Research Article

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Validation of a small-scale portable rainfall simulator on the simultaneous transport of sediments and pesticides in agriculture soils

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Abstract

BACKGROUND: Soil erosion and sedimentation accelerate land degradation, especially in East Asia. Surface runoff is a major pathway for pesticide transport into surface and groundwater, threatening aquatic ecosystems. This study investigated the runoff rate, sediment yield, pesticide transport, and pesticide concentrations across soil layers using a small-scale portable rainfall simulator (0.33 × 0.48 m) under laboratory and field conditions.

RESULTS: Cumulative sediment runoff reached 2.1 and 2.3 ton ha^{-1} in laboratory and field simulations, respectively. Maximum pesticide concentrations under laboratory conditions were 1.3 mg kg^{-1} (fipronil), 2.34 mg kg^{-1} (clothianidin), and 0.17 mg kg^{-1} (imidacloprid); field results were comparable. Over 2% of applied pesticides dissolved in runoff, while <1.2% adhered to soil particles. Fipronil exhibited the highest losses in runoff, posing acute toxicity risks for aquatic organisms, with toxicity unit values exceeding safe thresholds for bluegill sunfish.

CONCLUSION: Pesticide losses depend on solubility and soil adsorption. Fipronil, despite limited soil movement, poses significant aquatic toxicity risks compared to imidacloprid and clothianidin. This study highlights the role of portable rainfall simulators in understanding pesticide transport and provides valuable insights for mitigating the environmental risks of pesticide use.

Supporting information may be found in the online version of this article.

Keywords: runoff; soil erosion; rainfall; pesticides; contaminants

1 INTRODUCTION

Pesticides are essential components of high-input farming to expand agricultural production around the world. Although intensive pesticide use has improved agricultural production efficiency, it has also brought several negative impacts.[1] Despite the enormous amounts of pesticides used on crops, only a limited portion reaches the target pests.[2] Pesticides are lost either directly during spraying or indirectly through volatilization from plants and soil surfaces, leaching in soil, and runoff.[3–5] As a result, significant amounts of pesticides are discharged into lakes, rivers, and groundwater in agricultural watersheds, potentially affecting human health and ecosystems.[6] Imidacloprid, clothianidin, and fipronil are broadly used in fields such as veterinary medicine, forestry, urban gardening, and horticulture.[7,8] Sales of many individual neonicotinoid products have recently risen by 1.6–14.6 times, with overall sales increasing by 2.45 times.[9] Imidacloprid and clothianidin are systemic insecticides, while fipronil provides effective pest control primarily through contact and ingestion.[7,8] Several studies have demonstrated that neonicotinoid insecticides and fipronil are mobile in sediments and soils, with a high potential for runoff, leaching, and surface contamination.[10–12] Laboratory studies have shown that they can be directly toxic to non-target organisms.[13–17] Leaching and runoff of these pesticides from agricultural soils have resulted in the pollution of wetlands.[18–20] Many factors influence pesticide loss by surface runoff; these include properties of the pesticide and soil, climatic factors such as precipitation and evapotranspiration, topographical

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features, and the time between the pesticide application and the first rainfall occurrence.[21] Therefore, understanding the mechanisms that govern the transport of pesticides from agricultural fields to water resources is essential for mitigating pesticide discharge and ensuring appropriate usage of pesticides.

Soil erosion is also considered to be among the most significant challenges to the sustainability of natural ecosystems and has been recognized as the most prevalent cause of land degradation in East Asia, particularly in Japan and Thailand.[22–25] Annually, wind and water remove 75 billion metric tons of soil from the land, much of which is from farmland.[26] Soil erosion is a complex process that involves the detachment and outflow of topsoil from farmland, mainly due to water and wind. Moreover, the fine sediment eroded from agricultural fields that is carried to downstream areas may degrade aquatic ecosystems,[27–29] therefore there is a need to evaluate the dynamics of soil erosion.

Several studies have stated that the magnitude and frequency of pesticide pollution should be monitored through exposure evaluations.[9,16,30–32] It is also essential to understand the degradation and migration of pollutants to assess mitigation strategies and minimize the risks to non-target areas and organisms. Rainfall and the resulting runoff are dynamic processes that cause the transport and migration of sediment and agricultural chemicals from farmland to watersheds.[18,30] Many studies have emphasized the importance of understanding the relationship between rainfall and soil conditions with respect to runoff, as it reveals the dynamic fates of non-point sources of chemicals and sediment from agricultural soils.[33] Rainfall simulation has become an effective technique for conducting *in situ* and laboratory experiments to characterize the factors governing soil erosion and chemical transport.[30,34] The transport and fate of fipronil, imidacloprid, and clothianidin in urban applications have been studied minimally. Yadav and Watanabe[31] estimated the transport and fate of clothianidin and imidacloprid under a plot-scale rainfall simulator for a 1 × 5 m plot. However, the transport and leaching of fipronil under rainfall simulation have yet to be investigated.

Furthermore, this plot-scale rainfall simulator requires more time for setup and transportation, and a significant amount of water for the rainfall simulation. Instead of plot-scale (1 × 5 m) rainfall simulator trials that are challenging, time-consuming, and labor-intensive, rainfall simulations performed on small field plots (0.33 × 0.48 m) could provide valuable data. Moreover, small portable rainfall simulators offer advantages, including easy transport to inaccessible areas, lower cost, reduced water consumption, and the ability to collect data in a timely and organized manner within a short period.[34–36] Our previous study, by Saber *et al*.,[4] illustrated the small-scale portable rainfall simulator in simulating rainfall-induced runoff and transport of radioactive substances. This study hypothesizes that the small-scale portable rainfall-runoff simulator developed can generate realistic and comparable results to large-scale simulations, effectively capturing runoff, sediment yield, and pesticide transport dynamics. This hypothesis is based on the assumption that the simulator's design allows precise control of rainfall intensities and uniformity, making it suitable for environmental studies under both laboratory and field conditions. The objectives of this study were (1) to test and validate the performance of the small-scale portable rainfall-runoff simulator by comparing results under laboratory and field conditions, (2) to investigate the rate of runoff, sediment yield, and pesticide transport dynamics using the simulator, (3) to evaluate the downward mobility of the target pesticides (fipronil, clothianidin, and imidacloprid) in soil layers under simulated conditions, and (4) to provide insights into the potential environmental risks of pesticide and sediment transport, and their implications for aquatic ecosystems.

2 MATERIAL AND METHODS

2.1 Pesticides and reagents

Reference standards of clothianidin, imidacloprid, and fipronil were obtained from Wako Pure Chemical Industries (Tokyo, Japan), with a purity exceeding 99%. Analytical-grade solvents, including acetone, acetonitrile, methanol, and dichloromethane, were procured from Wako Pure Chemical Industries (Osaka, Japan) in HPLC-grade quality. Ultra-pure water was prepared using a Millipore system. Additionally, anhydrous magnesium sulfate, sodium chloride, and sodium sulfate were purchased in analytical grade from Wako Pure Chemical Industries (Osaka, Japan). The magnesium sulfate was activated by heating at 400 °C for 4 h in a muffle furnace and stored in desiccators prior to use. Primary secondary amine (PSA) and graphite carbon black (GCB) sorbents were sourced from Supelco (Bellefonte, USA).

The pesticides used in this study included clothianidin (trade name: Dantotsu, 16% SC), imidacloprid (trade name: Admire, 20% FL), and fipronil (trade name: Prince, 5% FL). Each formulation was applied at the recommended application rates of 134.4 g ai ha^{-1} for clothianidin, 330.6 g ai ha^{-1} for imidacloprid, and 71.9 g ai ha^{-1} for fipronil. These formulations were selected based on their availability in the local market and were applied according to the surfaces indicated in the product literature. The physicochemical properties of the pesticides are summarized in Table 1.

2.2 General design and characteristics of the rainfall simulator

In this study, a rainfall simulator was designed to generate controlled events in the laboratory or the field. The specific structure of the system was described previously.[4] This small-scale rainfall simulator is designed to provide consistent rainfall intensity and distribution, is fully portable, is constructed from low-cost and readily available materials, and requires minimal operation. The main components of the proposed rainfall simulator are a stainless-steel structural frame, droplet box, water supply system, lysimeter/plot frame, and two fans to homogenize rainfall distribution (Fig. 1). The rainfall uniformity, drop size, and kinetic energy at a rainfall intensity of 50 mm h^{-1} were measured following the procedure described in the previous report,[4] as outlined in the Supporting Information, Text S1.

2.3 Study design of the rainfall catchment areas

2.3.1 *Packed soil in the laboratory*

A micro lysimeter was used as a test plot, packed with Andisol upland soil. In this study, soil samples were taken from the trial farm of the Tokyo University of Agriculture and Technology (TUAT, Tokyo, Japan). The soil was collected from the surface layer (0–5 cm), then air-dried and crushed to pass through a 2-mm sieve to remove non-decomposed plant residues and large particles. The soil was packed in three replicates of lysimeters carefully and systematically to achieve a uniform density. At the bottom of each lysimeter, a 2-cm layer of glass beads provided a drainage system for collecting percolating water. The soil and glass beads were separated using two layers of 60-mesh stainless-steel mesh, serving as a static barrier within the experimental setup. The lysimeter (33 cm wide × 48 cm long × 13 cm high) was divided into five layers: four were 3 cm thick, and one was 1 cm thick, as

Table 1. Physical–chemical properties and toxicity of studied pesticides

Item	Fipronil	Imidacloprid	Clothianidin
Trade name	Prince	Admire	Dantotsu
Chemical class	Phenylpyrazole	Neonicotinoid	Neonicotinoid
Solubility in water (mg L^{-1})	1.9	610	304
Soil–water partitioning coefficient (K_d) (L g^{-1})	25	11	6.2
Stable to hydrolysis	PH 5–7	PH 5–11	PH 4.5–9
Octanol–water partition coefficient (log K_{ow})	4.0	0.57	0.7
Vapor pressure (mpa)	4×10^{-7}	4×10^{-7}	1.3×10^{-4}
Formulation used	5% Flowable (FL)	20% Flowable (FL)	16% suspension concentrate (SC)
Rate of application (g ai ha^{-1})	71.9	330.6	134.4
96-h LC_{50} *Lepomis macrochirus* (μg L^{-1})	83	105 000	117 000
48-h LC_{50} *Daphnia magna* (μg L^{-1})	190	850 000	>100 000

Physical property data is provided to ChemIDplus by SRC, Inc. The source of data information is from Bower and Tjeerdema (2020),[37] Clean Production Action (2015),[38] and Thuyet *et al.*[7]
FL; Flowable, SC; suspension concentrate.

Figure 1. The rainfall simulator.

shown in Supporting Information, Fig. S1. The soil in each layer was uniformly spread by hand over the lysimeter, followed by tamping with a wooden block. Water was added to each soil layer separately to achieve consistent water content and bulk density, similar to field conditions. The soil water content was set at 0.435 (±0.056) $cm^3\ cm^{-3}$, and the target bulk density was 0.683 g cm^{-3}. These values were measured at a depth of 0–5 cm at the soil's field capacity after 24 h of water saturation. Finally, the micro lysimeters were positioned with a 5% slope using a wooden block.

2.3.2 *Undisturbed soil in the field*

The field experiments were conducted in three uncultivated plots at the TUAT experimental farm. The soil was tilled before setting up the experimental plots. Stainless-steel frames were used to define the plot size, which was 1584 cm^2 (33 × 48 cm). The 5% slope was established using a spirit level and positioning the frame so that the outlet was at the lowest point. These plots were set up to avoid cross-contamination, with approximately 1-m wide buffer spaces between them (Supporting Information, Fig. S2). The runoff collector was attached to the plot frame after pounding the frame into the soil to collect surface runoff. At the lower end of each plot, a ditch was dug to collect runoff water. All plots were watered before the rainfall event by spraying with tap water until soil saturation was reached, then left for 24 h to measure the field capacity. In this case, the gravimetric water content was 0.637 (g g^{-1}) and the bulk density was 0.683 (g cm^{-3}).

2.3.3 *Soil characteristics*

The texture of the soils used in the laboratory and field experiments was classified as clay-loam Andisol according to the Soil Taxonomic Order of the International Union of Soil Sciences. It contains 43% silt, 33% sand, and 23% clay. This soil is characterized by short-range minerals, high organic matter, and good physical properties.[39] Table 2 illustrates the physicochemical properties of the soil used for the experiments.

2.4 Pesticides application and rainfall experiment

Before pesticide application, the soil was moistened to approximately field capacity and hand-tilled to ensure a uniform surface. The pesticides were sprayed onto the lysimeter and plot frames using a hand sprayer at the recommended application rates (134.4, 330.6, and 71.9 g ai ha^{-1} for clothianidin, imidacloprid, and fipronil, respectively). These rates were based on local agricultural practices in Japan, as outlined in the literature (e.g., Yadav and Watanabe[31]). Following application, the lysimeters and field plots were covered with plastic sheeting for 24 h to allow proper adsorption and minimize external interference.

Rainfall simulations were conducted 24 h after pesticide application under controlled conditions, with low wind speeds to prevent spray drift. The simulations replicated natural precipitation intensities observed in Tokyo, Japan, with an average intensity of 50 mm h^{-1}, corresponding to a 15-year return frequency.[4,7,40] Each simulation was conducted for 60 min to mimic real-world rainfall scenarios and assess pesticide transport.

2.5 Runoff monitoring and sample collection

Samples of runoff sediment were collected using well-cleaned and dried 1-L glass containers. The runoff was sampled for 10 min after it began and then every 10 min for a total of 60 min. The runoff rate (mm h^{-1}) was calculated based on the water volume and the sampling duration. Once the rainfall experiment was completed, all runoff-sediment suspensions were transported to the laboratory and vacuum-filtered (Whatman GF/C, 0.45 μm pore size, Cytiva, Japan) to separate the liquid phase from the sediment. After filtering, the sediment was dried in an oven at 105 °C for 24 h, and the amount of eroded sediment was measured gravimetrically. Meanwhile, soil samples were collected before and after the artificial rainfall to estimate the downward movement of the studied pesticides in the soil. Before the rainfall simulation, soil samples from the top 0–1 cm layer were collected from the laboratory and field plots. After the rainfall experiment, 24 soil-core samples were taken from each plot (lysimeter and plot frame) at depths of 0–1, 1–5, 5–10, and 10–13 cm (Supporting Information, Fig. S3). Before analysis, these samples were stored in small Ziploc plastic bags at −20 °C. All chemical analyses were completed within 7 days.

Table 2. Physicochemical properties of soil

Parameter	Value
Soil type	Andisol
Soil texture (International Union of Soil Sciences (ISUSS)	Clay loam
Average porosity	0.79%
PH	5.8
Organic carbon content	6.95%
Silt	43%
Sand	33%
Clay	23%
Cation exchange capacity (meq/100 g)	34.1
Specific gravity (mg m^{-3})	2.50
Bulk density (g cm^{-3})	0.683
Slope	5%

2.6 Analytical procedures

Pesticides were extracted from the filtered water phase using liquid–liquid extraction. A 200-mL water sample was extracted twice with 50 mL of dichloromethane. Anhydrous sodium sulfate was then used to dry the combined extracts, which were subsequently evaporated to dryness. Meanwhile, the homogenized sediment or soil sample (5 g) was extracted using the QuEChERS technique with slight modifications, as described in Supporting Information, Text S2.

The target pesticides in the extracts were detected using a Shimadzu HPLC with a VP-ODS analytical column (150 × 4.6 mm i.d., 4.6 μm) equipped with an autosampler injector and photodiode array detector (DAD). The mobile phase was water/methanol 80:20 (v/v) for fipronil and water/acetonitrile 40:60 (v/v) for imidacloprid and clothianidin, with a constant flow rate of 1 mL min^{-1}. The injection volume for all samples and standards was 20 μL. The DAD operated at fixed wavelengths of 270, 265, and 280 nm for imidacloprid, clothianidin, and fipronil, respectively. Under these analytical parameters, the retention times for imidacloprid, clothianidin, and fipronil were approximately 7.21, 6.34, and 7.07 min, respectively.

2.7 Quality control and quality assurance

Rigorous criteria were applied to ensure quality assurance and quality control. The analytical method was validated following the EU guideline SANTE/11312/2021[41] for residue analysis, assessing its linearity, accuracy, precision (both repeatability and reproducibility), and limit of quantification (LOQ). Field and laboratory/solvent blanks were collected and analyzed according to the existing samples to monitor interferences and/or possible contamination caused during sampling, transport, and storage. Clean sample bottles were filled with tap water and untreated soils for the field blanks and then processed concurrently with the real samples.

The linearity of the method was assessed through linear regression analysis of standard solutions and matrix-matched calibration curves across six concentration levels, covering a range from 0.03 to 3 mg L^{-1}. To prepare samples for pesticide recovery studies, known doses of tested pesticides were added to control soil samples and de-ionized water. The method's accuracy was checked by routine recovery assay at three fortification levels (0.03, 0.5, and 1 μg g^{-1}) of the pesticide tested in soil and water samples and replicated five times alongside a control. The mean recovery for clothianidin, imidacloprid, and fipronil ranged from 83.2% to 95.3%, 89.4% to 101%, and 93.4% to 99.8%, respectively, for water, and 94.5% to 99.1%, 93% to 106%, and 97% to 101%, respectively, for sediments/soil (Supporting Information, Table S1).

Relative standard deviation (RSD%) values were used to describe the precision of the procedure, which was determined through repeatability and reproducibility tests. The repeatability relative standard deviation (RSD_r) was calculated by contrasting the recoveries from spiked samples that were tested on the same day. Analyzing six spiked samples on 6 days provided the reproducibility relative standard deviation (RSD_R). The maximum RSD_r value for all compounds was 9.3% in terms of repeatability for the clothianidin compound in water, while the minimum value was 2.7% in samples of fipronil in soil. The highest reproducibility (RSD_R) value of recoveries was observed with fipronil in water

(8.91%), while the lowest one was with imidacloprid in soil (3.7%) (Supporting Information, Table S1). According to SANTE/11312/2021,[41] the LOQ is defined as the lowest fortification level measurable with acceptable precision (repeatability) and recovery under specified test conditions. In this study, the LOQs for imidacloprid, clothianidin, and fipronil were determined to be 0.03 μg g^{-1}, which aligns with the sensitivity thresholds required for detecting trace pesticide residues in environmental matrices. The results prove that the approaches established were suitable and repeatable for determining all tested pesticide residues in soil and water.

During the sample analysis (each run), the standards of the studied pesticide (external standard technique) were analyzed to calibrate and validate all the standard curves. The correlation coefficient (R^2) of the standard calibration curve for each target pesticide was more significant than 0.999 for the solvent as well as soil and water extracts (matrix). After analysis of 10–15 samples, one mid-level standard injection was done to confirm system stability. The back-calculated concentrations of reinjected mid-level standard during batch analysis were within ±15% of the nominal concentration, confirming the instrument's stability during the analysis. Additionally, a set of quality control samples (spiked samples) was injected at the beginning of each run, and every 10 real samples thereafter, to ensure system conditioning. The recovery for all quality control replicates for all tested compounds was higher than 80%, indicating the instrument was stable during the analysis of the samples.

3 RESULTS AND DISCUSSION

3.1 Performance of the portable rainfall simulator

Natural rainfall includes a wide range of drop sizes, from near-zero to almost 7 mm.[42] During the performance evaluation of the rainfall simulator in this study, a total of 1200 raindrops were estimated. At 50 mm h^{-1}, the simulated raindrop size was approximately 2.95 ± 0.029 mm, with a median volumetric drop (D50) diameter of 2.03 mm. These sizes are consistent with previous studies using other rainfall simulators.[19,34,40] The velocity of the raindrops produced by the proposed rainfall simulator was determined to be nearly 4.7 m s^{-1}, which is in accordance with previous results from Abudi *et al.*[35] (range 2.5–5.7 m s^{-1}), Kesgin *et al.*[36] (range 3.35–6.83 m s^{-1}), and Salem and Meselhy[34] (range 5.69–6.27 m s^{-1}). The findings indicated the excellent performance of the small-scale rainfall simulator in terms of raindrop size and velocity.

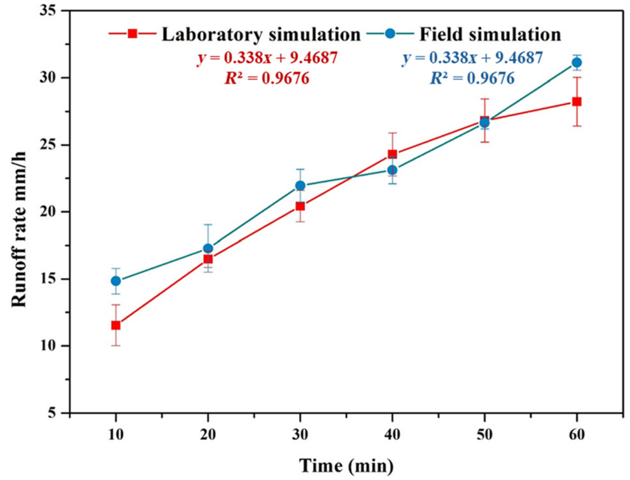

Figure 2. The hydrograph of runoff rate displaying surface runoff characteristics during rainfall experiments. Bars indicate standard errors (SE) of the measured concentrations.

The kinetic energy of the small-scale rainfall simulator was compared to that of natural precipitation in Japan. Due to the low fall height, it might be challenging for the drops to attain the terminal velocity of large, realistic raindrops. Based on the corresponding terminal velocity, the study's estimated kinetic energy (KE_{time}) was 0.15 J m^{-2} s^{-1}. Although this KE_{time} value is approximately 57.9% lower than the KEi_{NR} calculated for the natural rainfall for the 50 mm h^{-1} intensity, it is close to KE_{time} values measured by Borselli *et al.*[43] for 67 mm h^{-1} intensity (0.24–0.31 J m^{-2} s^{-1}), Boulange *et al.*[19] for 50 mm h^{-1} intensity (0.21 J m^{-2} s^{-1}), and Parsons and Stone[44] for 46–171 mm h^{-1} intensity (0.18–0.67 J m^{-2} s^{-1}). As a result, the proposed rainfall simulator can provide appropriate kinetic energy and be considered suitable for the experiment.

Before the experiment, the rainfall intensity was calibrated by measuring the water volume collected by the measurement tray over known time intervals. The rainfall simulator used in this work can simulate a consistent rainfall intensity of 50 mm h^{-1}. The Christiansen uniformity coefficient (CU) obtained in this study was 82%, which is consistent with earlier research by Aksoy *et al.*,[30] Luk *et al.*,[45] Martinez-Mena *et al.*,[46] and Salem and Meselhy.[34]

3.2 Characterization of surface runoff

In laboratory and field experiments, surface runoff began, on average, at 13.6 and 11.5 min following the onset of artificial rainfall, respectively. The runoff rate patterns in the lysimeter for the laboratory experiments and in undisturbed soil for the field experiments were similar, with rainfall initially infiltrating through soil profiles until the rainfall rates exceeded the soil's infiltration capacity. Such a short time to generate surface runoff considerably raises the risk of runoff from Andisol soils. This finding was corroborated by Boulange *et al.*,[19] who also found that surface runoff began at 14 min in Andisol soil at a rainfall intensity of 50 mm h^{-1} using a plot-scale rainfall simulator. The hydrograph of the surface runoff rate in the lysimeter and undisturbed soil is presented in Fig. 2.

The average final runoff rates at 60 min were 28.22 and 31.12 mm h^{-1} for the laboratory and field simulations, respectively. The laboratory simulation produced runoff coefficients with a maximum of 56.4%, while the field simulations reached 62.2%. Although the runoff volume was slightly higher in the undisturbed field soil compared to the laboratory lysimeter, statistical analysis using a paired *t*-test indicated no significant difference between the indoor and outdoor experiment sites ($P = 0.330$). This similarity could be attributed to the consistent initial soil moisture conditions at both locations, therefore the proposed rainfall simulator can produce a comparable rainfall-runoff response for both indoor and outdoor simulations.

3.3 Soil erosion

The concentration of sediment in runoff and cumulative sediment losses during rainfall experiments for the laboratory and field simulations is shown in Fig. 3. The changes in soil loss patterns could be divided into three stages. Sediment concentration reached its maximum when runoff started, then decreased throughout the rainfall event, and, finally, more surface soil erosion occurred by

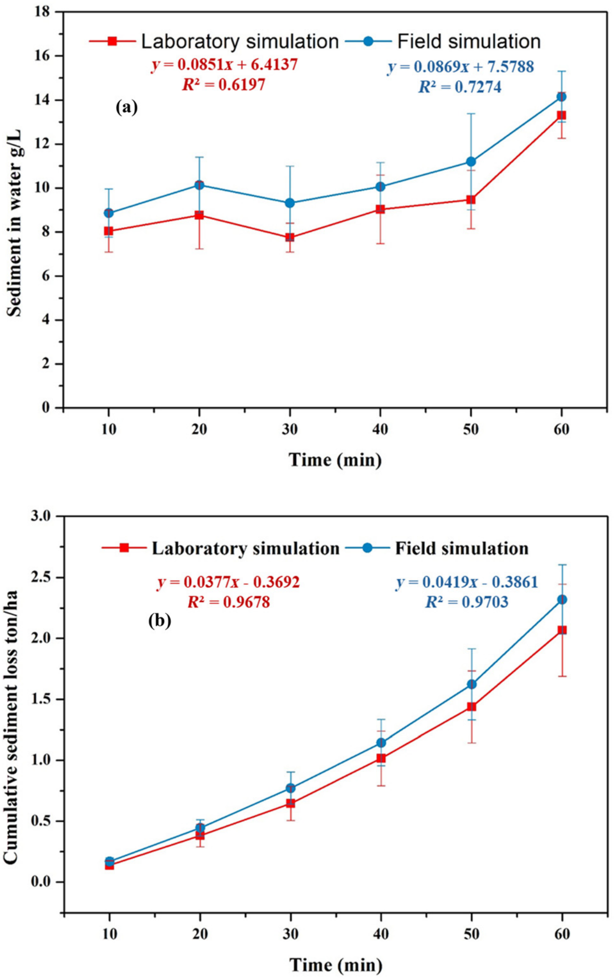

Figure 3. Sediment concentration in runoff (a) and cumulative sediment loss (b) during rainfall experiments. Bars indicate the standard error of the measured concentrations.

the end of the experiment. When the runoff rate begins, the impact of rainfall on readily detached particles in the exposed soil portions of the plots diminishes and soil transport reaches its maximum. Once intense rainfall exceeds the infiltration capacity of the field soil, the overland flow erodes the soil. Yadav and Watanabe[31] have also observed this sediment transport pattern. Overall, sediment yield in runoff ranged from 0.16 to 0.63 tons ha^{-1} in the lysimeter experiment and from 0.2 to 0.69 tons ha^{-1} in the undisturbed soil experiment. Sediment losses ranged from 0.1 to 0.532 tons ha^{-1} in other studies,[19,26,47] similar to the yields estimated in this study.

During this study, the accumulated sediment runoff was 2.1 and 2.4 tons ha^{-1} in the lysimeter and undisturbed soil experiments, respectively. The amount of soil erosion was slightly higher in the field than in the packed soil in the laboratory. A paired *t*-test on sediment concentration values confirmed a statistically significant difference between laboratory and field simulations ($P = 0.0286$). This suggests that although cumulative sediment yields were similar, there were significant differences in sediment concentration between the two setups. This may be attributed to the soil in the lysimeter being tamped with a wooden block, which may slightly reduce raindrop erosion compared to field soil. Comparing this result with the rainfall simulation used by Boulange *et al.*,[19] the cumulative sediment loss (1.25 tons ha^{-1}) with the plot-scale simulator was similar to that observed with the rainfall simulator used in this work. Although our findings fall within the range reported for similar rainfall experiments,[4,40] they were smaller than Japan's annual soil erosion rates (3.54–34 tons ha^{-1} per year).[48] Accordingly, these findings demonstrate that the small-scale portable rainfall-runoff simulator system can effectively simulate sediment transport dynamics and produce data comparable to those from large-scale experiments.

3.4 Pesticide loss in runoff

The pesticide concentrations measured in runoff water and sediment under laboratory and field simulations are presented in Fig. 4. Overall, higher concentrations of the studied pesticides in runoff sediment were observed in both laboratory and field simulations compared to those in runoff water. This may be due to reduced pesticide concentrations available for surface runoff, as some pesticides may have leached through the soil before runoff began.[26] An additional explanation for the low pesticide transport in runoff water may be due to the high organic carbon content in Andisol soil (Table 2), which increases the adsorption of these pesticides in the soil.[49,50] Furthermore, there may not be enough time to reach a steady-state equilibrium between adsorbed and dissolved substances in fast-flowing water. As a result, just a small portion of it could be dissolved.[51]

Figure 4 illustrates the temporal variation in pesticide concentrations in runoff water and sediment, highlighting a sharp increase in pesticide transport during the initial phases of runoff, followed by a gradual decline. This trend underscores the role of rapid desorption in the early stages of the runoff process, as indicated by the higher concentrations of pesticides at the beginning of the simulation. Furthermore, differences in the concentrations among fipronil, imidacloprid, and clothianidin reflect their distinct physicochemical properties, such as solubility and adsorption potential. The observed differences in pesticide concentrations can be attributed to the unique properties of fipronil, imidacloprid, and clothianidin. For instance, fipronil's lower water solubility and higher organic carbon adsorption coefficient (K_d) make it more likely to bind to sediment particles, resulting in higher concentrations in runoff sediment compared to water. On the other hand, imidacloprid, with its relatively higher solubility, exhibits more balanced transport between water and sediment. These findings align with those of a previous study[31] that emphasize the importance of pesticide physicochemical properties in determining their fate during runoff events.

The maximum concentrations were 1.36 mg kg^{-1} for fipronil, 2.33 mg kg^{-1} for imidacloprid, and 0.14 mg kg^{-1} for clothianidin in runoff sediment under laboratory conditions, while they were 1.63 mg kg^{-1} (fipronil), 2.22 mg kg^{-1} (imidacloprid), and 0.17 mg kg^{-1} (clothianidin) under field conditions (Fig. 4(c),(d)). Similarly, under laboratory conditions the maximum concentrations of fipronil, imidacloprid, and clothianidin observed in runoff water were 0.032, 0.033, and 0.034 mg L^{-1}, respectively, while under field conditions they were 0.053, 0.042, and 0.021 mg L^{-1}, respectively. As shown in Fig. 4(a),(b), the maximum dissolved concentrations of fipronil, clothianidin, and imidacloprid in runoff water were observed at the beginning of the experiment at both sites. This could be attributed to the rapid initial desorption of the applied pesticides in the first runoff samples. These findings are similar to those reported by Yadav and Watanabe,[31] where the maximum concentrations of clothianidin and imidacloprid in

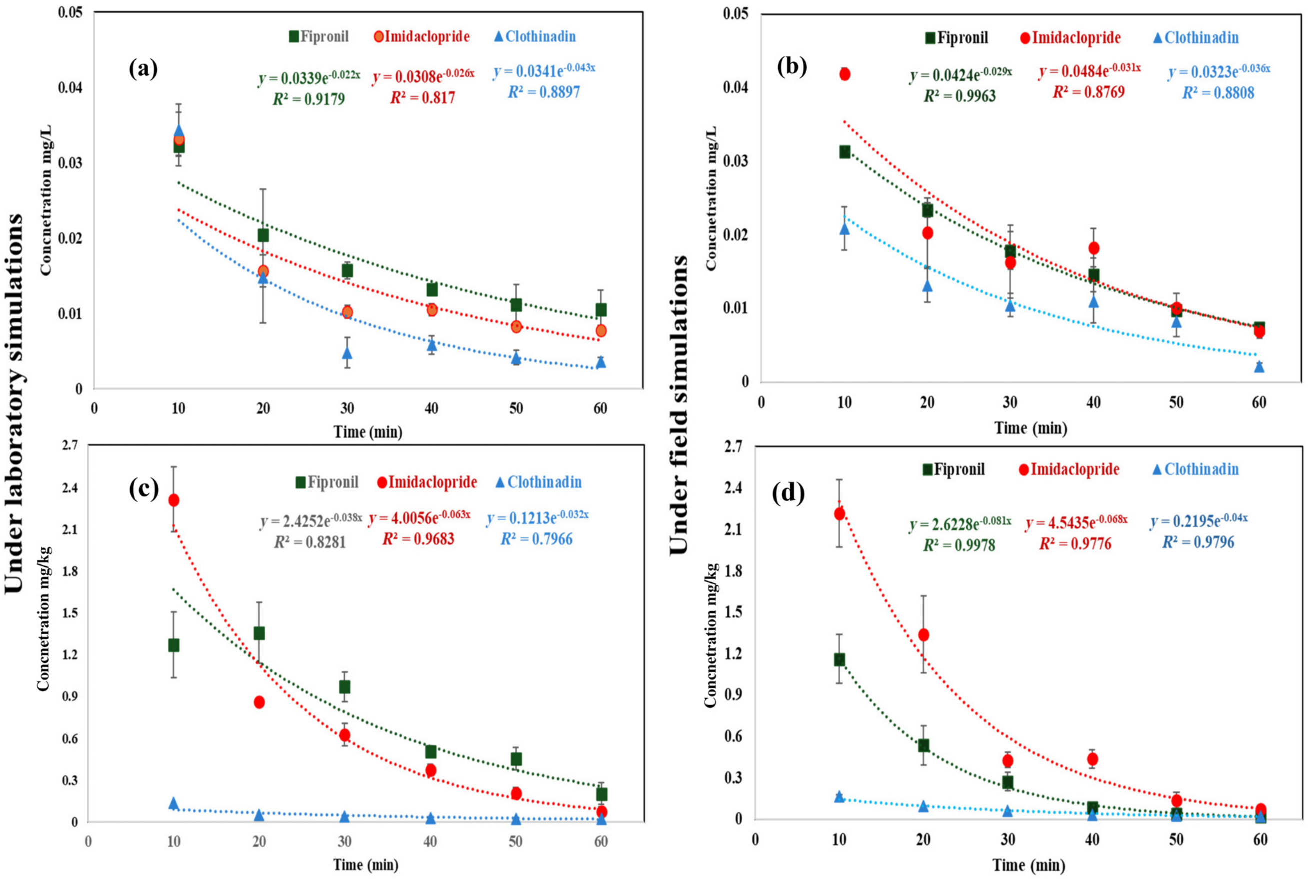

Figure 4. The concentration of fipronil, imidacloprid, and clothianidin as a function of time in water (a and b) and sediment (c and d) under laboratory and field simulations. Regression lines represent the exponential decay of pesticide concentrations over time, with equations and R^2 values indicating the strength of the fit. Bars indicate the standard error of the measured concentrations.

runoff water were 0.026 and 0.089 mg L^{-1}, respectively. In contrast, these values were lower than the maximum concentrations measured by Yadav and Watanabe[31] for clothianidin and imidacloprid in runoff sediment, which were 5.72 and 8.23 mg kg^{-1}, respectively. This difference could be the result of the high rainfall intensity (70 mm h^{-1}) in the study by Yadav and Watanabe,[31] which may have caused more substantial sediment runoff and, consequently, larger amounts of pesticides discharged during the runoff period.

The cumulative mass losses of fipronil, clothianidin, and imidacloprid in runoff water and sediment were 5.7%, 1.4%, and 0.9% of the applied mass under laboratory simulation, respectively (Fig. 5). Similarly, under the field simulation, the cumulative mass losses of fipronil, clothianidin, and imidacloprid in runoff water and sediment were 5.6%, 1.8%, and 1.5% of the applied mass, respectively (Fig. 5). Fipronil was shown to be more prone to surface runoff. The net loss was approximately four times larger than with clothianidin and imidacloprid. These data revealed that imidacloprid and clothianidin might quickly enter the soil profile with infiltrating water before surface runoff began. Under simulated rainfall experiments, similar patterns of removal of imidacloprid and clothianidin from turf surfaces have been documented.[7,31] The concentration of pesticide in runoff (water/sediment) is based on numerous factors, including the chemical characteristics of pesticides, the formulation of pesticides, the application rate, the rainfall pattern, the amounts of rainfall, and the type of soil surface.[7,52–54] The present study revealed that the losses of the studied pesticides followed similar trends across rainfall experiments. This indicates that the rate of runoff plays a significant role in the dynamics of pesticide transportation processes.[19,26]

Supporting Information, Fig. S4 illustrates the normalized detected mass (detected mass divided by applied mass, %, Test S3) of fipronil, clothianidin, and imidacloprid in runoff water and sediment collected from plots simulated in the laboratory and field. Under the laboratory simulation, the maximum average normalized masses of fipronil, clothianidin, and imidacloprid in runoff water were 0.862%, 0.491%, and 0.193%, respectively. In comparison, they were 0.29%, 0.01%, and 0.04% in runoff sediment, respectively (Supporting Information, Fig. S4(a),(c)). In the field simulation, the maximum pesticide losses through runoff water were 1.26%, 0.45%, and 0.37% of the applied mass for fipronil, clothianidin, and imidacloprid, respectively, while in runoff sediment they were 0.16%, 0.013%, and 0.07%, respectively (Supporting Information, Fig. S4(b),(d)). Over time, pesticide amounts decreased exponentially due to strong bonds between the soil matrix and the lower concentrations of applied pesticides. Additionally, soil aggregates were broken down through air slaking at the onset of rainfall events following the pre-wetting period, which created a new surface for pesticide desorption and led to higher concentrations in the initial rainfall intervals. The results showed that pesticide losses were lower than expected, which may be

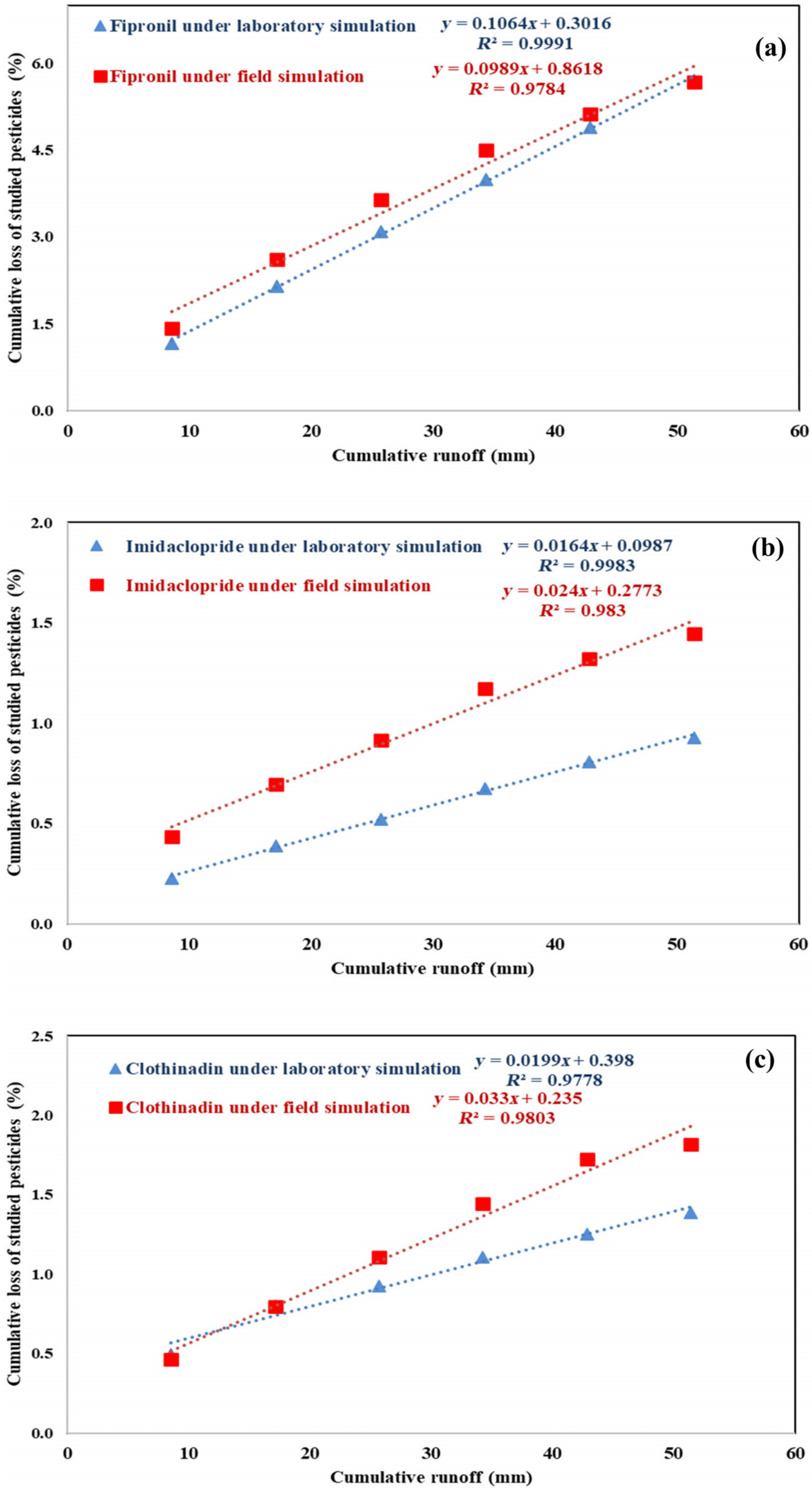

Figure 5. Fitting the relationship between cumulative mass loss of fipronil (a), imidacloprid (b), and clothianidin (c) and cumulative runoff under laboratory and field simulations. Laboratory and field data are displayed together for direct comparison. Regression equations and R^2 values are included to illustrate the relationship between cumulative pesticide loss (%) and cumulative runoff (mm) under both conditions.

due to stronger binding to organic matter in the Andisol or the possibility that the chemicals leached into the soil profile before runoff began. While similar results were unavailable, our findings were consistent with those reported by Müller *et al.*,[26] Yadav and Watanabe,[31] and Boulange *et al.*[19]

The proportion of pesticide leaching, interflow, and surface runoff is governed by their sorption behavior and water solubility.[31] Many pesticide molecules may be bound to the surface soil particles and are more vulnerable to transport through surface runoff than downward movement in the soil.[52,55] Pesticides with a high

KOC (log KOC > 4.5) have a low leaching potential because the potential for leaching in agricultural soil depends on the soil organic matter–water partition coefficient (K_{OC}). According to Müller *et al.*[52] and Freitas *et al.*,[55] many pesticide molecules can attach to soil particles on the soil surface, causing them to be more likely to be transported *via* surface runoff. Similarly, the adsorption–desorption distribution coefficient (K_d) affects environmental mobility and distribution across water, sludge, soil, and sediment compartments.[56] As shown in Fig. 5 fipronil had the highest cumulative mass loss in runoff water at both simulated sites despite its high sorption coefficient. The more pronounced first-flush effect for fipronil (flowable formulation) on soil surfaces may be attributed to either the higher surfactant concentration in the fipronil formulation or the characteristics of the Andisol surface soil, which adsorb and sequester most of the pesticide, decreasing its leaching potential. Conversely, the high solubility of imidacloprid and clothianidin compared to fipronil could explain why they leached more quickly with infiltration water and were transported out of the active runoff zone before runoff began. This variation in percentage loss is due to the complex interplay of different dissipation routes after application. The cumulative loads of fipronil, clothianidin, and imidacloprid for the entire trial are presented in Table 3. At the end of the rainfall events, the mass of fipronil, clothianidin, and imidacloprid lost *via* runoff water and sediments during the entire simulation period relative to the applied mass was 5.7%, 0.9%, and 1.4%, respectively, under laboratory simulation. Similarly, it was 6.6% for fipronil, 1.4% for imidacloprid, and 1.8% for clothianidin under field simulation. The results are not significantly different due to the same soil conditions at both simulated sites.

3.5 Distribution of pesticides in the soil profile

Figure 6 demonstrates the distribution of three pesticides in different soil layers (0–1 cm, 1–5 cm, 5–10 cm, 10–13 cm) in the lysimeter and plot frame after the rainfall-runoff simulation. The highest concentrations were detected at the 1–5 cm soil layer for all three insecticides in both laboratory and field simulations. The highest concentrations for fipronil, imidacloprid, and clothianidin were 1.03, 1.33, and 2.65 mg kg^{-1}, respectively, for the laboratory simulation, and 0.88, 1.48, and 2.64 mg kg^{-1}, respectively, for the field simulation. Both imidacloprid and clothianidin had the highest concentrations in the 1–5 cm layer, with concentrations decreasing in the deeper soil layers (5–10 and 10–13 cm). However, in both laboratory and field simulations, fipronil was not detected in soil layers deeper than 5 cm. Fipronil exhibits slower downward migration in soil than imidacloprid and clothianidin, possibly due to significant adsorption of fipronil onto soil particles and organic material and its lower solubility in water. The reported soil–water partitioning coefficients for fipronil, imidacloprid, and clothianidin are 25, 11, and 6.2 L kg^{-1}, respectively, and their corresponding water solubility values are 1.9, 610, and 304 mg L^{-1}, respectively (Table 1). The concentrations of fipronil in the soil profile were the lowest among the three pesticides, despite fipronil having the highest soil–water partitioning coefficient. These results are in agreement with those reported by Müller *et al.*,[26] and Yadav and Watanabe.[31]

Mass balance calculations were carried out to track the residual amounts of applied pesticides after laboratory and field rainfall simulations. The mass balance calculation considered the measured soil density at the surface and water content. Supporting Information, Fig. S5 shows the pesticide mass balance as a percentage of the applied pesticide mass under laboratory and field simulations. The two major dissipation pathways for the tested pesticides in both laboratory and field simulations were identified as degradation and adsorption to the soil. The amounts of degraded imidacloprid (80% and 79% under laboratory and field simulations, respectively) were higher than those of fipronil (38% and 53% under laboratory and field simulations, respectively) and clothianidin (29% and 28% under laboratory and field simulations, respectively). According to Pätzold and Brümmer,[57] pesticide degradation/dissipation during the rainfall simulations experiment could reduce the amount initially available for surface runoff. Additionally, the high relative mass of clothianidin in the soil could be attributed to its high soil–water partitioning coefficient (11 L kg^{-1}).

In summary, clothianidin and fipronil were predominantly adsorbed to the soil in the lysimeter and plot frame, with the least transportation in the runoff. Meanwhile, the losses of tested pesticides through water and sediment runoff ranged between 0.93–5.7% and 1.45–5.68% under laboratory and field simulations, respectively, therefore degradation is considered the major dissipation pathway for imidacloprid under rainfall simulation.

3.6 Toxicity of fipronil, imidacloprid, and clothianid

The growing usage of pesticides in urban areas has polluted urban streams and surface water bodies. In recent years, through anthropogenic activities and runoff into agricultural areas, environmental samples have revealed the presence of fipronil at concentrations predicted to cause acute toxicity.[58–60] Imidacloprid has been found in groundwater in Wyoming, and surface water surveys have been carried out in Florida, New York, and Washington.[61,62] Furthermore, the majority of urban streams in the 10 states under study showed fipronil concentrations at sub-part-per-billion levels, according to US Geological Survey monitoring studies.[63] Due to their large body size, water fleas—especially *Daphnia magna*—are among the most frequently used organisms for toxicity research,[64] therefore water fleas (*D. magna*) and bluegill sunfish (*Lepomis macrochirus*) have been used as sensitive

Table 3. Total loss of studied pesticides as function of applied mass after the runoff scenario

		Under laboratory simulation				Under field simulation			
	Applied mass	Loss in runoff water		Loss in runoff sediment		Loss in runoff water		Loss in runoff sediment	
Pesticides	Mass (mg)	Mass (mg)	%	Mass (mg)	%	Mass (mg)	%	Mass (mg)	%
Fipronil	1.14	0.051	4.50	0.013	1.20	0.059	5.25	0.005	0.42
Imidacloprid	5.24	0.041	0.78	0.007	0.15	0.064	1.23	0.011	0.22
Clothiandin	2.13	0.051	1.35	0.014	0.033	0.038	1.67	0.001	0.06

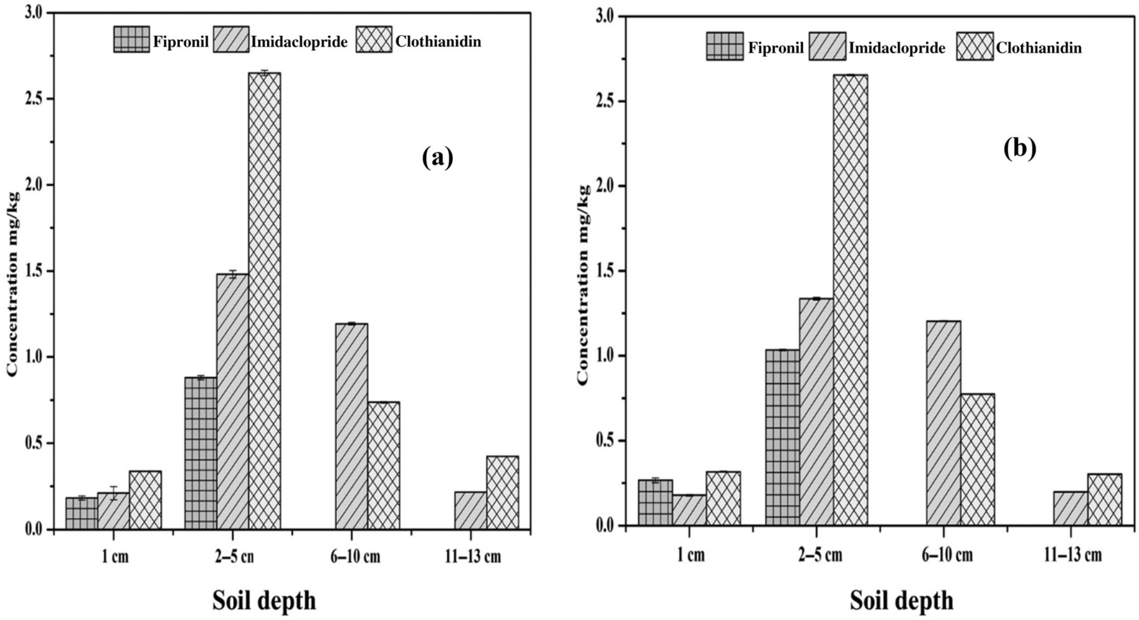

Figure 6. Fipronil, imidacloprid, and clothianidin pesticides transport in the soil layer during rainfall simulation under laboratory (a) and field (b) simulation. Bars indicate standard error of the measured concentrations.

indicators to assess the toxicity of synthetic detergents.[65] The toxic units (TUs) of each tested pesticide were determined to evaluate the cumulative impacts of the studied pesticides on the environment. The concentrations of fipronil, imidacloprid, and clothianidin were normalized using toxicity endpoints and these values were summed to calculate the total TUs in the sample.[7,66,67] A TU is defined as the actual concentration of the analyte in the runoff water divided by the 96-h median lethal concentration (LC_{50}) for bluegill sunfish (*L. macrochirus*) and the 48-h LC_{50} value for the water flea *Daphnia magna*, obtained from the literature. The sum of TUs represents the cumulative TUs of pesticides. The estimated concentrations of clothianidin and imidacloprid in runoff under laboratory and field simulations were below the 48-h and 96-h acute LC_{50} values for *D. magna* and bluegill sunfish (*L. macrochirus*), respectively (Table 1). Figure 7 shows the cumulative TUs of fipronil concentration under laboratory and field simulations. In comparison, the accumulated concentrations of fipronil in runoff water were 0.103 and 0.126 mg L^{-1} under laboratory and field simulations, respectively. These values were higher than the toxicity level for bluegill sunfish (*L. macrochirus*, 0.083 mg L^{-1}) and close to the 96-h acute LC_{50} value for the water flea *D. magna* (0.19 mg L^{-1}), therefore both simulation sites considered TUs and the sum of TUs for fipronil in runoff water. Throughout the rainfall events, the sum of TU values for fipronil to *L. macrochirus* ranged from 0.13 to 0.39 and 0.09 to 0.64 under laboratory and field simulations, respectively. Simultaneously, the TU values for fipronil to *D. magna* ranged from 0.06 to 0.17 and 0.04 to 0.28 under laboratory and field simulations, respectively (Supporting Information, Table S2). Meanwhile, the sum of TUs was greater than 1.0 for *L. macrochirus* under both simulation sites (Fig. 7). Consequently, the runoff losses of fipronil could pose a hazard for aquatic organisms. Attention should therefore be given to the application of this pesticide in upland fields. It is important to note that these estimates assume direct exposure of *L. macrochirus* and *D. magna* to runoff water without any attenuation between the application and exposure sites, such as dilution or degradation.

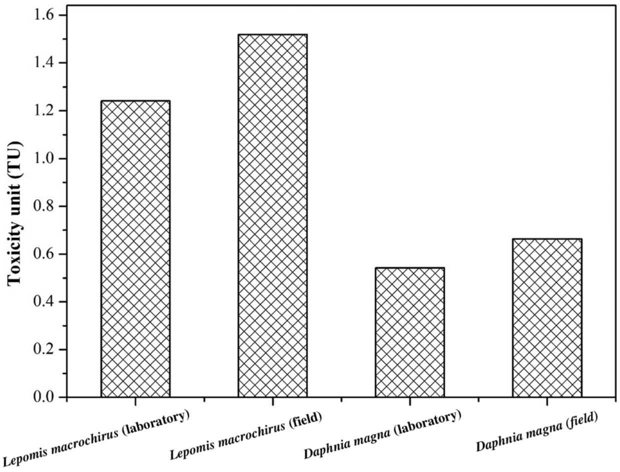

Figure 7. Toxicity unit calculations for fipronil in the runoff water to the bluegill sunfish *Lepomis macrochirus* and water flea *Daphnia magna*. This study used a small-scale portable rainfall simulator to investigate runoff rates, sediment yield, and pesticide transport under laboratory and field conditions. The findings provide insights into the environmental risks of widely used pesticides and the mechanisms driving their transport, aiding in developing effective mitigation strategies.

To our knowledge, this work is the first attempt to use a small-scale rainfall simulation to investigate the distribution and fate of certain hazardous pesticides through field and laboratory sampling. The findings of this study provide an overview of the potential environmental risks of these widely applied pesticides in urban environments and suggest possible modifications in application practices to mitigate their risks.

4 CONCLUSION

This study validates the small-scale portable rainfall-runoff simulator as a reliable tool for generating realistic rainfall intensities, enabling the study of runoff, sediment yield, and pesticide transport under controlled laboratory conditions. It also facilitates comparative analyses with field conditions, making it a valuable asset for environmental research, particularly in remote or resource-limited settings. The simulator's high precision in rainfall intensity and uniform distribution across the experimental area confirms its suitability for simulating key environmental processes. Designed to closely mimic field conditions within a controlled environment, the simulator allows for direct comparisons of runoff rates, sediment loss, and pesticide transport dynamics between laboratory and field scenarios. The results revealed higher runoff rates and sediment loss in field experiments compared to laboratory simulations, underscoring the influence of field-specific factors such as soil heterogeneity, slope, and natural variability.

The simulator effectively captured pesticide transport dynamics, with pesticide concentrations in runoff increasing during the initial stages of rainfall. Among the pesticides studied, fipronil exhibited the highest susceptibility to runoff, likely due to its lower solubility and higher soil adsorption coefficient (K_d) compared to clothianidin and imidacloprid. Additionally, the simulator enabled the assessment of pesticide movement within soil layers, revealing limited downward mobility for fipronil, in contrast to the greater mobility observed for the other pesticides. These findings highlight the simulator's ability to replicate critical field processes and provide valuable insights into sediment and pesticide transport dynamics, while acknowledging its limitations in fully replicating all aspects of natural field conditions.

The simulated rainfall experimental design provides critical insights into the environmental risks associated with pesticide transport, especially for fipronil, which poses higher toxicity risks to aquatic organisms. The study underscores the potential of this portable simulator for conducting realistic environmental studies, particularly in remote or resource-limited areas. Overall, this study demonstrates the reliability and practicality of the small-scale portable rainfall-runoff simulator for evaluating sediment and pesticide transport under diverse environmental conditions. The findings provide essential data for understanding and mitigating the environmental risks of pesticide use.

AUTHOR CONTRIBUTIONS

Conceptualization, methodology, formal analysis, software, data curation, investigation, visualization, writing—original draft, writing—review and editing: Ayman N. Saber: *Conceptualization, investigation, writing—reviewing and editing*: Farag Malhat. *Writing—review and editing*: Pabel Cervantes-Avilés. *Investigation*: Mostafa Mahmoud. *Conceptualization, supervision, writing—reviewing and editing, project administration*: Hirozumi Watanabe.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

ETHICS STATEMENT

Not applicable because this was not a research study involving animals or human beings.

CONSENT TO PARTICIPATE

Not applicable because this was not a research study involving human beings or animals.

CONSENT TO PUBLISH

Not applicable because this was not a research study involving human beings or animals.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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