each. A batch containing 7 such bags was prepared using millets from the same source. The first millet packet contained only millets and served as a blank control, while the second millet packet contained a specific concentration of triazophos (eg. 5 ppm or 10 ppm and so on) and served as a positive control. The remaining 5 millet bags were numbered 1–5 (for trials), and a specific concentration (ppm) of triazophos was added from the stock solution. The bags were left undisturbed for 30 minutes to allow the millets to absorb the triazophos, then the 7 bags were heat-sealed. Similarly, 13 batches with 7 bags each were prepared, with triazophos concentrations ranging from 5 ppm to 10000 ppm (5, 10, 50, 100, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000, and 10,000 ppm). For each batch, a negative control containing only the Triazophos at a concentration (eg. 5 ppm or 10 ppm and so on) the same as its batch was also prepared and tested.

Application of Mid-IR Generating Atomizer

MIRGA (mid-IR generating atomizer) (patent no. 401387) is a 20-mL capacity polypropylene plastic atomizer containing an inorganic water-based solution (containing approximately two sextillion cations and three sextillion anions). Specifications of MIRGA (MIRGA) and the process of generating mid-IR while spraying MIRGA are described by Umakanthan et al. [21, 22, 23] (Supplementary Figure F1).

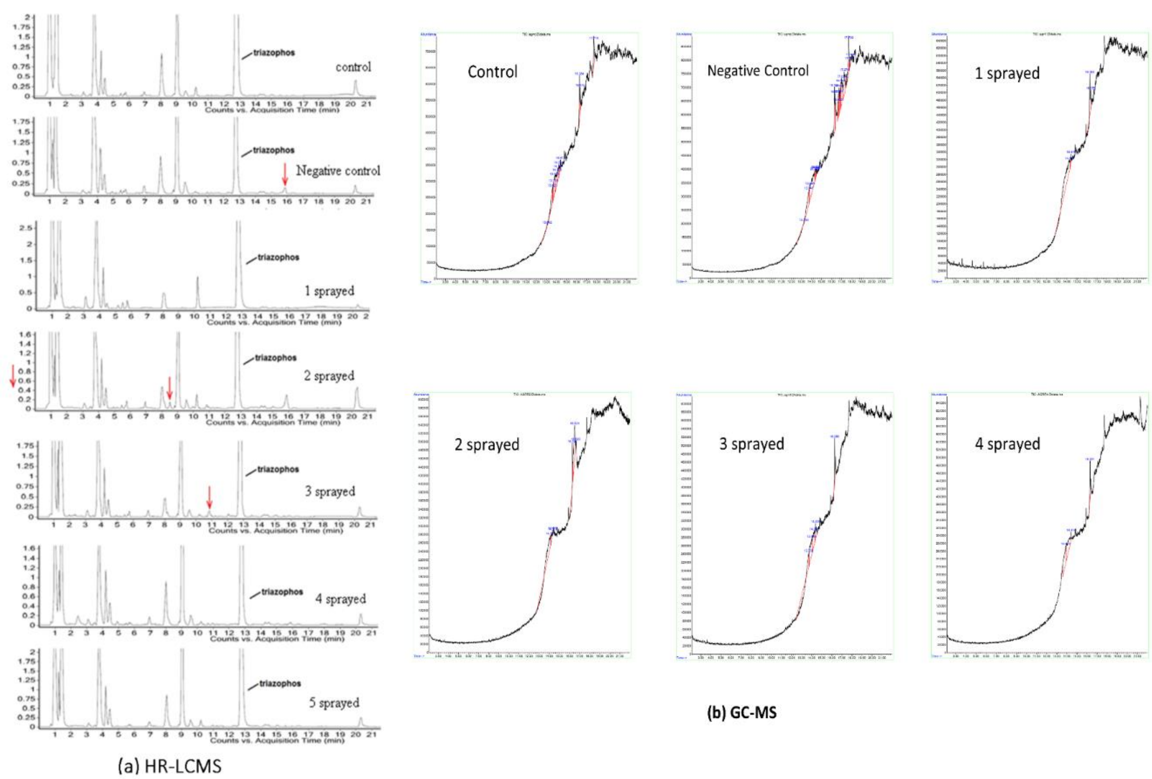


Figure 1: Instrumentation spectra images of agrochemical samples (a) HR-LCMS, (b) GC–MS

Each spray is designed to generate 2-6 µm mid-IR depending on the plunger pressure applied by the user [21] (supplementary Figure F2; data D1). Every time, spraying emits 0.06 ml, which contains approximately seven quintillion cations and eleven quintillion anions.

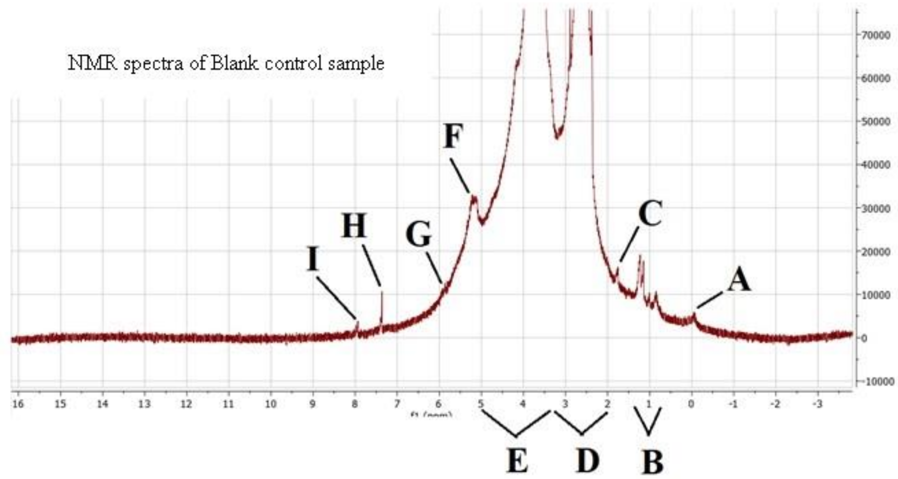


Figure 2: Regions on the NMR spectra of the blank control sample

To and fro motion of the particles is called oscillatory or vibrational motion. The emitted anions and cations while spraying generates the 2-6 µm mid-IR energy through to and fro oscillation in the following ways: i) repulsive energy generated while collision between anions; ii) repulsive energy generated while collision between cations; iii) attractive energy generated while collision between; iv) energy generated while the former two repulsive energies repel with each other; and v) energy generated while the repelling ions strike back the orifice of MIRGA sprayer at a particular pressure.

The inorganic compounds used in generating the mid-IR are a perspective for biomedical applications [24, 25]. It is also a new synthesis method for preparing functional materials (2-6 µm mid-IR) [26, 27]. It is well known that the combination of different compounds, which have excellent electronic properties, leads to new composite materials, which have attracted great technological interest in recent years [28, 29].

MIRGA spraying was performed from a distance of 0.25–0.50 meters toward the packaged (polythene) foxtail millet trial samples. This distance is essential for the solution to form ion clouds, associated oscillations, and 2-6 µm mid-IR generation; closer spraying did not generate the mid-IR. Trial packets numbered 1, 2, 3, 4, and 5 received 1, 2, 3, 4, and 5 MIRGA sprayings, respectively.

Determination of Ant Foraging Activity

Fire ants *Solenopsis geminata* (Fabricius) locally found in Sattur, Virudhunagar District, Tamil Nadu, India [30] were used in this study, as they were observed eagerly to eat foxtail millets. Ants are biological indicators [31], ecosystem engineers, and keystone species [32]. Any adverse behavioral effects due to agrochemical exposure have an impact not only on ants but also on other sympatric species [33].

Three months before the ant foraging trial, we selected different ant tunnels within a 2 km radius. Once per week at the brim of the ant tunnel, in virgin polythene sheets foxtail millet was placed. In the subsequent week, the foxtail millet mixed with Triazophos was placed in the same tunnel. Every alternate week, foxtail millet mixed with different concentrations of triazophos was placed at the brim of every tunnel of ants. The ants were thus trained to forage only on foxtail millet without triazophos. During the trial study, after MIRGA spraying, the trial and control packets of a batch were then opened, and 2.5 g millet was removed, kept in virgin polythene sheets, and placed around a fire ant tunnel. Enough time was allowed for fire ants to forage. Depending on foraging behavior preference, the samples were ranked as 1 – most preferred; 2 – highly preferred; 3 – moderately preferred, 4 – less preferred; 5 – least preferred; and 6 – refused. The same procedure was followed in all 13 batches of millets contaminated with different triazophos concentrations (5 to 10000 ppm). We hypothesized that ant foraging attraction to foxtail millet will decrease with increasing concentrations of triazophos residue. Thus, according to the degree of detoxification, the MIRGA-sprayed millets would attract foraging ants.

Instrumental Analysis

The following instruments were employed to study the changes caused by MIRGA spraying in the prepared millet samples that led to different foraging behaviors of ants. *(Details of instruments available in supplementary text T1 and their raw data in supplementary data D2)*

LC-MS Analysis:

Samples were ground and solved in methanol before the injection into the HPLC-MS system protocol as described by Khan, I. U., et al. [34]. The chemical compound transformation of sample was determined by LC-MS: from Agilent Technologies, USA. 1290 Infinity UHPLC System, 1260 Infinity Nano HPLC with Chipcube, 6550 iFunnel Q-TOFs. Column details: Hypersil GOLD C18 100 x 2.1 mm-3 micron. The millet samples were collected after MIGRA spraying and analyzed in an Agilent LC-MS Q-TOF system in ESI mode. Samples were injected into the MS with the mobile phase, ACN: 5 mM ammonium acetate (80:20), at a flow rate of 0.3 mL/min. The mass spectra were recorded in negative ion and positive mode from 50 to 1000 m/z at a capillary voltage and fragmentor voltage of 4500 and 200 V, respectively. The source gas temperature was 325°C, and the collision energy used was 5 V. After data acquisition, an extracted ion chromatogram was generated for all the samples.

GC–MS Analysis:

Samples were ground and solved in methanol before the injection into the HPLC-MS system protocol as described by Khan, I. U., et al. [34]. The chemical compound transformation of sample was determined by GC–MS: Agilent technologies, 7820A GC system, 5977E MSD, Column DB-5 MS, Detector MS, Flow rate 1.2, Carrier gas Helium, Solvent DMSO. The oven temperature started at 100°C to 200°C at 5°C/min and then ramped at 10°C/min to 270°C with a hold time of 6 minutes for conditioning purposes. The temperatures for the injectors and detectors were 250 and 300°C, respectively. The spectra were stored from 50 to 100 m/z, and peaks were identified using an in-built library of software.

FTIR Analysis:

Chemical bond changes were found using FTIR spectra of tested millet flours.

FTIR spectrometer: IR AFFINITY I – FTIR Spectrophotometer, FTIR 7600, Shimadzu.

1H-NMR Analysis:

The samples used in liquid NMR were prepared by solving the ground solid samples in Dimethyl sulfoxide (DMSO). Proton resonances mapped using proton nuclear magnetic resonance (1H-NMR): A Bruker AV-500 high-resolution multinuclear FT-NMR spectrometer equipped with a 5 mm rotor was used for 1H and 13C measurements. The number of scans varied from 8 to 64 for 1H measurements and 256-1024 for ^{13}C measurements. $CDCl^3$ or DMSO-d6 was used according to the sample's solubility. Bruker TOPSPIN software was used for integration and chemical shift calculations.

PXRD Analysis:

Structural changes of treated samples were ground and measured by PXRD: XRD diffractometer (powder) from Philips Xpert MPD Range (2θ): 3° to 136°; X-ray tube: Cu; JCPDF database; 2θ vs intensity plots/X-ray diffractograms. Source: Cu target X-ray tube. X-ray Power: 2 kW. Detector: Xe-filled counterplate or proportional detector. Software: JCPDF database for powder diffractometry. Goniometer. Operation Modes: Vertical & Horizontal. Accuracy: ±0.0025. 2° θ. Measurement range: from 30 to 136°. Diffractometer radius: from 130 to 230 m.

Transmission Electron Microscopy (TEM) Analysis

Particle configuration changes detected with transmission electron microscopy (TEM): An extremely small amount of material is suspended in a water/ethanol mixture (just enough to obtain a slightly turbid solution). The solution was homogenized using an ultrasonicator to disperse the particles, and a drop of the solution was then removed and drop cast on carbon-coated grids of 200 mesh where the grid was dried and fixed in the specimen holder. Instrument Make: Jeol Model JM 2100.

RESULTS

Foraging Behavior of Ants

The 2-6 μm mid-IR generated from MIRGA penetrated the intervening packaging material and acted on the inside foxtail millet. It was observed that MIRGA-sprayed foxtail millets with 5 to 3000 ppm triazophos and 6000 ppm were eagerly foraged by the ants. The 4000-5000 ppm and 7000-10,000 ppm samples were refused by the ants, but the blank controls were foraged by the ants. Understanding the cause of refusal behavior to 4000 and 5000 ppm but showing acceptance of 6000 ppm triazophos concentration is under investigation. (Table 1).

Table 1: Scoring the foxtail millet samples contaminated with triazophos based on the foraging behavior of fire ants

Batch	Pesticide ppm	Blank control (Only Millets)	Positive control (Millets + Triazophos) (Non-sprayed)	Rank* – Trial bags					Negative control (Only Triazophos)
				1 sprayed	2 sprayed	3 sprayed	4 sprayed	5 sprayed	
I	5	2	2	1	2	5	3	4	6
II	10	2	2	1	2	5	4	3	6
III	50	1	3	3	1	2	4	5	6

IV	100	2	2	3	1	2	4	5	6
V	500	1	2	4	2	3	4	5	6
VI	1000	1	3	5	2	5	4	1	6
VII	2000	2	5	5	5	1	3	4	6
VIII	3000	5	5	5	2	4	1	3	6
IX	4000	1	6	6	6	6	6	6	6
X	5000	1	6	6	6	6	6	6	6
XI	6000	2	6	5	4	3	1	2	6
XII	7000	1	6	6	6	6	6	6	6
XIII	10000	1	6	6	6	6	6	6	6

*Ranking score: 1 – most preferred; 2 – highly preferred; 3 – moderately preferred, 4 – less preferred; 5 – least preferred; 6 – refused

In this context to date, study showed that the 6000 ppm Triazophos 4 and 5 times sprayed samples showed some changes in lipid fraction and formation of sweeter sugars. These byproducts should have increased the ant foraging behavior. Interestingly these byproducts were not found in 4000-5000 ppm samples.

Control and trial samples were subjected to instrumentation tests, and their results were compared.

Instrumentation Results

HR-LCMS of Foxtail Millets Containing 2000 ppm Triazophos:

The presence of triazophos is expected to exert a repellent effect on the ants, as observed in the positive control sample. A lower number of MIRGA sprayings did not affect the toxic effect of triazophos since the ants showed a very low or null preference toward the millet in the 1 and 2 sprayed samples. However, a large change occurred in the 3 sprayed samples, where the foraging preference increased remarkably, which was related to the loss of triazophos toxicity.

The control sample (foxtail millet with 2000 ppm triazophos) (non-sprayed) contained dexpanthenol, meperidine acid, furegrelate, dihydrodeoxy streptomycin, albendazole (II), etc. The molecular masses detected for these compounds were in the range of 200-400 Daltons. The positive control contained millets and triazophos, and compounds such as betaxolol, ticlopidine, convallatoxin, and leukotriene F4 were present in this sample. This is correlated with very low or no preference for ant foraging.

One sprayed sample: Miglitol, pantothenic acid, histidinal, and dinorpromazine resulted in a major peak, which was not present in the control and thus attributed to being the reason for the low preference for ant foraging in this sample.

Two sprayed samples showed unique peaks of monoethylglycylxylidide (MEGX), monapterin, etc. The tri-peptide of Ser-Gly-Glu was seen in this sample compared to the control. These changes observed in this sample are responsible for the low preference for ant foraging.

Three sprayed samples were most favorable for ant foraging, in which the unique compounds 1-phenylbiguanide, sietenine, and hydroxytinidazole were found, though tri-peptide of Ser-Gly-Glu was also observed in this sample.

Four sprayed samples showed some peaks common to the control and positive control. Albendazole (II) was present in the control and 4 sprayed samples, while Convallatoxin and Leukotriene F4 were present in the positive control as well as in the 4 sprayed samples. This sample was less preferred by ants.

Five sprayed samples showed many unique peaks, such as the ketamine metabolite, metaproterenol 3-O-sulfate, and p-[N-propyl-N-(2 carboxyethyl)sulfamoyl]benzene. These compounds have played a role in the moderate preference for ant foraging. (Figure 1 (a); Supplementary Table L1)

Chromatograms and mass spectra results showed the presence of triazophos in every sample, with some variations in the peak intensity. The less intense peak of triazophos is observed in the 3-sprayed sample, which is interpreted as the ant's highest preference. This indicated some degradation or loss of the triazophos toxicity that occurred due to three cycles of MIRGA spraying. Concurrently, in the 3 sprayed samples, a few small peaks appeared in the chromatogram measurements, which indicated a transformation of the sample components, giving rise to new molecules [35] that exerted a more attraction on ants. More than 3 sprayings degraded some of these molecules, as few peaks were less intense in the 4 and 5 sprayed samples, and thus, the ants' preference was found to be reduced in those samples when compared to the 3 sprayed samples.

GC–MS of Millets Containing 2000 ppm Triazophos:

The control foxtail millet sample contaminated with 2000 ppm triazophos contained 1-nonadecene, cycloeicosane, 1,19-icosadiene, fatty acids such as oleic acid, and 9-octadecenoic acid. The positive control contained millets and triazophos, and 13-methyl-Z-14-nonacosene was a new and major peak that was correlated with very low or no preference for ant foraging.

One sprayed sample: Cis-9-hexadecenal was the major peak, and the content of this peak was nearly five times higher than that of the control. This is the reason for the low preference for ant foraging. Two sprayed samples showed a unique peak of hexahydropyridine, 1-methyl-4-[4,5-dihydroxyphenyl]. The oleic acid content in this sample was five times higher than that in the control and is inferred to be responsible for the low preference for ant foraging. The unique compounds found after 3 spraying were 9,12-octadecadienoic acid (Z, Z) and 1-nonadecene which could be the reason most favorable for ant foraging.

Four sprayed sample had the highest amount of oleic acid and some unique peaks, such as 1,2-benzothiazole, 3-(hexahydro-1H-azepin-1-yl), and 1,1-dioxide, which consequently resulted in a moderate preference for ant foraging. (Figure 1 (b)) (Table 2)

Table 2: GC–MS spectra analysis

R.T. (Min)	Name of Compound	% Area Present in each sample						
		Control	Positive control	1 sprayed	2 sprayed	3 sprayed	4 sprayed	Remarks
13.622	Oleic Acid	14.58	4.11	0.0	0.0	0.0	**43.61**	The most abundant

								peak in 4 sprayed
13.717	1-Nonadecene	**8.04**	0.0	0.0	0.0	0.0	0.0	Unique peak in control
13.74	Cyclohexane, 1-(1,5-dimethylhexyl)-4-(4-methylpentyl)	0.0	10.60	0.0	0.0	0.0	0.0	
13.821	Cycloeicosane	**13.58**	0.0	0.0	0.0	0.0	0.0	Unique peak in control
13.991	9,12-Octadecadienoic acid (Z, Z)-	0.0	0.0	0.0	0.0	**58.68**	0.0	The most abundant peak in 3 sprayed
14.076	cis-9-Hexadecenal	15.63	0.0	**72.78**	0.0	0.0	0.0	The most abundant peak in 1 sprayed
14.180	1,19-Eicosadiene	5.49	0.0	0.0	0.0	0.0	0.0	
14.246	Oleic Acid	5.68	0.0	7.36	25.17	0.0	0.0	
14.313	7-Pentadecyne	0.0	16.95	0.0	0.0	0.0	0.0	
14.407	Oleic Acid	3.60	2.00	0.0	9.77	38.96	0.0	
14.407	9,12-Octadecadienoic acid (Z, Z)-	0.0	0.0	0.0	0.0	20.52	0.0	
14.417	1,2-Benzisothiazole, 3-(hexahydro-1H-azepin-1-yl)-, 1,1-dioxide	0.0	0.0	0.0	0.0	0.0	**43.48**	The second most abundant peak in 4 sprayed
16.279	7-Pentadecyne	**14.40**	0.0	0.0	0.0	0.0	0.0	Unique peak in control
16.279	p-Menth-8(10)-en-9-ol, cis-	0.0	0.0	11.96	0.0	0.0	0.0	
16.289	Oleyl alcohol, heptafluorobutyrate	0.0	8.41	0.0	0.0	0.0	0.0	
16.289	1-Nonadecene	0.0	0.0	0.0	0.0	21.16	0.0	
16.374	6-Octadecenoic acid, (Z)-	6.65	0.0	0.0	5.37	0.0	0.0	
16.374	Oleyl alcohol, heptafluorobutyrate	0.0	8.45	0.0	0.0	0.0	0.0	
16.535	Hexahydropyridine, 1-methyl-4-[4,5-dihydroxyphenyl]-	0.0	0.0	0.0	**58.07**	0.0	0.0	The most abundant peak in 2 sprayed
16.620	3-Eicosene, (E)	0.0	5.17	7.90	0.0	0.0	0.0	
16.752	13-Methyl-Z-14-nonacosene	0.0	**17.23**	0.0	0.0	0.0	0.0	The most abundant peak in positive control
17.717	9-Octadecenoic acid,	**12.85**	0.0	0.0	0.0	0.0	0.0	Unique

	(E)-							peak in control
17.272	1-Bromo-11-iodoundecane	0.0	10.41	0.0	0.0	0.0	0.0	
17.707	22-Tricosenoate	0.0	11.53	0.0	0.0	0.0	0.0	

In the 4-sprayed sample, the oleic acid content increased from 14% to 43%, and a new peak of 9,12-octadecadienoic acid (58% increment) was observed.

In the literature, some compounds are described to be responsible for ant attraction in grains and plants. Some works have pointed out lipid compounds such as diglycerides. These kinds of compounds can be present in the samples, as they are methanol soluble. MIRGA spraying affected the nature of these compounds, transforming them into molecules with a lower or higher ant attraction potential. This, together with the degradation or loss of pesticide potency upon MIRGA spraying, supported our results observed for these samples.

Proton NMR of Millets Containing 2000 ppm Triazophos:

The regions on the NMR spectra of the control sample are shown in Figure 2. These regions and their general assignments are summarized in Table 3a. Table 3b provides the integral values of the peaks.

The spectra showed slight differences depending on the sample observed. For example, comparing the NMR spectrum of 1 sprayed sample with those of the control and positive control samples, some signals appeared at 4.7 ppm and between 5.2 and 5.7 ppm. These peaks were still observed in the 2, 3, 4, and 5 sprayed samples. Additionally, a peak at 8.2 ppm was observed only in the spectrum of the 2 sprayed samples. These observations indicate that MIRGA spraying involves the transformation of some of the components present in the samples. There were also some variations in the integral values, which meant that the concentration of some components was modified upon spraying. (Figure 3)

Table 3a: Summary of the regions and assignments of NMR spectra

Code	Chemical shift (ppm)	Assignment
A	0	Aliphatic protons (upfield by the effect of other groups)
B	0.75-1.40	Methyl groups
C	1.75	Aliphatic protons
D	2.00-3.20	Aliphatic protons next to other chemical groups (OH, C=O…)
E	3.20-5.00	Olefinic protons
F	5.00-5.50	Olefinic protons
G	5.90-6.00	Aromatic protons
H	7.40	Aromatic protons
I	8.00-8.20	Aromatic protons

Table 3b: Integral values of the peaks in NMR spectra

Code	Chemical shift (ppm)	Integral values of peaks						
		Blank control	Positive control	1 sprayed	2 sprayed	3 sprayed	4 sprayed	5 sprayed

				sample	sample	sample	sample	sample
A	0	0.0057	0.0014	0.002	0.0035	0.0067	< 0.0001	0.0067
B	0.75-1.40	0.024	0.0221	0.0085	0.0124	0.0177	0.0051	0.0173
C	1.75	0.0113	0.003	0.0009	0.0053	0.0079	< 0.0001	0.0087
D	2.00-3.20	1	1	1	1	1	1	1
E	3.20-5.00	1.23	1.41	1.23	0.97	0.97	1.78	0.96
F	5.00-5.50	0.0774	0.0342	0.0025	0.0009	0.0018	0.0563	0.0159
G	5.90-6.00	-	-	0.0012	0.0004	0.0006	0.0172	0.0059
H	7.4	0.0027	0.003	0.0011	0.0009	0.001	0.0062	0.0021
I	8.00-8.20	0.0013	0.0006	0.0005	0.0005	0.0004	0.0003	0.0006

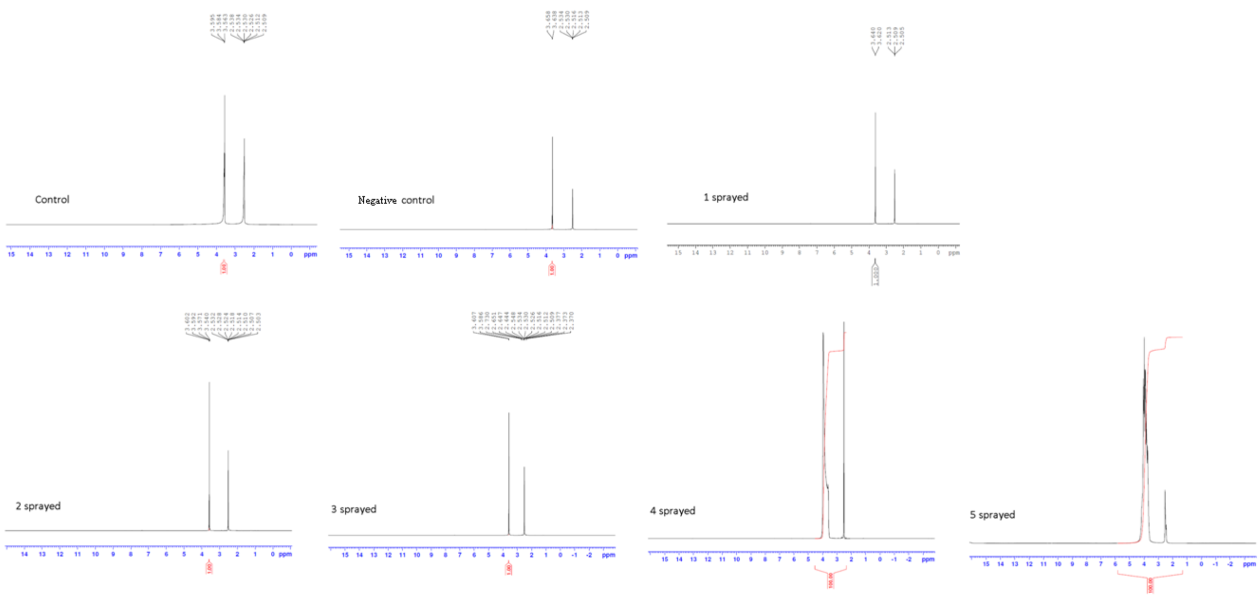


Figure 3: Instrumentation spectra images of agrochemical samples – 1H-NMR

Spraying caused a modification in the components summarized in Table 3a, such as aliphatic protons, methyl groups, olefinic protons, and aromatic protons in the samples. 1 and 2 sprayed samples are not preferred by ants because Triazophos is present and spraying did not affect their integrity yet. However, in 3 sprayed samples, the mid-IR had degraded triazophos; hence, the attractive potential of ants was recovered. Successive spraying led to the degradation of the molecules responsible for the ants' reduced attraction in 4 and 5 sprayed samples.

FTIR of Millets Containing 2000 ppm Triazophos:

The peaks in the FTIR spectra of the control sample are shown in Figure 4. The FTIR spectra from all the samples were quite similar in the number and position of the observed bands and peaks. In this study, with triazophos-contaminated foxtail millets, variation between samples is essentially found in the values of transmittance, which is directly related to the concentration of the compounds originating from those bands and peaks. The main observed bands in all the spectra are 3700-3000 cm^{-1} for O-H and N-H stretching, 3000-2750 cm^{-1} for C-H stretching, 1775-1575 cm^{-1} for C=O stretching, 1450-1250 cm^{-1} for C-N and C-O stretching and 1175-975 cm^{-1} for C-O stretching. For each observed band, samples were classified as a function of the magnitude of transmittance (or absorption), as reported in Table 4.

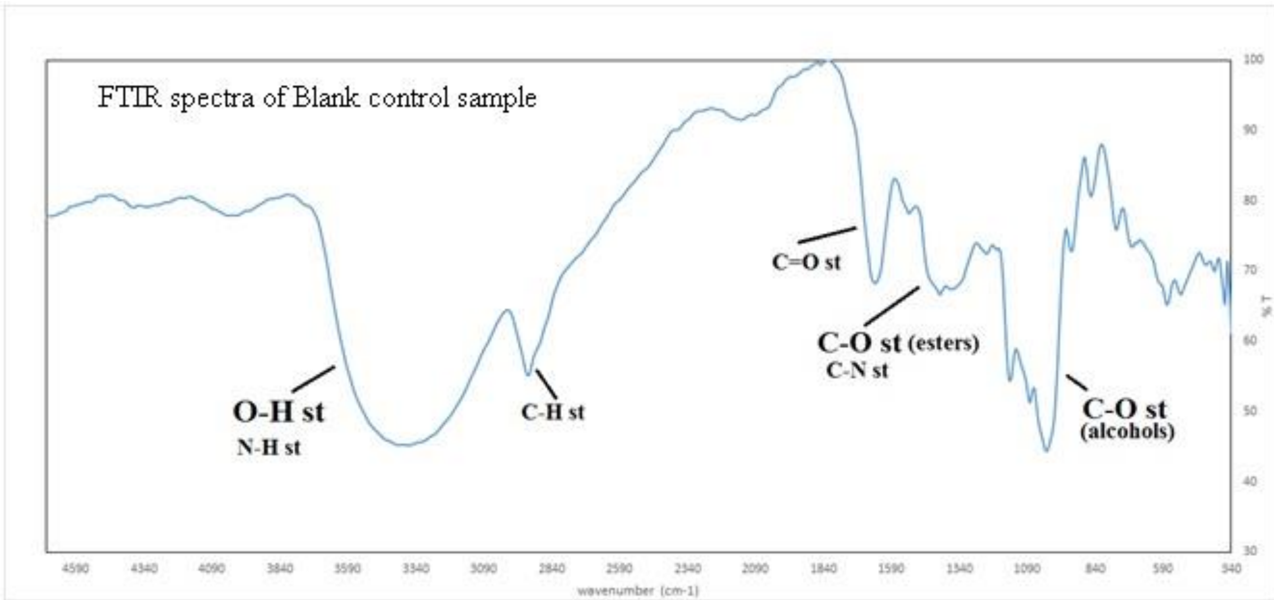


Figure 4: Peaks on the FTIR spectra of the blank control sample

Table 4: Samples in the order of magnitude of transmittance and absorption from FTIR bands

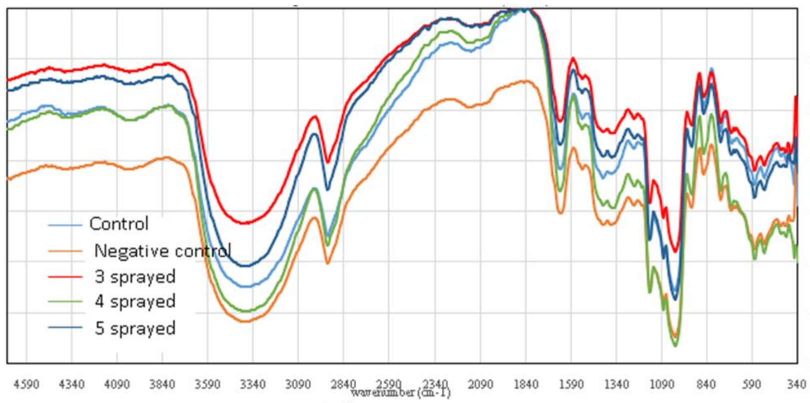
Band (position in cm^{-1})	% transmittance	Absorption
3700-3000 cm^{-1}	Positive control > 2 sprayed > 4 sprayed ≈ 1 sprayed> Control> 5 sprayed >> 3 sprayed	3 sprayed >> 5 sprayed > Control> 1 sprayed≈ 4 sprayed > 2 sprayed > Positive control
3000-2750 cm^{-1}	Positive control> 1 sprayed ≈ 4 sprayed > Control> 2 sprayed >> 5 sprayed>> 3 sprayed	3 sprayed >> 5 sprayed >> 2 sprayed > Control> 4 sprayed ≈ 1 sprayed > Positive control
1775-1575 cm^{-1}	Positive control > 1 sprayed> 4 sprayed > 2 sprayed > Control>> 5 sprayed>> 3 sprayed	3 sprayed >> 5 sprayed>> Control> 2 sprayed > 4 sprayed> 1 sprayed > Positive control
1450-1250 cm^{-1}	1 sprayed ≈ Positive control> 4 sprayed> 2 sprayed > Control> 5 sprayed> 3 sprayed	3 sprayed> 5 sprayed> Control> 2 sprayed > 4 sprayed > Positive control ≈ 1 sprayed
1175-975 cm^{-1}	1 sprayed < 2 sprayed ≈ 4 sprayed ≈ Positive control >> 5 sprayed ≈ Control>> 3 sprayed	3 sprayed >> Control ≈ 5 sprayed >> Positive control ≈ 4 sprayed ≈ 2 sprayed> 1 sprayed

A comparison between the control and positive control samples: Triazophos signals and bands were not identifiable in this comparison. This is possible because its bands and peaks overlapped with those emerging from foxtail millet. Nonetheless, the decrease in the transmittance observed in the positive control sample compared to the control sample was due to the contribution of the signals coming from triazophos to the signals observed in the control sample. The higher absorption in the region between 3100-2800 $cm^{-}1$ is caused by the additional contribution of the C-H stretching bands of aliphatic and aromatic moieties from Triazophos [36]. The same occurred in the 1600-1500 cm^{-1} region, with a contribution from the aromatic skeletal vibration from the triazophos. (Figure 5 (a))

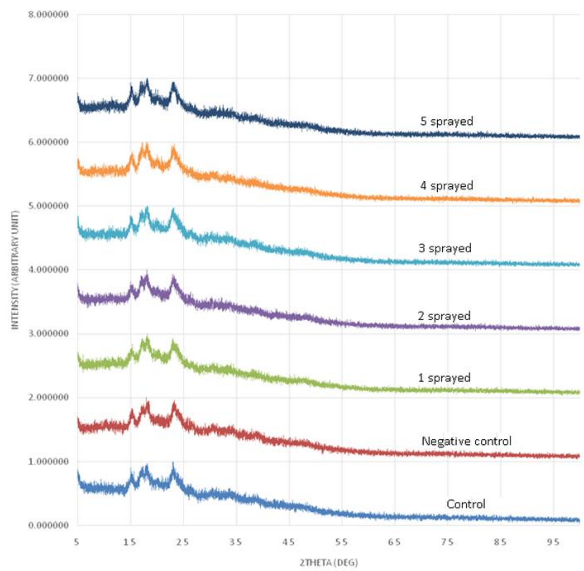
Regarding the sprayed sample, 1 and 2 spraying led to no changes in the ants' preferences compared to the positive control sample. Observing the overlay of the spectra corresponding to the control, positive control, 1 sprayed and 2 sprayed samples, 1 and 2 sprayings did not affect the activity of triazophos, and its pesticide activity remained intact. A marked change was observed in 3 sprayed samples since the ants' preference for the sample increased drastically. The main cause for this observation is attributed to the higher number of mid-IR sprayings applied to these samples that led to the complete degradation of the triazophos, eventually losing its activity. In addition, the mid-IR generated from spraying caused some degradation of some of the carbohydrates, releasing simpler sugars that are sweeter [37, 38] and known to naturally exert an attractive effect on ants. Observing the overlay of the spectra from the two control samples and 3 sprayed samples, transmittance values were different in the 3 sprayed samples compared to the control samples, especially when compared to the positive control sample. This supported our hypothesis, as appreciably notable changes in the transmittance were displayed in the regions where pesticide signals were expected to contribute.

The ants' preference was found to be reduced again with successively sprayed samples (4 and 5 sprays) compared to 3 sprayed samples. More intense spraying generated byproducts from triazophos degradation that regained some pesticide activity. These compounds are expected to retain some of the chemical groups present in triazophos, and for this reason, augmentation of the bands and peaks contributed by triazophos chemical groups was observed. Spectra from 4 sprayed and 5 sprayed samples showed lower transmittances than those displayed by 3 sprayed samples. The spectrum from the 4-sprayed sample was quite similar to the spectrum from the positive control sample; thus, it is not surprising that the observed ants' preference is comparable. In the case of the 5-sprayed sample, the spectrum is more similar to that of the control sample, and hence, the observed ant preference is more similar to that of the control sample. In this case, upon more spraying, part of the triazophos byproducts generated with pesticide activity are also degraded to nonactive compounds.

PXRD of Millets Containing 1000 ppm Triazophos:
All samples showed similar crystal structures. The XRD patterns measured agreed well with the signature peaks of millet starches. All samples, except 5 sprayed samples, exhibited typical *"A"-type* XRD patterns due to the presence of peaks at $^{15°}$, $^{17°\ 18°}$, $^{20°}$, and $^{23°}$ [39]. The 5 sprayed sample, on the other hand, exhibited a *"B"-type* XRD pattern due to the merged 17° and $^{18°}$ peaks. The low signal-to-noise ratio and high-intensity backgrounds in the XRD patterns indicated a mixture of amorphous and crystalline phases in the sample, such as contributions of irregularly small starch molecular chain aggregates, packed crystallites, and isolated single helices. (Figure 5 (b))



(a)FTIR



(b) PXRD

Figure 5: Instrumentation spectra images of agrochemical samples (a) FTIR, (b) PXRD

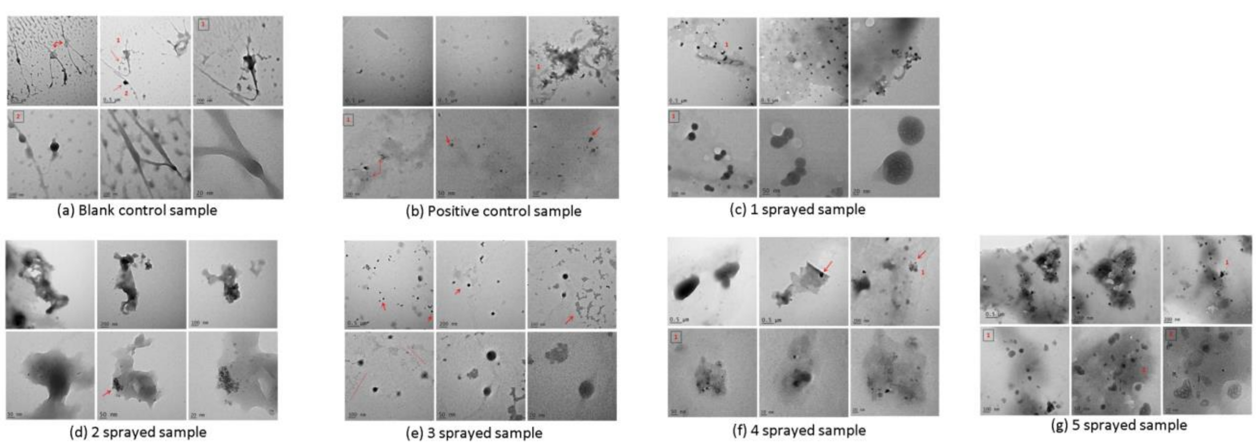


Figure 6: Transmission electron microscopy images of agrochemical samples

TEM of Millets Containing 3000 ppm Triazophos:

Bright-Field Images:

Significant differences were detected among all samples. This mainly concerns the type, reciprocal abundances, and spatial arrangements of the various particulate components observed. The particulate types detected in the control sample were not observed in any of the other samples, including the negative control. Conversely, more than one of the sprayed samples shows similarities with the latter (and, particularly, 2 sprayed, 3 sprayed, and, to a minor extent, 5 sprayed). The TEM images (Figure 6 (a)-(g)) also suggest that spraying of foxtail millet containing triazophos alters the millet structure at the micron level, as suggested by the agglomeration of the particles and loss of the long ribbon-like structures. In summary, the loss of ribbon-like structures is related to MIRGA spraying of foxtail millet with triazophos. In addition, the degree of agglomeration of the particles visible in the TEM images correlated with the ants' foraging preference. *(Detailed description of TEM data available in supplementary text T2 and figures F3 (a-g))*

DISCUSSION

Action of MIRGA on Pesticide Residues and Millets

Based on the background and the concepts described by Umakanthan *et al*., 2022a *(available in supplementary text T3)*, MIRGA designed to generate 2-6 μm mid-IR, altered the chemical bond parameters (Umakanthan *et al*., 2022a; Umakanthan *et al*., 2022b, Umakanthan T, Mathi M, 2023c), thereby detoxified the pesticide residues and potentiated the millets, rendering it preferable for ant foraging.

As displayed in the various instrument results, 2-6 μm mid-IR caused chemical and molecular level changes in the pesticide components. In this photodegradation process, chemical components of the pesticides absorb the mid-IR, and the absorbed mid-IR alters the chemical bonds of triazophos molecules; therefore, the triazophos molecules are degraded/transformed into another molecule or compound. According to the infrared results, three MIRGA sprayings received Foxtail millet samples ranging from 5 to 3000 ppm, were detoxified and hence increased ants foraging preference.

Proposed pathway of mid-IR-induced photodegradation of triazophos in foxtail millet

1. MIRGA containing inorganic salt solution.
2. Spraying of MIRGA equipment at 3900-pascal pressure.
3. Molecules in the salt solution oscillated.
4. Oscillation of and between the molecules generates 2-6 μm mid-infrared light.
5. 2-6 μm mid-IR falls on the packet containing foxtail millet contaminated with triazophos.
6. The mid-IR penetrates through the packet and coincides with the energy of the inside sample.
7. Molecules of the millet + triazophos absorb the mid-IR and are excited from ground state.
8. Nanostructured water layers of the sample triggered by the applied mid-IR, since water molecules absorb in this region.
9. Mid-IR causes elongation, contraction, formation, and breakage of the chemical bonds of the receptor molecules.

10. Pesticide components degrade into less/nontoxic forms depending on the quantum of MIR absorbed by them.
11. Simultaneous degradation of millet molecules, such as breaking complex sugars into simple sugars, further increases sweetness.
12. Thus, the foraging behavior of ants was attracted to detoxified and sweetened millet samples.

This study identified the detoxification of Triazophos pesticide and enhanced the sensory attributes of millets by applying 2-6 μm mid-IR. Depending on the number of MIRGA sprayings, the receptor's chemical bonds, configurations, and subsequent physical and chemical characteristics were altered.

The foraging behavior of ants as a marker to determine pesticidal toxicity in millet samples and their observed higher preference toward sprayed detoxified samples and lesser preference for non-sprayed samples, as observed in this study, are consistent with the results of Kwon, 2010 [40], in which organophosphate pesticides were shown to reduce the foraging activity of ants. Ants were able to discriminate between safe and potentially harmful prey and showed prophylactic avoidance of hazardous prey (Pereira *et al*., 2020).

Advantages of MIRGA Over the Existing Pesticide Degradation Methods

The methods described below have evolved over the years to remove pesticides from agro-products. Nevertheless, each of these methodologies possesses inherent constraints that hinder their implementation [41]. The MIRGA technology emerges as a potential solution to surmount these limitations, thereby endowing MIRGA with a comparative advantage over alternative methodologies.

Limitations surrounding the existing methodologies are as follows: Washing, blanching, peeling, and cooking are deemed appropriate solely for domestic and household applications. The utilization of Chemical treatment/Electrolyzed water leads to water wastage and the contamination of the environment with washed-off pesticide residue. The recent years have witnessed the rise of ozone as a relatively advantageous approach for pesticide elimination. Nonetheless, ozone presents several drawbacks: firstly, ozone decomposition targets exclusively water-soluble pesticides [14]; secondly, it effectively infiltrates the delicate skin of vegetables as opposed to the thick pericarp of fruits [14]; thirdly, ozone degradation proves effective under conditions of high humidity, low pH, and reduced temperatures [14]; fourthly, its innate oxidizing properties can lead to metal corrosion [14]; fifthly, the process of ozone treatment produces harmful ozonation byproducts that not only pose risks to human health but also contribute to secondary pollution, with these byproducts often exhibiting higher toxicity levels than the original pesticides [17]; and lastly, despite the relatively low cost associated with ozonation, such expenses are typically reflected in the retail prices of agricultural products, rendering them unaffordable for individuals with low to moderate incomes [14]. Presently, the application of the Pulsed light method is constrained to water treatment exclusively [41]. In the case of Irradiation, the common usage of gamma and UV rays results in the deterioration of the sensory and nutritional attributes of irradiated food items. Conversely, the Electron Beam method is hindered by its limited penetration depth [42]. While Bioremediation/Microbial degradation techniques can be employed for soil and environmental cleanup, they are unsuitable for food products due to their low degradation efficiency [43]. Cold plasma stands as an emerging technology, albeit with safety aspects that have not yet undergone comprehensive evaluation [44].

Application of MIRGA Technology in Field

Taking these methods and their limitations into consideration and comparison, MIRGA can be used under any atmospheric condition, is eco-friendly, safe, easy to use and easy to carry. The generated 2-6 μm mid-IR is nonionizing, harmless, and neither produces nor leaves any hazardous byproducts on the treated foods and nor cause adverse effect to user. The overwhelming advantage of the MIRGA technique is that it is sprayed externally from a distance of 0.25 to 0.50 meters over packaged agroproducts without any direct contact. The manufacturing cost of an atomizer is only USD 0.30, and it gives a minimum of 300 sprayings, which are enough to detoxify 1 to 2 tonnes of agro products within 5 minutes. MIRGA can be used at all levels from agro-farm to food industry to end-consumer to detoxify Triazophos from 5 to 3000 ppm range. Like photochemical and ozone treatments, MIRGA mid-IR altered the triazophos's chemical bonds. Thus, the chemistry of pesticidal residues changes, causing molecular degeneration (14; 15); therefore, their physicochemical properties are modified, leading to degradation and hence toxicity loss or reduction.

CONCLUSION

In the study, the impact of 2-6 μm mid-infrared spectrum irradiation in the detoxification of Triazophos was tried. Fire ants and instruments were employed, and the results are compared to current pesticide degradation technologies. The 2-6 μm mid-IR irradiation altered the chemical bonds and compounds of Triazophos concentrations ranging from 5 to 3000 ppm. As a result, the Triazophos was qualitatively detoxified, which more attracted ants for foraging. In comparison, this method was found to be economical and user-friendly, hence safer food. Although the quantitative changes in the pesticides are not investigated, the study has reached sufficient coverage to allow this technology in pesticide detoxification in foods. Further specific standardization studies for each pesticide, and agrochemical residues in agro product using 2-6 μm mid-IR will help to uncover numerous other issues posed by residues to the soil, soil microbiome, agriculture, and environment. In the future, it is possible to develop a pesticide cleaner that uses a mid-infrared spectrum.

Data and Materials Availability

Data included in article/supplementary material/ references in the article. Supplementary file available at: https://docs.google.com/document/d/1hdphmVg0qVyWJSnr1YEmQ6EnKD_JyINc/edit?usp=sharing&rtpof=true&sd=true

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Author Contributions

- *Umakanthan:* Conceptualization, Methodology, Project administration, Resources, Supervision, Validation.

- *Madhu Mathi:* Data curation, Investigation, Visualization, Writing - Original draft preparation.
- *Umakanthan, Madhu Mathi:* Writing- Reviewing and Editing.

Conflict of Interest

In accordance with the journal's policy and our ethical obligation as researchers, we submit that the authors Dr. Umakanthan and Dr. Madhu Mathi are the inventors and patentees of the Indian patent for MIRGA *(under patent no.: 401387),* which is a major material employed in this study.

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