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Field Assessment of Plant Growth Performance and Residue Persistence of Saponin-based Molluscicide Formulations

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ABSTRACT

This study evaluated the plant growth performance and environmental residue behaviour of saponin-based molluscicide formulations under field conditions. The findings were compared against two commercial chemical molluscicides: niclosamide and fentin acetate. Two saponin formulations, emulsifiable concentrate (EC) and wettable powder (WP) of saponin-based molluscicides, were applied at varying concentrations on rice crops, alongside chemical and water controls. Growth parameters, including plant height, tiller number, biomass, and harvest index, were recorded, while molluscicide residues were analysed in rice tissues, soil, and water using HPLC. Results showed no significant differences in growth performance among treatments. However, niclosamide exhibited the highest residue levels and most prolonged half-lives across all matrices, raising concerns over persistence and potential food safety risks. In contrast, saponin formulations demonstrated faster degradation with half-lives below 10 days and reduced environmental persistence. Despite detectable residues in polished grains, saponin is considered safe for human consumption due to its natural occurrence and rapid biodegradability. The findings supported the potential of saponin-based molluscicides as environment friendly alternatives to synthetic chemicals in rice cultivation. Further studies are recommended to improve formulation efficacy and understand their biochemical interactions with target pests.

Keywords: Apple snails, molluscicides residue, rice field, saponin

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INTRODUCTION

Pomacea maculata Perry, also known as the black apple snail, is one of the major pests that has drastically affected farmers in Malaysia's rice industry for decades. Due to their tremendous reproduction rate, they can now be abundantly spotted in all paddy fields throughout Peninsular Malaysia, igniting great concern in rice production and quality. Subsequently, they could trigger a greater threat to rice production due to their large size and great appetite (Arfan et al., 2014; Burks et al., 2011; Mokhtar et al., 2024). Various methods have been implemented to reduce the population of this pest, with chemical control being the most effective way to minimise them.

As technology in the agriculture industry advances, most farmers have decided that it is much easier to chemically control the apple snails' population in rice-growing areas by applying molluscicides to targeted areas. Additionally, chemical control is the most preferred approach in controlling pests due to its easy application, low labour costs, cost-effectiveness, and ability to kill pests quickly (Yigit & Velioglu, 2020). Metaldehyde, some carbamates such as methiocarb, niclosamide, and iron phosphate plus chelating agent were widely used as active ingredients in molluscicides (Andrews et al., 1982; Calumpang et al., 1995; Zhang et al., 2011). In Taiwan, metaldehyde, niclosamide, and triphenyltin acetate have been widely utilised for eradicating this invasive rice pest (Cheng & Kao, 2004; Wu et al., 2010). Applying chemical molluscicides reduced the number of apple snails but are highly toxic to non-target organisms such as fish and affected the environment (Roonjho et al., 2022; San Martín et al., 2008).

To assess potential phytotoxicity from molluscicides, key growth parameters (plant height, tiller number, and all rice cultivation stages) were monitored (DoA, 2008). Paddy cultivation has six stages. These include planting day (1-5 days), tillering stage (15-40 days), panicle initiation stage (40-69 days), heading stage (70-89 days), ripening stage (90-104 days), and harvest stage (105-112 days). These stages are identified and monitored through growth parameters, which are practical and fundamental in assessing the growth and tracking the health of the plants. They have also been used to estimate the final yield and act as a guide in decision-making regarding a suitable approach for the studied organism. These parameters are vital for assessing potential phytotoxicity caused by molluscicides on paddy plants by measuring plant height, number of tillers, fresh and dry weight of paddy straws and grains, total above-ground biomass, and harvest index. Phytotoxicity may affect plants' vigour by stunting the growth, leaf discolouration, chlorosis, necrosis, or yield decline (Dias, 2012).

Up to the present, rice research has focussed more on developing sustainable agricultural practices and restoring functional food webs for integrated pest management and nutrient cycling (Schmidt et al., 2015). However, the extensive use of pesticides has negatively impacted human and other life forms. Variations in pesticide residue levels in raw agricultural commodities are affected by several parameters, such as geographical locations, weather conditions, growing season, and growth rates (Fujita & Iijima, 2013). Ideally, a pesticide must be lethal to the targeted pests, but not to non-target species, including humans. Measuring pesticide residue levels in crops and aquatic life is vital for ensuring food safety. All assessed food must not exceed the maximum residue level (MRL) in the Codex, a guideline of the food code established by the FAO. Detecting and identifying various pesticide residues is becoming a significant public health concern and a vital procedure to be acknowledged as a guarantee of food safety (Hou et al., 2013; Teló et al., 2017; Zhang et al., 2011). While saponins are known, information on their field residue persistence and direct comparison with synthetics pesticides in a rice ecosystem is still lacking.

MATERIALS AND METHODS

Chemicals and Reagents

All standard compounds (saponin, niclosamide and fentin acetate) were purchased from the Thermo Fisher Scientific with more than 97% purity. HPLC grade acetone, acetonitrile (MeCN), and methanol (MeOH), analytical standard sodium chloride (NaCl), anhydrous magnesium sulphate (anhydrous $MgSO_4$), and Orthophosphoric acid were also acquired from the Thermo Fisher Scientific.

Treatments

Saponin emulsifiable concentrates, EC (T1), saponin wettable powder, WP (T2), two selected commercial molluscicides; niclosamide (T3) and fentin acetate (T4) as positive controls, and water (T5) as negative control, were used as treatments. All molluscicides were applied following the recommended rate, with five treatments.

Method Validation of Molluscicide Compounds

Quantification of saponin in molluscicide-containing saponin (Sapputra), niclosamide, and fentin acetate from commercial molluscicide compounds was done by referring to respective methods with modifications (Dong et al., 2017; Sun et al., 2012; Yang et al., 2003). The separation of saponin was executed using a C18 column, and the detection wavelength was set at 210 nm. The injection volume was 20 µL. A C18 column was used to quantify fentin acetate, and the detection wavelength was at 220 nm. The injection volume was 10 µL. Niclosamide was quantified using a C18 column with a 202 nm detection wavelength. The injection volume was 10 µL. For the recovery percentage, the values of spiked and unspiked samples were compared to evaluate the recovery and matrix effect in samples, accordingly. The percentage recoveries were determined by using the formula (Xu et al., 2012; Zaidon et al., 2019):

$$\text{Recovery percentage (\%)} = \frac{C_{spiked} - C_{unspiked}}{C_{added}} \times 100\% \qquad [1]$$

where C_{spiked} is the concentration of the target analyte measured in a spiked sample, $C_{unspiked}$ is the concentration of the target analyte measured in a blank sample, and C_{added} is the known concentration added to the sample.

Preparation of Stock Standard Solution

A stock standard solution of saponin, niclosamide, and fentin acetate was prepared at a concentration of 1000 ppm by dissolving 0.05 g of the respective standard in 10 mL of deionised water (saponin) and 10 mL of acetonitrile (niclosamide and fentin acetate) in a 50 mL volumetric flask. Then, intermediate working standard solutions were prepared by diluting the stock solutions in deionised water to obtain respective standards of 100 ppm. Finally, serial dilutions of the working standard solutions were prepared to obtain seven calibration solutions (50, 25, 10, 5, 1, 0.5, and 0.1 ppm) in deionised water. All the standard solutions were kept in scintillation vials at 4°C in the refrigerator.

Sample Preparation

The rice plants were ground into powder form using a table-type smashing machine. This step was crucial as it increased the surface area of the materials and helped facilitate solvent penetration into the cells. The material that passed through an 80-mesh screen was used for extraction purposes. The powder was kept in an airtight plastic bag in a refrigerator at 6 ± 1 ºC with 5% to 85% relative humidity for further analysis. Using a soil sampling apparatus, 200 g of soil sample was collected randomly at ten different sampling points in each plot with a zero to ten cm depth (Ma et al., 2012; Zhang et al., 2011). Stone and plant debris were manually removed, and the soil samples were stored at -20 ºC for further analysis. A 100 ml water sample was collected at intervals for each plastic container. Water samples were filtered using filter paper and concussion extraction before being reconstituted in 5 mL HPLC methanol for HPLC analyses (Huang et al., 2013).

Extraction of Rice and Soil Samples

Rice (1 g) and soil samples (5 g) were weighed separately in a 50 mL Teflon centrifuge tube, and an adequate standard was added to these blank samples. The centrifuge tubes with spiked samples were vortexed for 1 min. They were allowed to stand for 2 hours at room temperature to distribute and interact the molluscicide evenly with the sample matrix. 10 mL of acetonitrile was added to each centrifuge tube. After the tube was shaken vigorously for 10 min, 1 g NaCl and 4 g anhydrous $MgSO_4$ were added to the centrifuge tubes and again shaken for 5 min. Followed by centrifugation (4000 rpm, 5 min) of the sample containing centrifuge tubes, 1.5 mL of the upper layers (acetonitrile) supernatant was transferred to a 2 mL centrifuge tube containing 150 mg of $MgSO_4$ and 75 mg of Florisil for rice and 150 mg of $MgSO_4$ and 75 mg of C18 for soil samples, accordingly. Afterwards, the centrifuge tubes were vortexed for 1 min and centrifuged for 5 min at 5000 rpm. Finally, the upper acetonitrile layer was filtered from the individual tube through a 0.22 µm hydrophilic PTFE filter and transferred to an autosampler vial for HPLC analysis (Kaium et al., 2018).

Then, a 10 mL water sample was added to 50 mL Teflon centrifuge tubes, and the standard was added to the water samples. The centrifuge tubes were vortexed for 1 min and allowed to stand for 20 min at room temperature. Next, 10 mL of acetonitrile was added to each centrifuged tube and vortexed vigorously for 2 min. After the addition of 4 g $MgSO_4$ and 1 g NaCl, the tubes were immediately vortexed vigorously for 2 min and centrifuged for 5 min at 4000 rpm. Lastly, 1.0 mL of the supernatant (acetonitrile) from each tube was transferred into an autosampler vial with a 0.22 µm hydrophilic PTFE filter for HPLC analysis.

Data Collection and Analysis

Growth quality data, including plant height, number of tillers, fresh and dry weight of paddy straw and grain, total above-ground biomass, harvest index, and soil and water pH, were recorded during the field assessment. Total above-ground biomass and harvest index were derived by using the following formula (Saito et al., 2023):

$$\begin{array}{c}\text{Total above-ground}\\ \text{biomass (kg/ha)}\end{array} = \begin{array}{c}\text{Dry weight of grains}\\ \text{(kg/ha)}\end{array} + \begin{array}{c}\text{Dry weight of straws}\\ \text{(kg/ha)}\end{array} \quad [2]$$

$$\text{Harvest index} = \frac{\text{Dry weight of filled grains (kg/ha)}}{\text{Total above-ground biomass (kg/ha)}} \quad [3]$$

Residue level, degradation rate of molluscicides, half-lives, and maximum residue level (MRL) were recorded afterwards. The degradation rate refers to the time required for 50% of the initial dose of pesticides to dissipate or break down into simpler compounds or metabolites in the environment (Kah et al., 2007). It is also referred to as the first-order half-life or DT50. Degradation rate and half-lives of molluscicides were calculated using the following formula (Graebing et al., 2004):

$$C_t = C_0 e^{-kt} \quad [4]$$

Where:

C_t= concentration of pesticide at time t

C_0 = initial concentration of pesticide

k = degradation rate constant (in time^{-1}

t = time (typically in days).

Meanwhile, the degradation rate constant (k) was obtained using the formula:

$$k = \frac{\ln (C_0) - \ln (C_t)}{t} \quad [5]$$

Half-life was calculated as follows:

$$t_{1/2} = \frac{\ln (2)}{k} \quad [6]$$

The statistical significance between molluscicide treatments was interpreted by an Analysis of Variance (ANOVA) test using the Statistical Analysis System 9.4 (SAS).

RESULTS AND DISCUSSION

All graphs showed linear and reproducible calibration curves, with the R^2values nearly approaching 1 (saponin: 0.9971, niclosamide: 0.9991, and fentin acetate: 0.9991). These values indicated that the responses of the HPLC detector towards residues of all compounds were good, where the linearity factors were at $R^2 > 0.99$. The retention times obtained from HPLC analysis for saponin, niclosamide, and fentin acetate were 2.9, 4.3 and 5.3 min, respectively, showing a slight difference compared to reference retention times. However, Sun et al. (2017) explained that the actual chromatogram may vary from the reference chromatogram due to factors such as the type of columns used, flow rates, and the mobile phase. These factors may contribute to the difference between measured and predicted retention time. In addition, the recovery of saponin for grains, leaves and stems, water and soil ranged from 58% to 118% whereas for niclosamide, the percentage values ranged from 71.3% to 113.9%, respectively, as shown in Table 1. Meanwhile, for fentin acetate, all samples' recovery ranged from 71.3% to 94.1%. The recovery results were acceptable, compared to the guidelines for residue analysis quality control (Corley, 2003; Fitri et al., 2017). The percentage of recovery values accepted at the global stage was between 60% and 140% (Pihlström et al., 2021). It is recommended that when outliers are identified, they should be excluded from the statistical calculation of the mean, SD and RSD, with justification and statistical significance. Nevertheless, all individual recovery data (including those excluded) should be reported (Fitri et al., 2017). Hence, the extraction methods were validated and used to determine paddy, soil, and water compound residues.

No significant ($p \leq 0.05$) differences were observed among treatments for all measured growth parameters (plant height, tiller count, biomass, and harvest index) at any sampling stage (Table 2). The average plant height ranged from 126.7 to 118 cm for all treatments, respectively. However, the plant treated with niclosamide (T3) gave the lowest reading in plant height. Paddy plants treated with the negative control treatment (T5) showed the highest number of tillers, with 24 tillers during 110 DAA. This was followed by T2

Table 1
The average recoveries of molluscicides in rice plants, soil and water (value within the range 60-140% is considered as reliable (Pihlström et al., 2021))

Molluscicides	Spiking level (ppm)	Mean value of molluscicides recovery (%)			
		Leaves	Grain	Soil	Water
Saponin	0.5	78	58	89.6	80.1
	1	76	119	71	82.1
	5	118	64.7	104	94.0
Niclosamide	0.5	71.3	75.7	113.9	94.9
	1	76.8	81.3	90.2	96.5
	5	83.2	84.5	93.9	112.8
Fentin acetate	0.5	94.1	86.1	82.1	70.9
	1	88.7	91.2	81.9	71.3
	5	92.2	84.7	80.5	79.4

(saponin WP) and T4 (fentin acetate), with 22 and 21 tillers, respectively, indicating better branching and potential productivity for these treatments. Meanwhile, the lowest number of tillers was detected in the sample treated with niclosamide, 17 tillers. There were no significant differences between treatments for fresh and dry weight of paddy straw and grains, the total above-ground biomass, and harvest index.

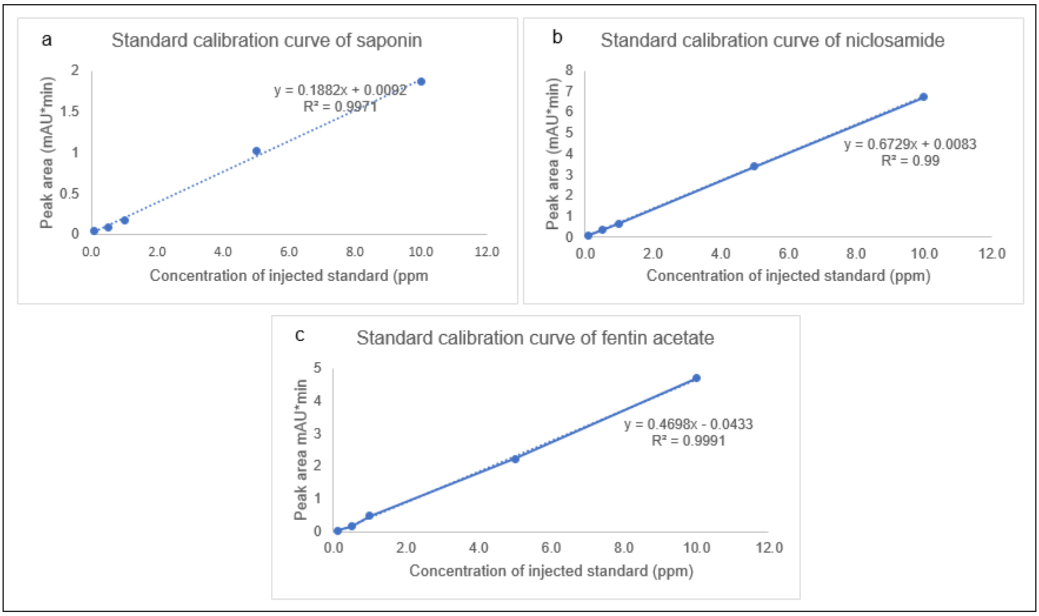

Figure 1. Standard calibration curve of (a) saponin, (b) niclosamide, and (c) fentin acetate

Ramli et al. (2019) stated that observing paddy growth through plant height, width of leaves, number of leaves, and number of tillers is crucial in determining the harvest yield. Overall, good performance of paddy growth contributed to high grain yield harvested (Kamarulzaman et al., 2017; Ramli et al., 2018). As mentioned in Table 2, the highest plant height and number of tillers were exhibited in T5 (water, negative control), but it gained almost a similar yield compared to other treatments. Tillering capacity may influence the yield potential of a paddy cultivar (Krishnan et al., 2011; Yoshida, 1973). Generally, paddy plants with more tillers may experience a greater inconsistency in the nutrient distribution among tillers, leading to a dissimilar pattern in grain development and yield between tillers (Krishnan et al., 2011; Yoshida, 1973).

Residue levels in paddy straws and grains, soil, and water samples collected from the field assessment were determined by HPLC and shown in Table 3, 4, and 5, respectively. These results were based on the findings of Aktar et al. (2009), in which pesticide residues were discovered in soil, air, surface, and groundwater across the plant cultivations. Subsequently, the residue levels decreased over time as the volatilisation of the compound took place. During harvest, which was at 110 DAA, plants treated with niclosamide (T3) exhibited the highest residue with 86.0 ppm in paddy straw, followed by T2 (74.3 ppm), T4 (66.0 ppm), and T1 (48.0 ppm). The highest declination regarding residue dissipation was observed in T1 (saponin EC), as it lost 2,091.7 ppm throughout the assessments, from 30 to 110 DAA. This declination was probably due to a more volatile compound than other molluscicide compounds.

Referring to Table 3, compound residues were determined in unpolished and polished grain. Residue levels in unpolished grain at 110 DAA showed T2 (90.0 ppm) having the highest residue, followed by T1 (72.7 ppm), T3 (72.0 ppm), and T4 (71.3 ppm). However, these measurements were statistically similar, with no significant residual level differences across the treatments. Polished grain residues showed a general reduction compared to unpolished grain. Treatment 3 (37 ppm) had the highest residue, followed by T2 (26.7 ppm), and then T4 (21.0 ppm). Apart from that, the half-life data reflected how long it took for the pesticide residue to degrade to half of its initial concentration. Both positive controls represented the most prolonged half-life recorded during the assessment, in which T4 (fentin acetate) had an approximate half-life of 70 days, followed by niclosamide (T3) at 32 days. For saponin formulations, both showed a short half-life of less than ten days.

Detecting pesticide residues in food commodities has significantly hindered international trade (Bajwa & Sandhu, 2014). The migration of pesticide compounds into the grains may occur based on their chemical characteristics, the concentration of pesticides used and other biotic and abiotic conditions. According to recommendations, pesticides should only be present on the outer layer and eliminated during grain milling, mostly in coproducts such as bran and husk (Dors et al., 2011). In this assessment, molluscicide residues still existed

Table 2
Growth data of paddy plants and grains between molluscicide treatments

Treatment	Plant										Grain		Harvest index	Total above biomass (kg/ha)
	Average plant height (cm)				Average no of tillers				Fresh weight (kg)	Dry weight (kg)	Fresh weight (kg)	Dry weight (kg)		
	30 DAA	60 DAA	90 DAA	110 DAA	30 DAA	60 DAA	90 DAA	110 DAA						
T1	46.8 a	93.8 ab	111.9 a	118.6 a	11 a	19 bc	19 bc	19 bc	1.32 a	0.59 a	0.71 a	0.46 a	0.44 a	1.04 a
T2	44.4 a	89.5 b	116.6 a	121.3 a	13 a	22 ab	22 ab	22 ab	1.45 a	0.52 a	0.65 a	0.45 a	0.46 a	0.97 a
T3	45.1 a	95.3 a	114.2 a	118.0 a	11 a	17 c	17 c	17 c	1.14 a	0.40 a	0.77 a	0.45 a	0.53 a	0.85 a
T4	46.6 a	95.8 a	115.9 a	119.4 a	12 a	21 abc	21 abc	21 abc	1.37 a	0.54 a	0.87 a	0.66 a	0.55 a	1.2 a
T5	48.5 a	91.8 ab	118.8 a	126.7 a	13 a	24 a	24 a	24 a	1.07 a	0.48 a	0.93 a	0.56 a	0.54 a	1.04 a

Note: Means comparison followed by the same letters are insignificant among types of molluscicides against residue level at $p \leq 0.05$, according to Tukey's.
*Note that DAA is the day after the application. (T1= Saponin EC, 23 333.33 ppm, T2= Saponin WP, 23 333.33 ppm, T3= Niclosamide EC, 3 300.00 ppm, T4= Fentin acetate WP, 01 118.5 ppm, T5= Water)

Table 3
Average amount of residue, half-life, and degradation rate of paddy straw, polished, and unpolished grains from field assessment

Treatment	Residue in paddy straw (ppm)		Unpolished grain (ppm)	Polished grain (ppm)	Half-life (day)	Degradation rate constant ($days^{-1}$)
	30 DAA	**110 DAA**	**110 DAA**	**110 DAA**		
T1	2109.7 a	48.0 b	72.7 a	18.0 bc	9	0.08
T2	1632.3 a	74.3 ab	90.0 a	26.7 ab	8	0.09
T3	1724.7 a	86.0 a	72.0 a	37.0 a	32	0.02
T4	1574.0 a	66.0 ab	71.3 a	21.0 ab	70	0.0099
T5	0 b	0 c	0 b	0 c	-	-

Note: Means comparison followed by the same letters are insignificant among types of molluscicides against residue level at $p \leq 0.05$, according to Tukey's. *Note that DAA is the day after the application. (T1= Saponin EC, 23 333.33 ppm, T2= Saponin WP, 23 333.33 ppm, T3= Niclosamide EC, 3 300.00 ppm, T4= Fentin acetate WP, 01 118.5 ppm, T5= Water)

in the Polish grain and exceeded the MRL permitted in food. The MRLs for niclosamide and fentin acetate in rice were 2 mg/kg and 5 mg/kg, respectively (China Food and Drug Administration, 2017). As for Malaysia, if there is no established national MRL, CODEX MRLs will be first adopted, followed by MRLs established by the Association of Southeast Asian Nations (ASEAN). If neither administration has established MRLs, a default MRL of 0.01 ppm will be applied. Hence, it can be concluded that all compound residues obtained from this study exceeded the MRL stated by the administration, which is not suitable for human consumption in the long term. However, even though saponin residues are high in the grains, it is considered safe to be consumed as saponin is rapidly dissipated and broadly found in many plants used for the daily diet and medicinal purposes for humans (Oleszek & Oleszek, 2020; Sharma et al., 2023).

Data from Table 4 demonstrated the soil sample's residue level, half-life, and degradation rate constants. There were significant differences between treatments at 7, 30 and 110 DAA. The soil treated with niclosamide (T3) had a high initial residue at 7 DAA (6,012.3 ppm). At 110 DAA, the residue value was high at 1,373.7 ppm, showing slower degradation. Additionally, the long half-life of 35 days and the low degradation rate constant (0.02) indicated a slower degradation compared to T1 and T2, suggesting the persistence of niclosamide in the soil. On the contrary, T4 (fentin acetate) had the highest residue (6,981 ppm at 7 DAA) but experienced a sharp decline from 110 DAA to 1,093 ppm. Despite the high initial residue, the relatively short half-life of 11.3 days and a high degradation rate constant (0.06) suggest a faster breakdown than other treatments.

Meanwhile, the residue values in water significantly differed between treatments at 30, 60 and 110 DAA, as shown in Table 5. As per result, saponin WP (T2) residue was slightly

Table 4
Average amount of residue, half-life, and degradation rate of soil sample from field assessment

Treatment	Soil residue (ppm)					Half-life (day)	Degradation rate constant (day^{-1})
	7 DAA	30 DAA	60 DAA	90 DAA	110 DAA		
T1	4 975.0 b	4 389.7 b	3 110.0 a	1 689.7 a	431.3 c	13	0.05
T2	5 413.0 ab	3 700.7 b	2 431.7 a	1 413.7 a	978.0 b	14	0.049
T3	6 012.3 ab	4 801.0 b	2 723.7 a	2 211.0 a	1 373.7 a	35	0.02
T4	6 981.0 a	6 596.7 a	3 310.7 a	2 134.3 a	1 093.0 ab	11	0.06
T5	0 c	0 c	0 b	0 b	0 d	-	-

Note: Means comparison followed by the same letters are insignificant among types of molluscicides against residue level at $p \leq 0.05$, according to Tukey's. *Note that DAA is the day after the application. (T1= Saponin EC, 23 333.33 ppm, T2= Saponin WP, 23 333.33 ppm, T3= Niclosamide EC, 3 300.00 ppm, T4= Fentin acetate WP, 01 118.5 ppm, T5= Water)

Table 5
Average amount of residue, half-life and degradation rate of water sample from field assessment

Treatment	Water residue (ppm)					Half-life (day)	Degradation rate constant (day^{-1})
	7 DAA	30 DAA	60 DAA	90 DAA	110 DAA		
T1	8 065.7 a	5 078.7 b	3 261.7 b	1 837.7 a	326.7 ab	19	0.035
T2	6 911.3 a	5 765.0 b	3 402.3 b	1 919.0 a	707.3 a	17	0.04
T3	7 688.7 a	6 051.7 ab	3 988.0 b	2 297.7 a	684.0 a	25	0.02
T4	8 140.7 a	7 369.0 a	5 667.7 a	3 214.0 a	459.3 ab	11	0.07
T5	0 b	0 c	0 c	0 b	0 b	-	-

Note: Means comparison followed by the same letters are insignificant among types of molluscicides against residue level at $p \leq 0.05$, according to Tukey's. *Note that DAA is the day after the application. (T1= Saponin EC, 23 333.33 ppm, T2= Saponin WP, 23 333.33 ppm, T3= Niclosamide EC, 3 300.00 ppm, T4= Fentin acetate WP, 01 118.5 ppm, T5= Water) higher than T1 at 110 DAA, suggesting slower breakdown at later stages despite its faster rate in the early period. T3 (niclosamide) showed the slowest degradation, with 684 ppm remaining by 110 DAA. The long half-life of 25 days and a low degradation rate constant of 0.02 suggest a much slower degradation than other treatments. Meanwhile, T4 initially had the highest residue (8 140.7 ppm at 7 DAA) but showed rapid degradation, with 459.3 ppm remaining at 110 DAA. It exhibited the fastest degradation among other treatments, with the shortest half-life of 11 days and the highest degradation rate constant of 0.07.

As given in Tables 4 and 5, the residue in soil was relatively higher than the residue in water at 110 DAA. This condition proves the dissipation theory of chemical compounds from water to soil in most field studies regarding various crops, making the soil more acidic and infertile in the long term. Similar results were obtained in a study by Tang et al. (2018) in which pyrethroid (synthetic organic insecticide) residues were relatively higher in sediments than in surface water. As explained by Vryzas (2018), the dissipation of pesticides can be induced physically, chemically and biologically, including volatilisation, absorption by soil colloids or transported off-site through surface runoff and leaching. These processes may influence the quantity of each pesticide detected in soil, sediments, or water bodies. According to Zhang et al. (2012), pesticide residues in soil raise several potential harmful effects, such as adverse impact on subsequent crops and groundwater contamination. Pal et al. (2006) also stated that pesticide residues may affect non-target soil microorganisms, thus impairing the pesticide degradation process and eventually inducing its persistence in soil.

Biopesticides are biodegradable, which enables them to decompose rapidly and does not severely affect surface and ground water (Alliance, 2015). This statement is based on the findings from this field assessment, which found that saponin residues were lower than niclosamide residues in paddy straws, grains, soil, and water. In addition, Frank et al. (2002) suggested that the half-life of niclosamide should be 2 to 5 times longer in dry soil compared to those in moisture-maintained soil. This is probably the cause of the persistence of niclosamide in dry conditions, as there is a low risk of water leaching and runoff of materials. Likewise, the half-life of soil exposed to fentin acetate obtained from field assessment was 11 days, which is similar to the study done by Yen et al. (2001), who discovered a shorter half-life of fentin acetate of 8.3 to 19.4 days in clay loam soil. In contrast, Paton et al. (2006) assessed the half-life of fentin acetate to be 27 and 33 hours in non-sterile soil. In the past, as suggested by Loch et al. (1990), the half-life of fentin acetate ranged from 47 to 140 days, depending on the soil type. Hence, it is vital to monitor the dissipation of pesticides in soil and water due to their significant and severe impacts towards paddy growth, as they can hinder some key parameters that may impose a decline in grain yield afterwards. The mechanism behind the effect of saponin molluscicides towards apple snails using biochemical approaches must be further studied for better understanding and substantial evidence on the biochemical pathways of saponin intervention towards the internal system of apple snails.

CONCLUSION

All growth and residue parameters of rice exposed to different concentrations of saponin-based molluscicides were assessed. From the result obtained in this experiment, it can be concluded that niclosamide (T3) demonstrated the highest amount and most prolonged half-life of compound residues in paddy straw, polished grains, soil, and water. Both saponin formulations exhibited a higher dissipation rate as they lost 50% of their residue in less than 10 days, compared to niclosamide and fentin acetate, which need more time to dissipate by half. Therefore, saponin-based formulations are suitable as an alternative approach to control the apple snails and minimise the application of chemical molluscicides for rice cultivation in Malaysia. Additional research is recommended to refine saponin-based formulations further, optimising their concentrations, and application methods for different agricultural settings. This will help maximise pest control efficacy while reducing costs and labour inputs for farmers.

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