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Organic Water-Soluble Fertilizers Enhance Pesticide Degradation: Towards Reduced Residues

Dongsheng LIU[a], Weizhen LI[b], Haixiang GAO[b]*, Changsheng HUANG[a], Shihong XU[a], Wenqi LIU[c]

[a]*Guangxi Penshibao Co., Ltd. CHINA*
[b]*China Agricultural University. CHINA*
[c]*Soil Fertilizer Work Station of Guangxi Zhuang Autonomous Region. CHINA*

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Corresponding Author: Haixiang GAO, E-mail: hxgao@cau.edu.cn
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ABSTRACT
This scientific undertaking meticulously inspected chlorpyrifos degradation kinetics when interacts with assorted organic water-soluble fertilizer formulations. Through rigorous field experimentation, we evaluated the modulatory effects of organic water-soluble fertilizers on the kinetics of pesticide degradation. Under specific conditions, organic water-soluble fertilizers can promote the degradation of pesticides. The integration of distinct fertilizer dilutions conspicuously enhanced degradation, alluding to intricate concentration-dependent mechanisms. In our quest to decipher the underlying mechanisms, we delved into both the biochemical and physicochemical facets. Notably, we monitored plant peroxidase activity across varying concentrations of these fertilizers throughout the investigative period. Temporal tracking displayed escalated plant peroxidase activity, mirroring bolstered detoxification. The results of the UV degradation experiment showed no significant difference in the acaricide degradation rate, regardless of the presence or absence of organic water-soluble fertilizers. However, illumination-induced degradation remained unperturbed by fertilization. Simulated rainwater cleansing was enacted on farmer’s market produce, spanning crucifers, asters, chenopods, and amaranths. Our assays pertaining to washing elucidated the capability of organic water-soluble fertilizers to curtail pesticide residues across representative vegetable taxa. Fertilizer supplementation substantially reduced chlorpyrifos residuals, especially in crucifers. This inquiry underscores the inherent botanical mechanisms of detoxification, which, when augmented by judicious fertilizer supplementation, culminate in the diminution of chlorpyrifos pesticide residues. While promising, extensive multi-crop trials are required to optimize assimilation strategies. Harnessing the intrinsic synergy between agricultural enrichment and pest mitigation, as expounded in this study, heralds a paradigm shift towards sustainable agriculture, ensuring both food security and ecological stewardship.

Keywords: Chlorpyrifos degradation, Peroxidase-mediated detoxification, Pesticidal residue diminution, Photolysis and UV effects, Agricultural sustainability

1. Introduction

Plants possess the ability to synthesize carbohydrates via photosynthesis; however, essential elements such as nitrogen, phosphorus, and potassium, which are integral for the formation of vital biomolecules like proteins, must be procured through mineral elements present in the soil. Continuous harvesting of plants inevitably leads to a decline in these mineral elements, resulting in soil impoverishment. Fertilizers, serving as a crucial constituent of agricultural chemicals, assume the responsibility of providing plant nutrition. Fertilizers play a pivotal role in fortifying soils with mineral elements that are inherently deficient, a step that ensures plant growth remains unhindered by elements such as nitrogen, phosphorus, and potassium (Savci 2012). It is imperative to acknowledge that while these inorganic compounds are vital in compensating for nutrient scarcities, their excessive application may culminate in deleterious consequences such as soil acidification and aquatic pollution (Medel et al. 2022). Fertilizers derived from organic, water-soluble sources present a viable alternative, addressing these detriments via a mechanism characterized by the gradual release of nutrients.

Pesticides arise as indispensable constituents within the anthology of agricultural amalgamations, their cardinal purpose being the protection of harvests from pernicious pestilent organisms. Despite its utility, the pronounced toxic attributes of chlorpyrifos residues, coupled with their persistent manifestation within both plant structures and aquatic domains, invite substantial trepidation. The precipitous accrual of such chemical vestiges upon agricultural yields, antithetical to rigorous safety prerequisites, spotlights an imperative for expeditious diminution (Medel et al. 2022; Senthilkumar et al. 2022). Though efficacious in pest control, the implications encompass potential degradation of soil matrices, contamination of aquatic conduits, threats to human health, and the fiscal implications of their synthesis and administration (Bonmatin et al. 2021; R. Ramadevi et al. 2022; Senthilkumar et al. 2022). Although the protective role of pesticides in plant health is indisputable, a lack of knowledge among farmers often leads to over-application of pesticides, and in some instances, products are sold within the safety interval of the pesticide, potentially jeopardizing consumer health (Philippe et al. 2021) As a consequence, there is a pressing need for the development of scientifically sound methodologies to reduce pesticide residues and curtail the safety interval of pesticides (Adhikari 2017).

The organophosphorus pesticide, chlorpyrifos, known for its role in obstructing nerve impulse transmission through the inhibition of acetylcholinesterase enzymatic functions, has been corroborated for its efficacy against a diverse spectrum of pests plaguing various crops. However, abundant trepidations pervade surrounding chlorpyrifos' overt toxicity and persistence within botanical and aqueous environments, underscoring the necessity of minimizing accumulations on consumable crops to uphold exacting safety standards. Given the concerns, we explored how organic water-soluble fertilizers might enhance microbial and enzymatic activities, thereby reducing chlorpyrifos residues and shortening pre-harvest intervals. This study unveils new insights into the synergistic interactions between fertilizers and pesticides, enriching current knowledge. Rigorous experimentation verified that synergistic co-applications can effectively diminish pesticide accumulations, consequently abbreviating pre-harvest intervals. Our experiments confirmed that using organic water-soluble fertilizers with pesticides effectively reduces pesticide residues and safety intervals (Niu et al. 2021). The outcomes elucidate that the synergistic application of organic water-soluble fertilizers in conjunction with pesticides paves the way for diminished pesticide residues, consequently abbreviating the safety interlude necessary before the harvested yield can be adjudicated as fit for intake. In charting the intricate coordinates of this scholarly passage, the undertaken empirical maneuvers have unfurled illuminating glimpses into a cardinal quandary that lies firmly ingrained within the expansive realm of agricultural sustainability.

2. Material and Methods

2.1. Experimental reagents and materials

The reagents and materials were obtained from commercial sources:

Acetamiprid emulsion concentrate (480g/L, Jiatong, Jiangsu Baoling Chemical Co., Ltd.) for its pesticidal properties, and acetamiprid (Aladdin Reagent Co., Ltd., Shanghai, China) as a reference standard for comparison purposes. Organic water-soluble fertilizer (water-based) (Guangxi Penshibao Co., Ltd.) for its plant nutrient content. (Detailed Information on the Fertilizer: (1) Composition: The fertilizer is an organic multi-element compound water-soluble type, abundant in essential crop nutrients such as nitrogen, phosphorus, potassium, boron, zinc, manganese, and other minerals. Moreover, it encompasses organic nutrients like fulvic acid, amino acids, vitamins, and polysaccharides. (2) Product Features: This fertilizer grants crops with thorough and balanced nutrition throughout their growth cycle. It aids in tissue repair, growth promotion, and product quality enhancement. It's known to elevate crop immunity, catalyze enzymatic activity, bolster resistance against environmental adversities, augment chlorophyll content, enhance photosynthesis efficiency, and promote fruiting and flowering. (3) Chemical Properties: Organic Matter: ≥125g/L; Nitrogen (N): ≥100g/L; Phosphorus (P2O5): ≥50g/L; Potassium (K): ≥20g/L; Zinc (Zn): ≥20g/L; Boron (B): ≥8g/L; Manganese (Mn): ≥2g/L; (4) Safety and Quality Standards: The fertilizer adheres to stringent safety standards, with specific thresholds set for insoluble matter, heavy metals, microbial contamination, among other potential contaminants. The pH for a 1:250 dilution resides between 3.0 to 5.0.)

Acetonitrile, methanol, and acetone (chromatographically pure, Beijing Dimachem Technology Co., Ltd.) as organic solvents for extraction and analytical processes. Sodium chloride, sodium dihydrogen phosphate, and sodium phosphate monobasic (analytical grade, China National Pharmaceutical Group Chemical Reagent Co., Ltd., China) as reagents in the analytical process. Cleanert SC18-SPE (Bonna-Agela Technologies Co., Ltd.) as a sorbent material in sample preparation. Guaiacol (Tokyo Chemical Industry Co., Ltd., Japan) and 30% hydrogen peroxide (China National Pharmaceutical Group Chemical Reagent Co., Ltd., China) as reagents in the analytical process. A ceramic small grinding bowl (Guangda Hengyi Co., Ltd., China) for grinding and homogenizing samples, and a 2 mL centrifuge tube (Guangda Hengyi Co., Ltd., China) for sample storage and processing.

The vegetables used in the experimental procedure, including rapeseed, lettuce, Chinese kale, spinach, and amaranth (Meili Meijia Supermarket, Beijing, China), were procured for use as samples. All of the aforementioned reagents and materials were used in the described experimental procedure, and their properties and sources have been accurately reported for transparency and repeatability purposes.

2.2. Experimental Instruments

The Agilent 1200 infinity series high-performance liquid chromatography instrument with a UV-visible light detector (Agilent Technologies, Palo Alto, California, USA) was used for detection, separation, and quantitative analysis. The chromatographic column used was the Spursil C18 column (5μm, 4.6×250mm) and the Spursil C18 guard column (5μm, 2.1×10mm).

Other instruments included an analytical balance, a circulating multi-functional water pump, a rotary evaporator, a freezer, an organic membrane, latex gloves, sterile disposable syringes, a nitrogen concentrator, a manual adjustable pipette, an ultrapure water system, a CNC ultrasonic cleaner, a high-speed centrifuge, a micro-injector, an electric heating blast drying oven, a vortex mixer, a homogenizer, a UV lamp, a homemade UV box, a UV-visible spectrophotometer, a temperature-controlled high-speed centrifuge, an automatic tension meter, and a CNC ultrasonic cleaner.

2.3. Field trial

2.3.1. Overview of the trial site

The trial field for this field experiment is located in Houzhang Village, Shangzhuang Town, Haidian District, Beijing. It is surrounded by many villages, such as Qianzhang Village, Bajia Village, Shuangta Village, and Xixinlitun Village, and is located in the northwest corner of Shangzhuang. The soil in this area is fertile and belongs to the good quality loam soil of the North China Plain. The area has a temperate monsoon climate with little water and strong winds in spring, rainy and humid in summer, short and dry in autumn, and cold and frozen in winter. The average annual temperature is 12 °C, the annual precipitation is 630 mm, with 60-70% concentrated in July and August, the annual evaporation is 1500mm, and the average annual wind speed is 2.4 m/s.

2.3.2. Experimental method

The land was divided into 10 plots, each plot measuring 6 m^2 with a safety zone between each plot. Plots 1, 2, and 3 were recommended for high doses of Chlorpyrifos, with 900 mL of Chlorpyrifos diluted 1000 times applied. Plots 3, 4, and 5 were also recommended for high doses of Chlorpyrifos, with 900 mL of diluted Chlorpyrifos and 900μL of 1000-fold diluted organic water-soluble fertilizer added (Chang et al. 2020; Sun et al. 2018). Plots 5, 6, and 7 were recommended for high doses of Chlorpyrifos, with 900 mL of diluted Chlorpyrifos and 600 μL of 1500-fold diluted organic water-soluble fertilizer (Penshibao) added. Plot 10 was left as a blank control group without any Chlorpyrifos application. When the rapeseed plants were approximately 10 cm tall, the spraying was carried out on a windless morning. Samples were collected 3, 5, and 7 days after spraying.

The pesticide detection method referred to GBT 20769-2008 (Pang 2018) (Determination of 450 Pesticides and Related Chemical Residues in Fruits and Vegetables).

According to the experimental needs and the prediction of sample content, a standard substrate solution of Chlorpyrifos with five concentrations of 1mg/L, 0.8mg/L, 0.5mg/L, 0.1mg/L, and 0.05mg/L were prepared with small rapeseed as the substrate. The chromatographic peak area of each concentration was detected and the standard quantification curve of Chlorpyrifos was plotted, with the concentration of the Chlorpyrifos standard substance on the x-axis and the chromatographic detection integral area on the y-axis.

The linear regression equation for the standard substrate solution of Brassica rapa subsp. chinensis is:

Chlorpyrifos, $y = 116.16x + 28.673$, $R^2 = 0.9971$ (Figure 1).

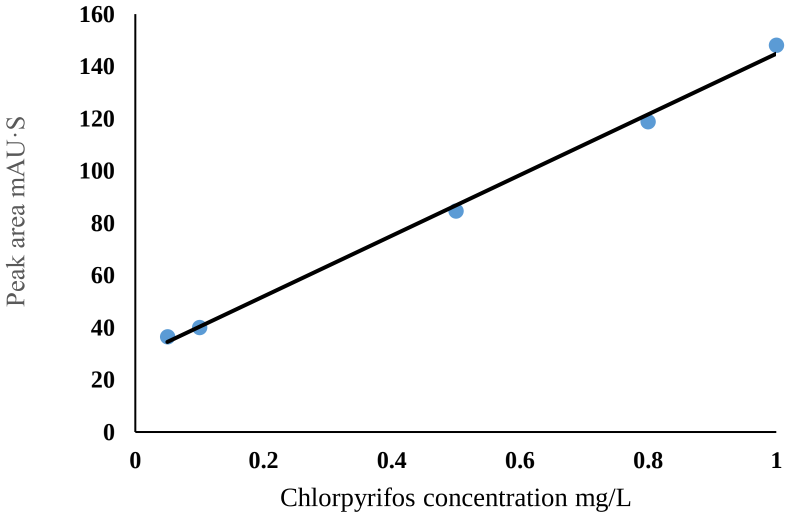


Figure 1- Calibration Curve of Chlorpyrifos in Real Sample Brassica rapa subsp. chinensis

Table 1- The recovery and RSD of added analytes in real vegetable sample

Samples	*Added concentration (mg/kg)*	*Recovery rate (%)*					*Average recovery rate (%)*	*RSD (%)*
Brassica rapa subsp. chinensis	0.005	88.7	94.8	101.4	93.2	95.3	94.7	4.8
	0.1	94.0	89.3	94.6	91.1	88.7	91.5	2.9
	0.5	97.7	94.1	95.5	86.6	93.2	93.4	4.5

2.4. Biological factor - peroxidase activity

The experimental area was partitioned into ten distinct plots, each encompassing 6 m² and separated by safety zones (Andreu & Picó 2004; Hossain et al. 2022; Pal et al. 2010; Pavlidis et al. 2020; Shalaby & Abdou 2010). Plots 1-3 were subjected to elevated concentrations of Chlorpyrifos, achieved by administering 900 mL of 1000-fold diluted Chlorpyrifos. Plots 4-6 received a similar treatment, with the addition of 900 µL of at a 1000-fold dilution. In plots 7-9, 900 mL of diluted Chlorpyrifos was supplemented with 600 µL of at a 1500-fold dilution. Plot 10 served as an untreated control group. When the rapeseed plants reached approximately 10 cm in height, the spraying was conducted on a calm morning. Samples were procured on days 3, 5, 7, and 14 post-spraying, with experiments executed immediately following sample collection.

Initially, a mortar, phosphate buffer solution, and rapeseed samples were precooled, with the mortar situated in an ice bath to maintain a low temperature, thereby preserving enzyme activity. A rapid weighing balance was employed to measure 0.200 g of fresh rapeseed leaf samples, which were subsequently added to the mortar in the ice bath for grinding. Peroxidase extraction was achieved using a 50 mmol/L precooled phosphate buffer solution (pH 6.0). A pipette was used to extract 600 µL of the phosphate buffer solution, which was then transferred to a 2 mL centrifuge tube. Following this, 500 µL of enzyme solution was extracted twice, ultimately combining with the initial extract. The resulting mixture was subjected to temperature-controlled high-speed centrifugation at 4°C and 12,000 g for 20 minutes. The supernatant was then aspirated and stored in a refrigerator.

The instrument was zeroed using a blank phosphate buffer solution. A 3 mL aliquot of the reaction solution was withdrawn using a pipette, and 40 µL of the test enzyme solution was introduced. The solution was promptly mixed with a pipette and positioned within a UV-visible spectrophotometer. The enzyme-catalyzed reaction ensued, yielding a colored product quantifiable by the UV-visible spectrophotometer. The OD470 alteration curve within 15 minutes was constructed using the spectrophotometer, with the curve's slope signifying the reaction rate. Peroxidase activity can be denoted as the change in OD470 per minute multiplied by 100, with the unit being U. Lastly, enzyme activity was converted to the per gram of fresh weight of rapeseed enzyme activity value (Singh et al. 2004).

2.5. Non-biological factor - light exposure

2.5.1. Experimental design

A 175 W UV mercury lamp served as the light source for the investigation (Hossain et al. 2013), Plots 1-3 comprised a 5 ppm solution of Chlorpyrifos (water: methanol = 1:1), while plots 4-6 contained a 5 ppm solution of Chlorpyrifos combined with a 1000-fold diluted organic water-soluble fertilizer. Plots 7-9 were treated with a 5 ppm solution of Chlorpyrifos and a 1500-fold diluted organic water-soluble fertilizer. Plots 10-12, which housed a 5 ppm solution of Chlorpyrifos, were maintained in darkness as a control group. Following 0, 10, 25, and 45 minutes of exposure, samples were collected and analyzed using high-performance liquid chromatography (HPLC).

2.5.2. Standard curve

An external standard method was employed, with Chlorpyrifos concentration plotted on the x-axis and chromatographic peak area on the y-axis to construct a standard curve for subsequent quantitative analysis.

Standard Curve: $y = 9.8016x + 0.0478$ $R^2 = 0.9999$ (Figure 2)

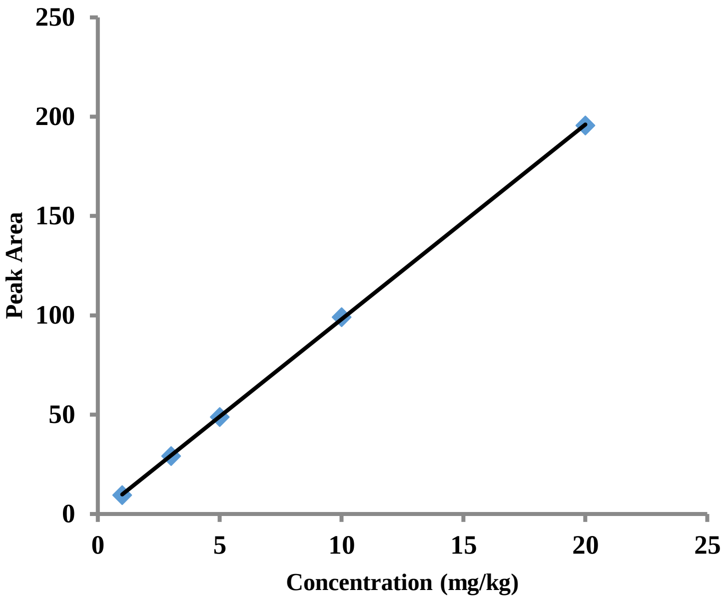


Figure 2- Calibration Curve of Chlorpyrifos

2.6. Surface activity verification experiment

2.6.1. Instrumentation

A JK99B automatic tensiometer (brand: POWEREACH, Shanghai Zhongchen Digital Technology Equipment Co., Ltd.) was utilized for the experiments.

2.6.2. Experiment

The gradient dilution method was implemented: The organic water-soluble fertilizer, sourced from Guangxi Penshibao Co., Ltd., was chosen for its specific nutrient composition, which plays a pivotal role in its properties and efficacy. A 2% organic water-soluble fertilizer solution was prepared and successively diluted by 2-fold to generate a series of gradient solutions, specifically 2%, 1%, 0.5%, 0.25%, and 0.125%. The platinum plate method was employed to measure surface tension values, with three parallel measurements executed for each group (a platinum plate is immersed in the test solution and subsequently lifted, with the surface tension value recorded upon detachment from the liquid surface). The surface tension of pure water at room temperature is 72 mN/m.

2.7. Non-biological factor - facilitates pesticide dissolution experiment

2.7.1. Experimental method

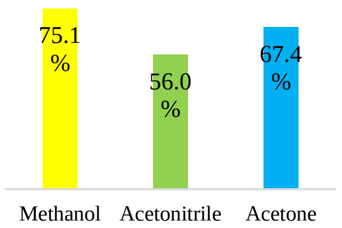
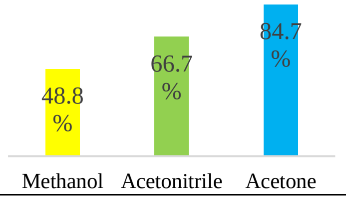
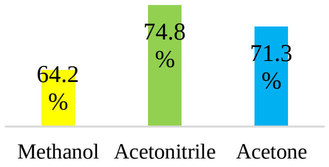
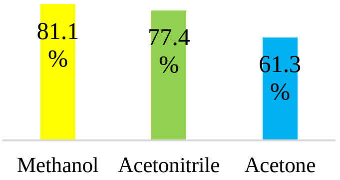
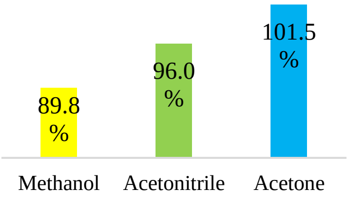
Experimental Design

Four experimental groups were established using four stainless steel pans, each containing 2 L of deionized water and 2 mL of Chlorpyrifos emulsion (formulated as a 1000-fold diluted solution of Chlorpyrifos). Groups 1 and 2 did not incorporate organic water-soluble fertilizer. Group 3 introduced 2 mL of a 1000-fold diluted solution of organic water-soluble fertilizer, while Group 4 added 665 µL of a 1500-fold diluted solution of organic water-soluble fertilizer, administered twice. Equal quantities of oilseed rape were submerged in the pesticide solution in each stainless-steel pan, stirred thrice, and subsequently removed and dried.

Upon drying, the samples were cleansed. Group 1 remained unwashed, whereas the other groups were rinsed with 2 L of deionized water, employing the same soaking and stirring protocol, and then dried. Ultrasonic extraction was utilized for analysis (Balkan & Yılmaz 2022; Ikeura et al. 2011). The oilseed rape plants chosen for the experiments were specifically in the vegetative growth stage, at the rosette phase, ensuring uniform developmental progression among all specimens. Each plant consistently presented an average of 8-10 leaves. Three oilseed rape plants were randomly chosen for each group as parallel samples. Each plant was accurately weighed to 0.800 g in a centrifuge tube, and 8.00 mL of methanol was introduced to extract the Chlorpyrifos residue on the leaf surface. The solution was sonicated for 20 min and analyzed via liquid chromatography.

Solvent optimization

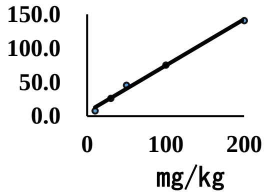
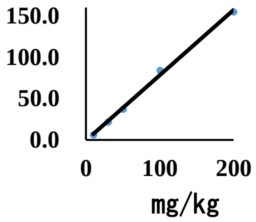
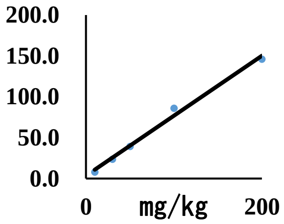
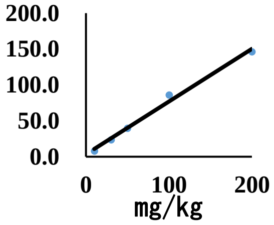
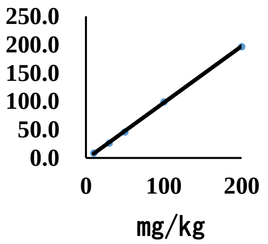
Table 2- The influence of different solvents on extraction recovery of chlorpyrifos

Vegetables (Family)	*Vegetables (Species)*	*Solvent optimization*	*Optimization result*
Brassicaceae	*Brassica rapa subsp. Chinensis*		Methanol
Asteraceae	*Brassica napus subsp. oleifera*		Acetone
	Lactuca sativa		Acetonitrile
Amaranthaceae	*Spinacia oleracea*		Methanol
Amaranthus tricolor	*Amaranthus spp.*		Acetone

Precisely weigh 0.800 g of intact vegetable leaves and use a microsyringe to draw up 80 µL of a 1000 mg/kg stock solution of chlorpyrifos in methanol, achieving a concentration of 100 mg/kg. Gradually dispense one drop in 40 steps, with each drop approximately 2 µL, lightly touching the leaf surface to establish contact with the droplet. Repeat this process 40 times to uniformly coat the leaf surface with 40 small droplets. Allow the leaves to rest for 20 minutes for methanol evaporation before placing the pesticide-treated leaves in a 10 mL centrifuge tube. Add 8 mL of ultrasonic extraction solvent (methanol, acetonitrile, or acetone, with three replicates for each solvent) and sonicate for 20 minutes. Analyze the methanol extract using high-performance liquid chromatography to calculate the recovery rate. The solvent exhibiting the highest recovery rate is selected as the optimal solvent for subsequent experiments.

Calibration Curve

Table 3- Calibration curve of chlorpyrifos on different vegetables

Vegetables （Family）	*Vegetables （Species）*	*Calibration Curve**	*R^2*
Brassicaceae	*Brassica rapa subsp. Chinensis*	**y=0.6831x+6.0689** 	0.9946
Asteraceae	*Brassica napus subsp. oleifera*	**y=0.7885x-0.6840** 	0.9969
	Lactuca sativa	**y=0.7338x+0.3889** 	0.9911
Chenopodiaceae	*Spinacia oleracea*	**y=0.7143x+0.3889** 	0.9985
Amaranthaceae	*Amaranthus spp.*	**y=0.9970x-2.3032** 	0.9996

*: The adding concentrations are 10mg/kg, 30mg/kg, 50mg/kg, 100mg/kg, 200mg/kg

The specific experimental procedure entails the following steps: accurately weigh 0.800 g of vegetable leaves and utilize a micro-syringe to draw the appropriate volume of the stock solution for each desired concentration. Gradually dispense a droplet multiple times, with each droplet measuring approximately 2 μL, gently touching the leaf surface such that the droplet merely contacts the surface and is adsorbed onto the leaf due to surface interactions. This process is repeated numerous times to uniformly coat the leaf surface with small droplets. Allow the leaves to rest for 20 minutes for methanol evaporation before placing the treated leaves in a 10 mL centrifuge tube. Add 8 mL of ultrasonic extraction solvent, sonicate for 20 minutes, and analyze the solvent extract using high-performance liquid chromatography to calculate the recovery rate and construct the standard curve.

3-Results and Discussion

3.1. Results of field control trials

The empirical outcomes suggest that subsequent to the administration of the organic water-soluble fertilizer, there was a marked diminution in the remnants of pesticides. Specifically, pesticide residue levels after adding 1500-fold diluted organic water-soluble fertilizer for 3 and 7 days were approximately half of those without its addition. In contrast, the concentration of 1000-fold diluted organic water-soluble fertilizer did not exhibit any noticeable change in pesticide residue in comparison to samples without the fertilizer (Figure 3). This intimates a potential dependency on concentration. Subsequent experimental designs might explore the precise interplay between the promotion of degradation and the gradations of organic fertilizer dilution, aiming to discern the ideal dilution for optimal efficacy. The meticulous calibration of such dilution models is of utmost importance for the articulation of efficacious application protocols.

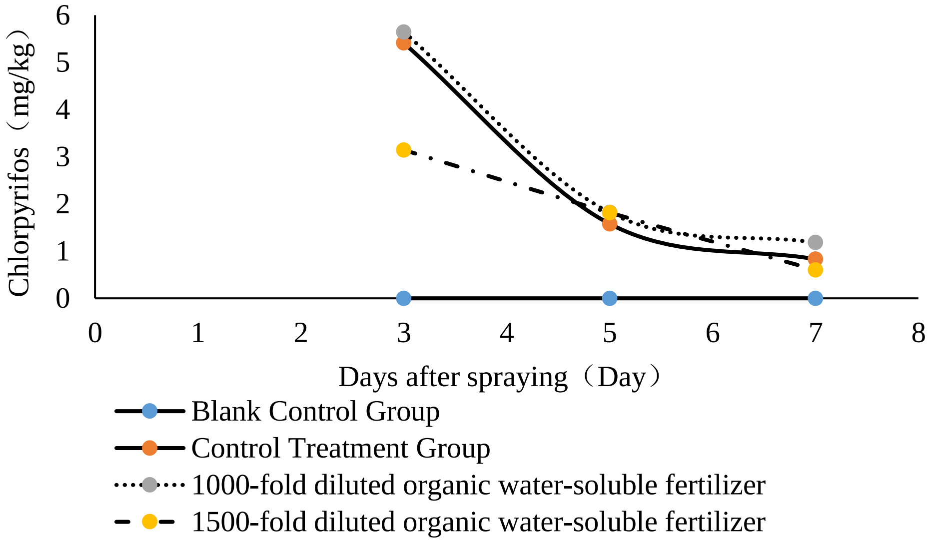


Figure 3- The influence of organic water-soluble fertilizer on degradation curve of chlorpyrifos

3.2. Biological factor - peroxidase activity results

The experimental data underscore that during the initial 7-day period, the peroxidase activity remained relatively constant across all vegetable samples, irrespective of the application of organic water-soluble fertilizers. (Figure 4) However, as the days progressed, a noticeable difference emerged. Particularly after the 7-day mark, vegetables that received the organic water-soluble fertilizer treatment showed a surge in peroxidase activity. The peak difference was observed at 14 days, suggesting that the organic water-soluble fertilizer might be playing a more pronounced role in influencing enzyme activity over extended periods. This could potentially be attributed to the gradual absorption and utilization of the nutrients present in the fertilizer by the plants.

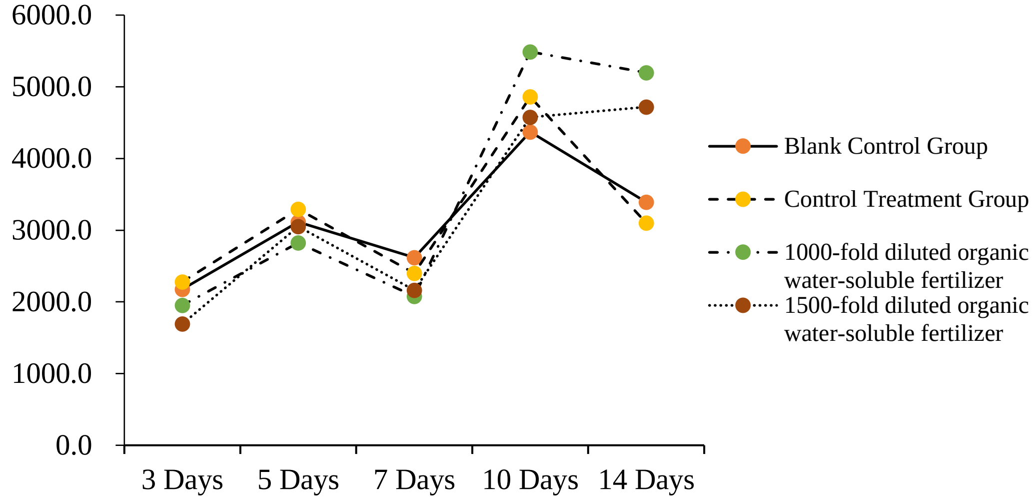


Figure 4- The influence of organic water-soluble fertilizer on the activity of peroxidase

The meticulous calibration of such dilution models is of utmost importance for the articulation of efficacious application protocols. Enzymes of the peroxidase family are instrumental in plant detoxification endeavors. The surge in their activity suggests an augmented detoxification apparatus, aligning seamlessly with the documented diminution in pesticide residues.

The organic water-soluble fertilizer may be catalyzing this detoxification process in the oilseed rape leaves, thereby ensuring a healthier vegetable yield with reduced pesticide content. The specific mechanisms could involve upregulation of certain detoxification enzymes or metabolic pathways by active ingredients in the fertilizer.

Advanced transcriptomic or proteomic analyses could potentially elucidate the genetic underpinnings bolstering detoxification in the presence of fertilizer supplementation. This insight aligns coherently with prior scholarly endeavors highlighting the versatile roles of peroxidases in plant defense mechanisms. These enzymes, besides their role in detoxification, are integral to the reinforcement of plant cellular architectures and enhancing adaptability to a plethora of stress conditions. It becomes compelling to theorize that organic water-soluble fertilizers may be magnifying these intrinsic vegetal defense systems, thus furnishing an augmented barrier against pesticide accrual.

In synthesizing the observations, the evident amplification in peroxidase activity, modulated by the presence of organic water-soluble fertilizers, necessitates additional academic exploration. A profound exploration of the constituents within these fertilizers and their nexus with plant biochemistry could illuminate pioneering tactics for sustainable agronomy. Through judicious tailoring of fertilizer compositions, we might envision a scenario wherein flora not merely assimilate vital growth nutrients but concurrently fortify their innate defensive armamentarium against extrinsic contaminants, including pesticides (Saparrat et al. 2010).

3.3. Non-biological factors - light exposure experiment results

As demonstrated in the Figure 5, the chlorpyrifos concentration stored in the dark remained stable throughout the experiment, indicating that pesticide hydrolysis during this period was markedly slower than photolysis, which underscores the difference between hydrolytic and photolytic degradation processes. Specifically, hydrolysis, which occurs in the absence of light, is often a slower process when compared to photolysis, where light serves as a catalyst to promote degradation. Nonetheless, the addition of various concentrations of organic water-soluble fertilizer did not significantly accelerate the photolysis reaction compared to the chlorpyrifos solution without organic water-soluble fertilizer. While these constituents might have a role in nourishing the soil or promoting plant health, their interaction with pesticides, in this case chlorpyrifos, seems minimal with respect to photodegradation. A plausible conclusion here is that the organic matter present in the fertilizer does not engage in any significant interactions leading to the indirect photolysis of chlorpyrifos, as supported by references (Graça et al. 2017; Wang et al. 2000). Thus, the overarching degradation effect of the organic water-soluble fertilizer on chlorpyrifos might be facilitated through other mechanisms, potentially biological or chemical, rather than the promotion of photolysis. Ensuing investigations might navigate these ancillary routes, facilitating a comprehensive comprehension of the dynamic interplay between organic fertilizing agents and pesticidal compounds.

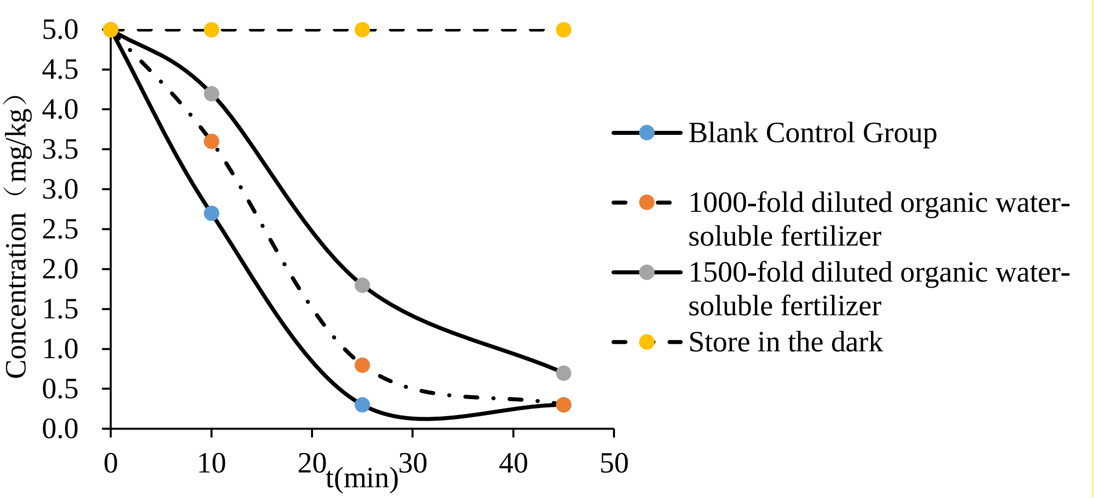


Figure 5- The influence of organic water-soluble fertilizer on photodegradation curves of chlorpyrifos

3.4. Surface Activity of Organic Water-soluble Fertilizer

Figure 6 delineates the intricate interplay of surface tension dynamics associated with organic water-soluble fertilizers, accentuating a pronounced surfactant-like behavior. Upon systematic escalation of the fertilizer's mass fraction, an unequivocal attenuation in surface tension becomes manifest, culminating in a stabilization plateau at a 2% threshold. Such observations not only attest to the inherent amphiphilic nature of the fertilizer but also insinuate a labyrinthine compositional matrix. Predominantly, specific molecular entities, perhaps surfactants or analogous amphiphilic moieties within the fertilizer, emerge as the plausible catalysts orchestrating this surfactant-like behavior.

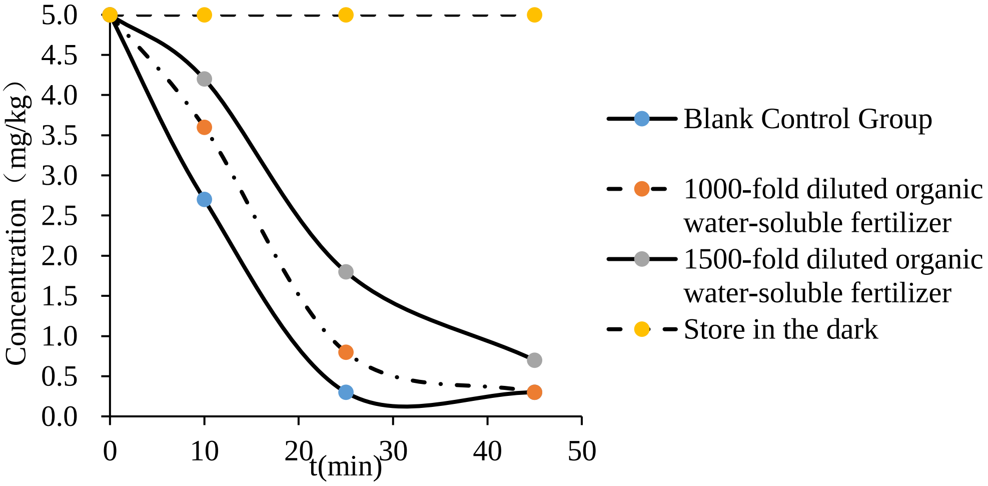


Figure 6- surface tension curves of organic water-soluble fertilizer

This amphiphilic characteristic, intrinsically embedded within the fertilizer, fosters a propitious milieu for synergistic interactions with hydrophobic pesticidal agents, epitomized by chlorpyrifos. Envisage an intricate dance where the lipophilic factions of the fertilizer entwine with the non-polar pesticide moieties, concurrently, the polar factions are immersed in an aqueous continuum. This orchestrated interplay precipitates a marked diminution in pesticide residues, accentuated post-aqueous events such as precipitation or intentional irrigation, thereby truncating the requisite safety interludes preceding vegetable ingestion. Such a mechanism proffers an avant-garde stratagem to efficaciously modulate pesticide residues.

Contemporary scholarly treatises, as corroborated by references (Sundaram & Sundaram, 1994; Pinto et al.2015), resonate with this narrative, spotlighting the synergistic interplay of humic acid vis-à-vis chlorpyrifos. These molecular dalliances can be adeptly leveraged to further mitigate pesticidal residues on flora, particularly subsequent to ablution in the presence of organic water-soluble fertilizers.

3.5. Non-biological factors - Effects of Spraying Organic Water-soluble Fertilizer on Pesticide Dissolution

3.5.1. Results and analysis of cruciferous vegetables (rapeseed)

In this study, rapeseed specimens imbued with pesticides underwent aqueous ablution to quantify residual pesticide levels. Comparing the experimental group treated with organic water-soluble fertilizer to the group without it, a decrease in residual pesticide concentration was observed with the addition of Organic water-soluble fertilizer. The residual rate after washing was 76%, a 28% reduction compared to the group without Organic water-soluble fertilizer.

The notable decrement in persistent pesticidal contaminants accentuates the formidable potential of organic water-soluble fertilizers, positing them as an efficacious paradigm in the pursuit of agricultural products of heightened purity and security. Concurrently, this underscores an emergent trajectory toward the attenuation of an entrenched reliance upon synthetic chemical agents in pest deterrence.

An examination of the experimental groups with different concentrations of Organic water-soluble fertilizer revealed that the group with a higher 1000-fold concentration exhibited the least pesticide residue, with a residue rate decrease of 41%.

The postulated mechanism responsible for this discernment is predominantly anchored in the surfactants that are intrinsic to the composition of organic water-soluble fertilizers. These surfactants, esteemed for their amphiphilic characteristics, are posited to augment the dissolution of pesticides, particularly in the context of natural rainfall or controlled irrigation techniques. Such a supposition aligns seamlessly with the venerated role of surfactants in augmenting the solubility of hydrophobic entities within aqueous mediums.

Consequently, it can be concluded that adding Organic water-soluble fertilizer organic water-soluble fertilizer to rapeseed reduces pesticide residues. The reduction mechanism may involve surfactants in organic water-soluble fertilizer dissolving more pesticides into water during natural rainfall or artificial cleaning. Organic water-soluble fertilizer, a water-soluble organic fertilizer, contains organic matter such as humic acid. Evidence indicates that humic acid can increase the apparent solubility of pesticides, with a linear correlation between the apparent solubility of pesticides and humic acid concentration. Empirical data indicates that humic acid demonstrates an aptitude for elevating the ostensible solubility of pesticides, with linear correlation observed between pesticide ostensible solubility and humic acid concentration. Thus, it can be inferred that organic water-soluble fertilizer organic water-soluble fertilizer reduces pesticide residues and decreases the safety interval for rapeseed.

3.5.2. Results and analysis of asteraceae vegetables (lettuce)

Amaranth, a member of the Asteraceae family, is relatively easy to wash, exhibiting a residue rate of 78% after washing with water. The inherent ease of washing Amaranth might be attributed to its leaf structure or the nature of its epidermal layer, which might be less adhesive to pesticide residues compared to other vegetables.

Upon the addition of a 1500-fold concentration of organic water-soluble fertilizer, the pesticide residue rate decreased by 11%. Whereas a modest decrement in residual concentrations suggests that even at augmented concentrations, the organic hydrophilic nourishment manifests a non-trivial influence upon the dissolution dynamics of pesticidal residues. More strikingly, with a 1000-fold concentration of the organic water-soluble fertilizer, the residue rate decreased by 32%. This substantial drop at a lower concentration might hint at an optimal concentration range where the fertilizer exhibits maximal efficiency in aiding pesticide dissolution.

Among the four vegetable types examined, organic water-soluble fertilizer demonstrated a significant effect in reducing pesticide residues on Amaranthaceae vegetables such as amaranth, second only to cruciferous vegetables.

Such specificity in action suggests that different vegetable families, due to their unique anatomical and biochemical traits, might interact differently with the organic water-soluble fertilizer. For instance, the waxy cuticle of cruciferous crops could facilitate surfactant interactions, while certain secondary metabolites in Asteraceae vegetables may preferentially bind with humic acids. Discerning attributes idiosyncratic to discrete categories could pave the way for a more tailored formulation of nutriments. The paramount inference drawn from these rigorous experiments is the revelation that organic water-soluble fertilizers precipitate a substantive diminution in pesticide residues. This is most salient in the context of cruciferous vegetables and those of the Amaranthaceae family. The empirical evidence presented furnishes a persuasive justification for prudently incorporating organic hydrophilic supplements within established agricultural frameworks, particularly for botanical varieties exhibiting a pronounced susceptibility to pesticidal treatments.

As for the underlying mechanism, it's postulated that surfactants and humic acid present in the organic water-soluble fertilizer play pivotal roles in promoting pesticide dissolution in water. Surfactants, by their nature, reduce the surface tension of water, potentially allowing for better penetration and removal of pesticide residues from the vegetable surfaces. Humic acid, on the other hand, might be binding to the pesticide molecules, enhancing their solubility and consequently their ease of removal. For a holistic epistemological panorama, it stands to reason that the orchestration of further investigative undertakings, plumbing the depths of these postulated mechanistic underpinnings, will either vindicate or challenge these suppositions, thereby amplifying our grasp of the cardinal function of organic water-soluble fertilizers in residue diminishment.

3.5.3. Summary of vegetable experiments

The results shown in Figure 7 demonstrate that the utilization of water soluble fertilizer has an effect, on decreasing the levels of pesticide residue in different kinds of vegetables belonging to the Cruciferae, Asteraceae, Chenopodiaceae and Amaranthaceae families. This corresponds with the pattern we observed in our research, where organic water soluble fertilizers successfully lower pesticide residues, across plant groups. Cruciferous vegetables represent the most abundant and diverse edible vegetable group. For a holistic epistemological panorama, it stands to reason that the orchestration of further investigative undertakings, plumbing the depths of these postulated mechanistic underpinnings, will either vindicate or challenge these suppositions, thereby amplifying our grasp of the cardinal function of organic water-soluble fertilizers in residue diminishment. This could explain the pronounced pesticide residue reduction observed in crucifers. Organic water-soluble fertilizer organic water-soluble fertilizer exhibited the strongest effect in reducing pesticide residues on cruciferous vegetables, indicating potential applicability in agricultural production for residue reduction.

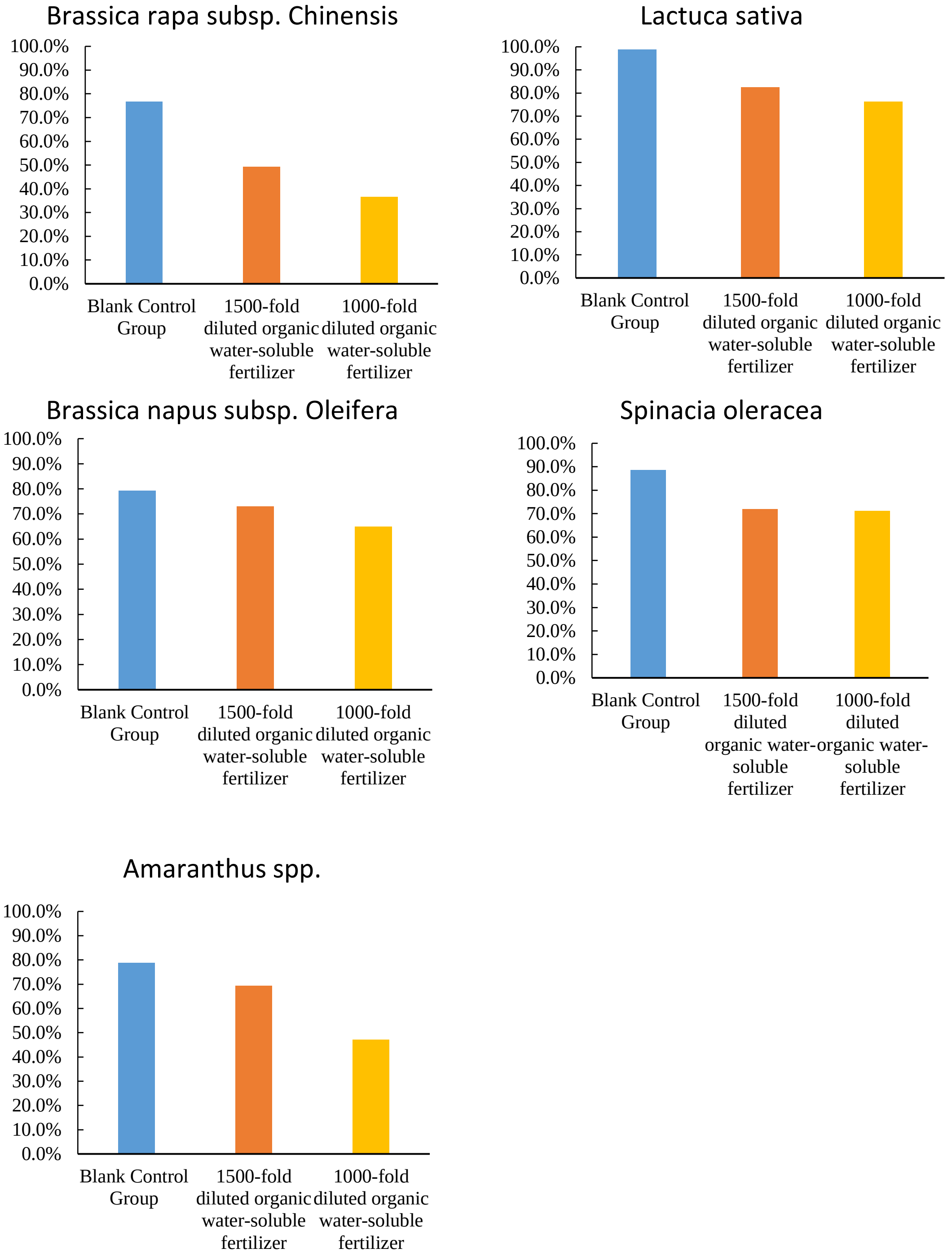


Figure 7- The influence of organic water-soluble fertilizer on the quantity of pesticide residue on Cruciferae vegetables, *Asteraceae* vegetables, Chenopodiaceae vegetables, *Amaranthaceae* vegetables

Additionally, the organic hydrophilic nourishment delineates a salient influence in attenuating pesticidal remnants on verdant consumables hailing from the taxonomies of Asteraceae and Amaranthaceae, as well as other taxonomic groupings. These discernments evoke the nuanced versatility of this approach across a diverse spectrum of botanical classifications, signifying a pivotal evolution in approaches to ameliorating challenges associated with pesticide residues. The broad efficacy across botanically diverse vegetables implies that the mechanisms of pesticide dissolution promoted by organic water-soluble fertilizers are not strictly limited to specific plant taxa. The phenomena of surfactant-mediated effects coupled with humic acid complexations seem to be ubiquitously exhibited across an array of foliaceous vegetables. However, fine-tuning fertilizer compositions to match the properties of certain vegetable groups could further maximize pesticide residue removal.

4. Conclusions and Outlook

Traditionally, agricultural chemicals have been distinctly categorized into two groups: pesticides for plant protection and fertilizers for plant nutrition. With advancing research, the scientific community has proposed the novel concept of integrating fertilizers and pesticides. A growing body of evidence suggests that the combined application of pesticides and fertilizers can yield higher crop productivity or improved quality compared to the sole use of fertilizers. This study explores the integration of fertilizers and pesticides to reduce pesticide residues, thus enriching the theory of fertilizer and pesticide integration. This erudite inquiry delves into the intricate confluence between nutrient supplements and pesticidal entities, aiming to diminish the persistence of pesticidal traces, thus rejuvenating the theoretical underpinnings of their symbiotic orchestration.

Initially, this study confirmed through field experiments that organic water-soluble fertilizer promotes the degradation of the insecticide imidacloprid. Subsequently, the underlying mechanism of this promoting effect was examined, focusing on two primary factors - biological and non-biological factors. Biological factors were primarily illustrated through field experiments demonstrating that, after a certain period, organic water-soluble fertilizer can enhance peroxidase activity, thereby augmenting its detoxification effect and reducing pesticide residues. Non-biological environmental factors are divided into photolysis and rainwater washing. Photolysis experiments indicated that the addition and concentration of organic water-soluble fertilizer did not significantly influence pesticide degradation. Washing experiments, simulating rainwater washing, were conducted on five common vegetables from four families - cruciferous, Asteraceae, Chenopodiaceae, and Amaranthaceae - and demonstrated that the residue rate of imidacloprid in vegetables with added organic water-soluble fertilizer decreased.

This decremental phenomenon was conspicuously manifest in cruciferous species, insinuating singular interplays between their ceraceous exteriors and the active moieties of the nourishment. In summation, this investigative endeavor, wielding a quintessential organic hydrophilic nourishment in tandem with a conventional insect deterrent, riveted its focus upon its prowess to catalyze pesticide degradation. The empiricism affirms that such nourishments can be instrumental in attenuating imidacloprid remnants, thus fortifying the theoretical edifice of nourishment and pesticidal integration. While this scholarly pursuit bequeaths seminal empirical foundations, the clarion call for additional investigative depth remains, aimed at unraveling the intricate tapestry underpinning pesticidal residue diminution via organic nourishments. Nuances encompassing optimal nourishment matrices, dosage interplays, and temporally calibrated applications warrant exploration across an expansive spectrum of pesticidal-crop dyads. The symbiotic deployment of pesticidal agents and nourishments, especially those of the hydrophilic foliar ilk, looms as an indomitable fulcrum in the odyssey toward agronomic modernization.

The seamless integration of plant nutrition, plant protection, health concerns arising from pesticide use, and soil issues caused by fertilizers theoretically aligns with the developmental requirements of modern agriculture and supports the exploration and advancement of innovative agricultural technologies in the future.

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