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Ecological risk assessment of pesticides on soil biota: An integrated field-modelling approach

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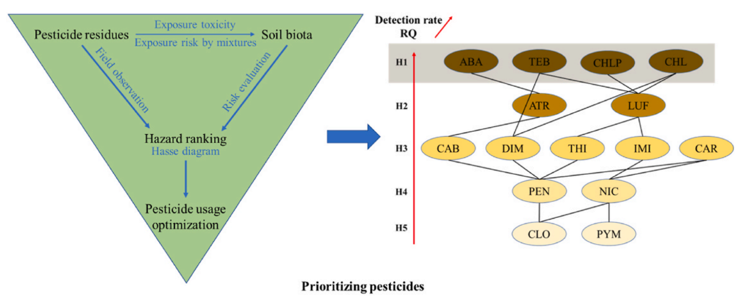
HIGHLIGHTS

- Nearly half of samples showed high ecological risk to soil biota due to pesticides.
- *Eisenia fetida* suffered exposure risk from multiple pesticides.
- Higher ecological risks were found in apple and wheat-maize rotation fields.
- A pesticide hazard ranking model was proposed based on the Hasse diagram.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticide residues in soils can cause negative impacts on soil health as well as soil biota. However, research related to the toxicity and exposure risks of pesticides to soil biota are scarce, especially in the North China Plain (NCP) where pesticides are intensively applied. In this study, the occurrence and distribution of 15 commonly used pesticides in 41 fields in Quzhou county in the NCP were determined during the growing season in 2020. The ecological risks of pesticides to the soil biota, including earthworms, enchytraeids, springtails, mites and nitrogen mineralization microorganisms, were assessed using toxicity exposure ratios (TERs) and risk quotient (RQ) methods. Based on pesticide detection rates and RQs, pesticide hazards were ranked using the Hasse diagram. The results showed that pesticides were concentrated in the 0–2 cm soil depth. Chlorantraniliprole was the most frequently detected pesticide with a detection rate of 37%, while the highest concentration of 1.85 mg kg^{-1} was found for carbendazim in apple orchards. Chlorpyrifos, carbendazim and imidacloprid posed a chronic exposure risk to *E. fetida*, *F. candida* and *E. crypticus* with the TERs exceeding the trigger value. Pesticide mixtures posed ecological risks to soil biota in 70% of the investigated sites. 47.5% of samples were ranked as high-risk, with the maximum RQ exceeding 490. According to the Hasse diagram, abamectin, tebuconazole, chlorantraniliprole and chlorpyrifos were ranked as the most hazardous pesticides for soil biota in the study region, indicating that alternative methods of pest management need to be considered. Therefore, practical risk

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mitigation solutions are recommended, in which the use of hazardous pesticides would be replaced with low-risk pesticides with similar functions from the Hasse diagram, or with biopesticides.

1. Introduction

Pesticides have been used intensively worldwide to protect crops and increase yields. For the past 30 years, farmers have been steadily increasing pesticide application rates to meet the demands of growing populations worldwide, with 4.16 million tons of pesticides used in 2019 (FAO, 2017). Due to their toxicity, pesticides can cause multiple negative effects on an ecosystem. For instance, increasing pesticide residues in environmental matrices can reduce the abundance of beneficial species and disrupt food webs (Allgeier et al., 2019). With successive field applications, the soil can be contaminated by pesticides, especially persistent pesticides (Hvezdova et al., 2018; Tsaboula et al., 2016). The bioaccumulation and biomagnification of pesticides in the food chain poses a significant exposure risk to soil biota, and further increase pesticide ecotoxicity in the soil (Kianpoor Kalkhajeh et al., 2021; Yuantari et al., 2015).

Soil biota, including micro-organisms and soil fauna, play essential roles in maintaining soil functions, such as regulating nutrient cycling and maintaining soil quality, and contribute to soil biodiversity, which is another vital indicator of soil health (Bhandari et al., 2021; Lavelle et al., 2006). Pesticide residues threaten soil biota by affecting gene expression and enzyme activities that can inhibit fecundity, reduce growth and influence survival rates (Lyons et al., 2018; Wang et al., 2019; Ye et al., 2016). Therefore, it is essential to investigate the residual levels of pesticides in soil and assess the ecological risks these pesticides pose to soil biota.

The EFSA (European Food Safety Authority) has recommended the use of assessment methods such as risk quotients (RQ) and toxicity exposure ratios (TERs) (EFSA et al., 2017). To obtain holistic assessment results for soil species, exposure to both individual pesticides and mixtures should be considered. The TER approach aims to assess the species-specific exposure risks to individual pesticide compounds. For hazard characterization, these individual compounds have been given trigger values, 10 for chronic and 5 for acute exposure (EC, 2018). However, since regional studies have shown that pesticides are mostly detected as mixtures in arable soil, the ecological risks posed by mixtures should also be considered in order to reflect the actual exposure risks to soil biota (Bhandari et al., 2020; Hvezdova et al., 2018; Silva et al., 2019). The RQ-based assessment was developed to assess the ecological risks of exposure to multiple pesticide mixtures in the study locations with the concentration-addition (CA) method. The CA method is widely accepted and provides a conservative assessment to address the exposure risk from multiple compounds and has been frequently used in pesticide risk assessments (Baqar et al., 2018; Carazo-Rojas et al., 2018; Zheng et al., 2016). Up until now, the ecological risks that pesticides pose to non-target species in aquatic environments has been well studied. However, information concerning the risks to soil biota is limited. Vašíčková et al. (2019) and Bhandari et al. (2021) used a combined TERs and RQ-based approach to reveal the ecological risks of pesticide residues to soil biota, especially to *F. candida* and *E. crypticus*. Due to the severe lack of information and the threats posed by specific pesticides, we need to develop a hazard ranking framework to identify hazardous compounds in mixtures of pesticides found in the soil and explore possible alternative low-risk pesticides.

Pesticide application in China has increased from 0.77 million tons in 1990 to 1.7 million tons in 2019 (FAO, 2017). Based on a national estimation carried out by the government, only about 40% of the applied pesticides actually reach and protect the target crop (MOARA, 2021a,b), indicating that a considerable amount of pesticide drift ends up in the surrounding and off-field environment (Ryberg et al., 2018). Researchers reported that pesticides have been intensively sprayed in the North China Plain (NCP), which is a major cereal crop producing area in China (Sun et al., 2019). Quzhou county, a typical agricultural county located at the center of the NCP, was selected as the case study site in this study. It is studied that overuse pesticides and using forbidden pesticides contributed to Pesticides were found to be largely applied in the field with overuse and using forbidden ones occur in roughly 50% of pesticide application events in the NCP, which is asking for highlights the need for proper regulation to supervise pesticide use, as well as potential systemic monitoring of pesticides in the soil, and a comprehensive risks assessment for in soil biota (Mu et al., 2022a, 2022b). (Mu et al., 2022a, 2022b). Ranking the pesticides to be used based on multiple critical and quantitative criteria is important for the sustainable management and risk mitigation of pollutants (Li, 2022; Sang et al., 2022). Thus, the objectives of this study are to (1) investigate the occurrence of pesticides in the soil in Quzhou county, (2) assess the ecological risks that individual pesticides and pesticide mixtures pose to soil biota and (3) propose a hazard ranking framework of pesticides based on their ecological risks to soil biota and their detection rates in the soil. The findings of this study can provide guidance for further risk mitigation measures, and data that will help to contribute to a more sustainable regional pesticide management strategy.

2. Materials and methods

2.1. Study area

Quzhou county (36°34′45″ N - 36°57′57″ N, 114°50′30″ E – 115°13′30″ E), a typical agricultural county with a subtropical humid monsoon climate, is located in the central area of the NCP. Quzhou covers an area of 667 km^2, of which over 80% is farmland. The average temperature and annual precipitation are 13.4 °C and 556.2 mm, respectively. Grain crops, mainly maize and wheat, as well as vegetables, apples and grapes make up the majority of the crops grown in this region.

2.2. Sampling

To determine the concentration of pesticides in the soil, soil samples were taken from wheat-maize rotations as well as vegetable fields, grape vineyards and apple orchards before pesticide application and 1 or 2 days after harvesting (Table S1). In this study, we randomly selected 10 fields of wheat-maize rotation, 9 vegetable fields, 10 grape vineyards, and 12 apple orchards. Pesticide concentrations in samples taken from the pre-application (PA) period are marked as background values, while the concentrations in samples taken from the post-harvest period are referred to as accumulation values.

Soil samples were taken with an auger at two depths: 0–2 cm and 2–10 cm. In each sampling field, soil samples were taken from 6 to 8 points in the field and then mixed together into one sample. During the sampling process, irrelevant materials such as stones, roots and leaves were removed. All samples collected were then placed in self-sealing plastic bags and stored at −20 °C until the chemical analyses were performed.

2.3. Pesticide determination

2.3.1. Chemicals and solvents

Prior to the chemical analyses, farmers were interviewed and asked to list the pesticides that they commonly used on their fields. From these lists of pesticides, 15 commonly used pesticides in 13 groups were selected for lab analysis: benzimidazole (carbendazim), organophosphate (chlorpyrifos), neonicotinoid (clothianidin, imidacloprid, and thiamethoxam), morpholine (dimethomorph), anthranilic diamide (chlorantraniliprole), micro-organism derived compounds (abamectin), sulfonylurea (nicosulfuron), benzoylurea (lufenuron), pyridine (pymetrozine), dinitroaniline (pendimethalin), triazine (atrazine), triazole (tebuconazole) and carbamate (carbofuran). The analytical reference standards for chemical analysis were purchased from Alta Scientific Co., Ltd. The standard stock solution was prepared in acetonitrile at a concentration of 1000 mg L - ^{1}. The mixed standard solution was then prepared at a concentration of 100 mg L - ^{1} from the individual stock solutions. The calibration curve for instrumental analysis was prepared by diluting the mixed standard solution and following the concentration gradients of 0.01, 0.05, 0.1, 0.5, 1 and 2 mg L - ^{1} in acetonitrile. All the solutions prepared were stored in a refrigerator at −20 °C until use. Untreated bare soil was collected in Quzhou county to use in blank samples. The blanks were then fortified with the mixed standard solution at concentrations of 0.01, 0.05, 0.1, 0.5 and 1 mg L^{-1} for recovery assessment and method validation.

2.3.2. Extraction and clean-up

The pre-treatment procedure was modified from our previous study (Mu et al., 2022a, 2022b). Briefly, 5.0 ± 0.05 g of a soil sample was weighed and placed in a centrifuge tube with 10 mL water, 5 mL of acetonitrile and 3 g NaCl before being placed in a vortex. After vortexing for 15 min at a rotation rate of 2500 rpm, the tube was then centrifuged for 5 min at a rotation rate of 3800 rpm. The remaining supernatant (roughly 1 mL) was transferred into a 2 mL centrifuge tube for further treatment.

The purifying agents, 100 mg $MgSO_4$ and 50 mg C18, were added to each centrifuge tube along with the extracts. The tubes were then vortexed for 30 s and centrifuged in a high-speed centrifuge at a speed of 10,000 rpm. The upper layer supernatants were passed through 0.45 μm filters and stored in glass vials at −20 °C for further instrumental analysis.

2.3.3. LC-MS/MS

All measurements were performed using liquid chromatography coupled with a triple quadrupole mass spectrometer (LC-MS/MS; Shimadzu LCMS-8045, Shimadzu Corporation, Tokyo, Japan). An Athena C18-WP 100 Å column (50 mm × 2.1 mm id, 3.5 μm particle size) was used, and the temperature kept at 40 °C for separation. Analysed compounds were separated with the mobile phase, including eluent A (100% acetonitrile) and B (ultrapure water with 0.1% formic acid). The temperature and flow rate of dry gas (N_2) were 300 °C and 11.0 L/min, respectively. The nebulizer pressure and the electrospray voltage were 15.0 psi and +4000 V, respectively. The precursor and corresponding product ions for the multi-reaction monitoring detection of each target compound are presented in Table S2. The gradient elution was optimized at a flow rate of 0.25 mL/min as follows: 0–0.2 min 20% A, 0.2–2 min from 20% to 60% A, 2–6 min 80% A, 6–6.5 min from 80% to 20% A, 6.5–7.5 min 20% A. The injection volume was 2 μL. The limit of qualification (LOQ) for analysed chemicals was 0.01 mg kg^{-1}.

2.3.4. Quality assurance and quality control

The calibration curve solutions were injected a total of three times, once at the beginning, the middle and the end of the sample sequences. Recovery rates of analysed pesticides for fortified blank samples and calibration curve solutions were both acquired within a range of 70%–110%. Also, the calibration curves were fairly linear, with linear correlation coefficients over 0.99.

2.4. Ecological risk assessment

2.4.1. Toxicity exposure ratios

The toxicity exposure ratios (TERs) approach aims to assess if the accumulation level of pesticide residues in the soil results in exposure risks to soil biota. The TERs were calculated based on the measured pesticide concentrations (average or maximum value) and the toxicity data of pesticides for certain soil species (equation (1)). When maximum and average values of measured concentrations are used in the assessment, the TERs can indicate the related acute and chronic exposure risks posed by certain pesticides. This method can provide species-specific results based on toxicity data and measured pesticide concentrations (MCs).

$$TER_{species} = \frac{NOEC_{species} \ or \ LC50_{species}}{MC_{mean \ or \ max}} \tag{1}$$

$NOEC_{species}$ and $LC50_{species}$ represent the no observed effect concentration (mg kg^{-1}) and 50% lethal concentration (mg kg^{-1}) for certain combinations of pesticides and soil species. MC_{mean} and MC_{max} represent the mean value and the maximum value of measured pesticide concentrations. Species-specific NOEC and LC50 were derived from the PPDB database (PPDB, 2021) and literature (Bhandari et al., 2021) and listed in Table S3.

In the assessment, general scenarios and worst-case scenarios (Dabrowski et al., 2014) were developed by assuming the input of MCs at average and maximum concentrations (Bhandari et al., 2021). In the present study, the five EFSA soil organisms (*Eisenia fetida*, *Enchytraeus crypticus*, *Folsomia candida*, *Hypoaspis aculifer* and nitrogen mineralization organisms) were selected as indicative species for pesticide exposure risk (OECD 216, 2000). EC (2002) has defined trigger values (cut-off values) of 5 and 10 for acute and chronic exposure risk, respectively. If the calculated TER is above the trigger values, the exposure risk to certain species can be interpreted as negligible.

2.4.2. Ecological risks due to pesticide mixtures

The ecological risks of pesticide mixtures to soil biota were assessed using the risk quotient (RQ) method in which the risk quotient of mixtures was quantified by concentration addition (equation (2) and (3)).

$$RQ_i = \frac{MC_{soil}}{PNEC_{mss}} \tag{2}$$

$$\sum RQ_{site} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MC_i}{PNEC_i} \tag{3}$$

$$Contribution \ \% = \frac{RQ_i}{\sum RQ_{site}} \tag{4}$$

Here, the $PNEC_{mss}$ represents the predicted no effect concentration to the most susceptible species among earthworms (*Eisenia fetida)*, enchytraeids (*Enchytraeus crypticus)*, springtails (*Folsomia candida)*, mites (*Hypoaspis aculifer)* and nitrogen mineralization microorganisms. The $PNEC_{mss}$ can be calculated as the ratio of the endpoint (LC50, EC50 or NOEC) of the most susceptible species and the assessment factor (AF). The assessment factor can be set as 10, 50, 100 or 1000 according to the amount of toxicity data available (Vašíčková et al., 2019). Briefly, (1) the AF is defined as 1000 if at least one LC50 is available at a single ecological level; (2) the AF is defined as 100 if long-term assays are available and (3) an AF of 50 or 10 is given if there are two or three or more available NOECs, respectively. Toxicity data, AF and calculated $PNEC_{mss}$, derived from PPDB and literature, are listed in the supplementary information (Table S3). $\sum RQ_{site}$ quantifies the ecological risks posed by detected mixtures at a location, which can be classified into four levels of severity: negligible risk ($\sum RQ_{site} < 0.01 =$, low risk ($0.01 \leq \sum RQ_{site} < 0.1 =$, medium risk ($0.1 \leq \sum RQ_{site} < 1 =$ and high risk ($\sum RQ_{site} > 1$).

2.5. Hazard ranking of pesticides in soil

This study proposes a 2-step hazard ranking model that uses a Hasse diagram, a graphical methodology that ranks objects in a way of partial

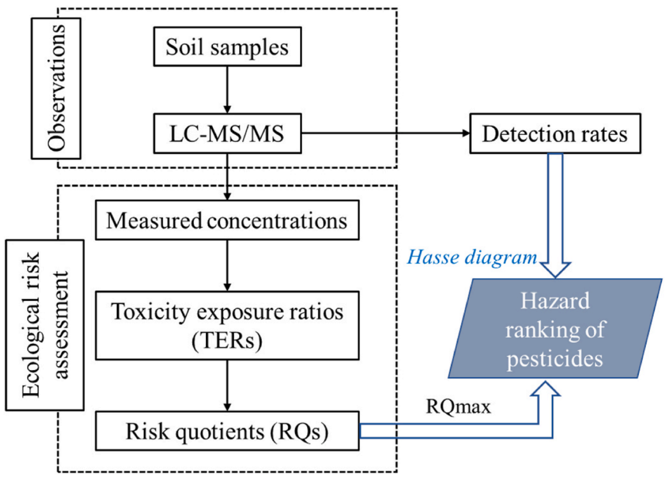

Fig. 1. The framework of the pesticide hazard ranking model.

order and visualizes the connections between these objects (Brüggemann and Patil, 2011). The ecological risk indictor (RQ) and detection rates of pesticides in soil samples were ranked using the Hasse diagram (Fig. 1). The calculated RQ_i represents the severity of the exposure risk posed to soil biota by single pesticides, while the detection rates of pesticides in soil were considered to reflect how easily non-target soil species were exposed to the pesticides. The maximum values of RQ_i for each pesticide were defined as RQ_{max}. Briefly, the detection rates and RQ_{max} of pairs of pesticides were initially compared. In the diagram, pesticides with both higher detection rates and RQ_{max} were placed in upper levels, relative to the other pesticide. Therefore, the compound located higher in the diagram is more hazardous to soil biota in the study region, and a compound located lower in the diagram is less hazardous. If the value of pesticide was not high neither from eco-risk nor from detection rate, the paired of pesticides under consideration cannot be directly compared and even linked.

2.6. Statistical analysis

Only concentrations above the LOQ were included in the further statistical analysis. The Kolmogorov-Smirnov test was performed first to examine the normality of the distribution of data. When data distribution was normal and skewed, one-way ANOVA and Mann-Whitney U tests were performed to compare the differences in the measured concentrations in samples taken from different crops, fields, depths, and sampling times. One-way ANOVA was performed to identify significant differences in the number of detected residues in the samples taken from different crop fields, depths and sampling times. The Spearman's correlation test was performed to examine the correlations between the detected concentrations of pesticides. A linear regression model was applied to examine the correlations between measured pesticide concentrations and pesticide application rates.

3. Results

3.1. Overview of pesticide residues in soil

Multiple residues were detected in 57% of collected soil samples. Pesticides were detected in over 80% of collected samples, and 12% of collected samples contained more than 5 residues, with a maximum of 8

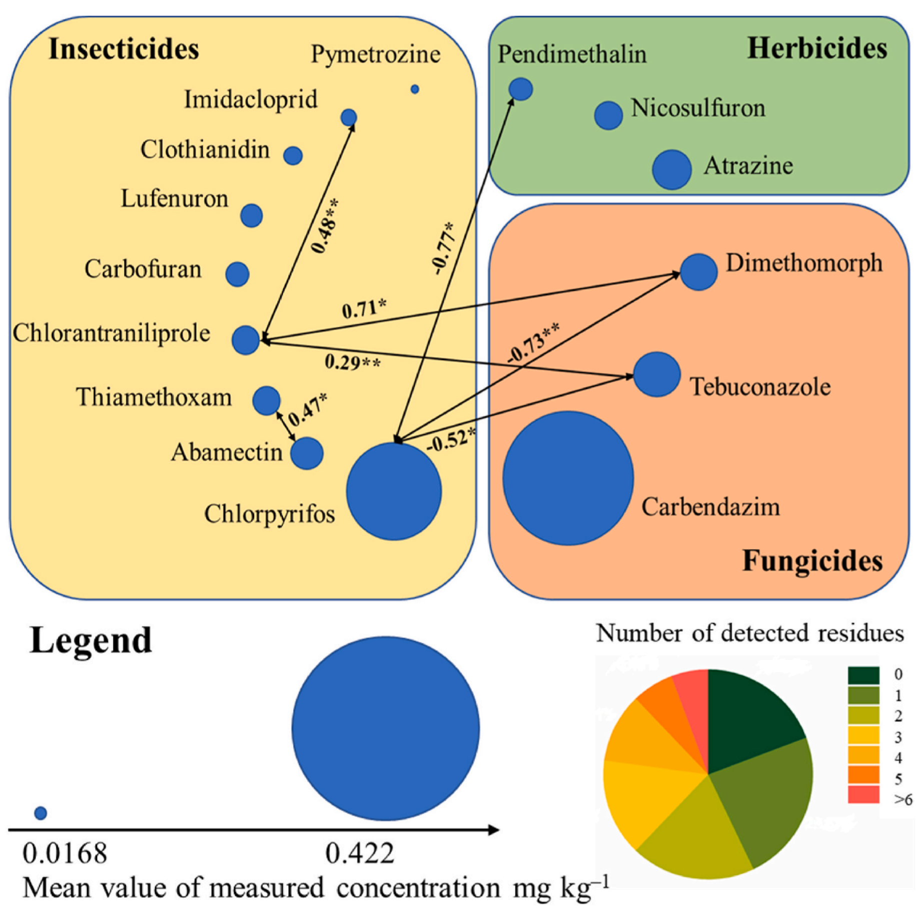

Fig. 2. Measured pesticide concentrations in soil samples and the internal correlations between paired pesticides. Note: The arrows represent correlations between connected pesticides. Only significant correlations were displayed. * Significant level at $p < 0.05$, ** Significant level at $p < 0.01$.

Table 1
Descriptive statistics of pesticide concentrations (mg kg^{-1}) in soils.

Pesticide	Type	Class	Overall				0–2 cm depths			2–10 cm depths		
			Detection rate (%)	MC_{mean}	Median	MCmax	Detection rate (%)	MCmean	MCmax	Detection rate (%)	MCmean	MCmax
Chlorpyrifos	Insecticide	Organophosphate	11.5	0.274	0.0269	1.55	11.6	0.395	1.55	8.60	0.112	0.545
Carbendazim	Fungicide	Benzimidazole	5.71	0.422	0.0198	1.85	7.20	0.452	1.85	4.30	0.371	1.09
Clothianidin	Insecticide	Neonicotinoid	3.57	0.0304	0.0276	0.0661	4.30	0.0329	0.0661	4.30	0.0193	0.0284
Imidacloprid	Insecticide	Neonicotinoid	24.5	0.0254	0.0215	0.782	26.1	0.0276	0.0782	24.3	0.0219	0.0453
Thiamethoxam	Insecticide	Neonicotinoid	13.7	0.0559	0.0273	0.281	15.9	0.0706	0.281	11.4	0.0357	0.0752
Dimethomorph	Fungicide	Morpholine	7.85	0.0758	0.0213	0.426	14.5	0.0761	0.426	1.40	0.0723	0.0723
Chlorantraniliprole	Insecticide	Anthranilic diamide	37.4	0.0541	0.0275	1.53	37.7	0.0252	0.0661	3.71	0.0829	1.53
Abamectin	Insecticide	Micro-organism derived compounds	17.3	0.0750	0.0218	0.319	26.1	0.0662	0.257	17.1	0.0532	0.319
Nicosulfuron	Herbicide	Sulfonylurea	5.71	0.0381	0.0270	0.759	11.6	0.0381	0.0759	nd	nd	nd
Lufenuron	Insecticide	Benzoylurea	21.4	0.0397	0.0276	0.202	34.8	0.0463	0.202	11.4	0.0201	0.0370
Pymetrozine	Insecticide	Pyridine	5.00	0.0168	0.0171	0.243	5.80	0.0175	0.0243	4.30	0.0158	0.0183
Pendimethalin	Herbicide	Dinitroaniline	4.29	0.0275	0.0169	0.556	8.70	0.0275	0.0556	nd	nd	nd
Atrazine	Herbicide	Triazine	11.4	0.0627	0.0207	0.627	18.8	0.0736	0.370	5.70	0.0273	0.0413
Tebuconazole	Fungicide	Triazole	35.3	0.0120	0.0529	0.684	3.91	0.129	0.506	31.4	0.104	0.684
Carbofuran	Insecticide	Carbamate	7.14	0.0447	0.0186	0.203	8.70	0.0629	0.203	5.70	0.0182	0.0194

Note.
nd, not detected.

residues (Fig. 2). Chlorantraniliprole and tebuconazole were the most widely detected pesticides in the soil, with the detection rates exceeding 35% (Table 1). Pesticides were more frequently detected in apple orchard soils, followed by vegetable fields and grape vineyards. After a growing season, the number of detected residues in samples taken after harvesting from apple orchards and grape vineyards were significantly lower as compared to the samples taken before pesticide application (Fig. S1). More residues (2.7 residues on average) were found in the topsoil than from deeper layers (2.3 residues on average) (Fig. S1). Pesticide concentrations were widely distributed ranging from 0.01 to 1.85 mg kg^{-1} (Table 1). Among all collected samples, the highest concentration was found for carbendazim, followed by chlorantraniliprole and chlorpyrifos at roughly 1.50 mg kg^{-1} (Fig. 2 and Table 1). No significant differences were found in pesticide concentrations in samples taken from different crops, depths and times (Fig. S2). The application rates of the analysed pesticides (displayed in Table S4) were obtained via farmer interviews in the study region that were carried out prior to the field sampling (Mu et al., 2022a, 2022b). The measured pesticide concentrations were found to be positively correlated with the pesticide application rates in the field (Fig. S3).

3.2. Ecological risk assessment

3.2.1. Risk assessment of single pesticides using TERs

To address the single pesticide exposure risks to the soil biota, a TER approach was performed for selected in-soil species and microorganisms in the 0–2 and 2–10 cm soil layers. The maximum value and means of measured pesticide concentrations in 0–2 and 2–10 cm soil layers are presented in Table S5. The TERs for the soil samples from different layers under the general scenario and worst-case scenario were separately calculated (Tables 2 and 3). Nicosulfuron and pendimethalin were excluded from the TER assessment in the 2–10 cm soil depth due to their absence in these soil samples.

TER values were more frequently found to exceed the trigger values in 0–2 cm soil depth samples. Based on the TERs, *E. fetida* is the most susceptible soil biota in all depths, as it suffers chronic exposure risks from multiple pesticides under worst-case scenario. Carbofuran presents the most severe exposure risks to *E. fetida* (TER = 0.01), and there were 7 additional pesticides with TERs lower than 1 under worst-case scenario at a depth of 0–2 cm. For the acute exposure risk, only chlorpyrifos had a TER lower than the trigger value for *E. fetida* at a depth of 0–2 cm. It should be noted that chlorpyrifos and carbendazim had lower TERs than the trigger value under general scenarios for *E. crypticus* and the worst-case scenario for *F. candida* at all depths. Multiple pesticides including abamectin and chlorpyrifos exhibited potential exposure risks to N/C mineralization organisms at all depths under the worst-case scenario.

3.2.2. Risk assessment of pesticide mixtures by RQ

As shown in Fig. 3, the calculated $\sum RQ_{site}$ indicates a high level of ecological risk posed by pesticide mixtures at the sampled locations. The ecological risks were recognized as high risks in nearly half of the collected samples, while only around 30% of samples showed negligible risk.

The highest $\sum RQ_{site}$, which was 490, was found in apple orchards. The ecological risks posed by pesticide mixtures varied among the fields with different crop types. Over 67% of samples from vegetable fields were recognized as high risk, while the proportion for apple orchards was around 39% (Fig. 3). In line with the detection rates, the calculated RQs were significantly lower at the 2–10 cm depth. It is also worth noting that the ecological risks significantly decreased after harvest (Fig. S4).

The contributions (%) of pesticides to the ecological risks at the sampled locations were calculated and the major contributors to this risk were further examined (Fig. 4 and Fig. S5). The major risk contributors varied due to different pesticide accumulation patterns across the sampled fields. For the wheat/maize rotation fields, the ecological risks

Table 2
TER_{max} and TER_{mean} calculated based on the selected species and single pesticides in the 0–2 cm soil depth. Trigger value: 10 for acute risk, 5 for chronic risk, TERs below trigger value are presented in bold font.

Pesticides	*E. fetida* acute		*E. fetida* chronic		*E. crypticus* Chronic		*F. candida* chronic		*H. aculeifer* chronic		N/C mineralization organisms	
	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}
Carbendazim	317	77.7	8.84	**2.17**	NA	NA	**0.220**	**0.0500**	NA	NA	14.2	**3.47**
Chlorpyrifos	37.2	**9.46**	**1.01**	**0.260**	**0.250**	**0.0600**	NA	NA	NA	NA	5.06	**1.29**
Clothianidin	282	200	53.0	**0.0400**	NA	NA	NA	NA	NA	NA	NA	NA
Dimethomorph	140	25.1	**2.34**	**0.420**	13.1	**2.35**	16.4	**2.94**	NA	NA	NA	NA
Thiamethoxam	LR	LR	75.6	**0.0200**	NA	NA	NA	NA	NA	NA	NA	NA
Chlorantraniliprole	LR	LR	776	**0.300**	NA	NA	NA	NA	317	121	NA	NA
Abamectin	LR	LR	LR	LR	NA	NA	LR	388	NA	NA	7.23	**2.72**
Nicosulfuron	734	368	6.56	**3.29**	262	132	6.56	**3.29**	NA	NA	NA	NA
Lufenuron	LR	LR	LR	LR	NA	NA	NA	NA	NA	NA	17.3	**3.97**
Pymetrozine	LR	LR	NA	NA	NA	NA	11.4	8.22	NA	NA	NA	NA
Carbofuran	LR	LR	22.3	**0.0100**	NA	NA	LR	LR	NA	NA	107	32.9
Imidacloprid	LR	LR	837	**0.300**	NA	NA	NA	NA	NA	NA	NA	NA
Tebuconazole	LR	LR	260	**0.0700**	NA	NA	596	152	LR	758	94.0	23.9
Pendimethalin	LR	LR	NA	NA	36.40	18.00	NA	NA	NA	NA	NA	NA
Atrazine	LR	605	11.4	**2.27**	NA	NA	**2.85**	**0.570**	NA	NA	NA	NA

Note.
NA, data not available.
LR means the corresponding TER value above 1000, for which the exposure risk from pesticides could be perceived as low.

Table 3
TER_{max} and TER_{mean} calculated based on the selected species and single pesticides in the 2–10 cm soil depth. Trigger value: 10 for acute risk, 5 for chronic risk, TERs below trigger value were presented in bold font.

Pesticides	*E. fetida* acute		*E. fetida* chronic		*E. crypticus* Chronic		*F. candida* chronic		*H. aculeifer* chronic		N/C mineralization organisms	
	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}	TER_{mean}	TER_{max}
Carbendazim	387	132	10.8	**3.68**	NA	NA	**0.270**	**0.0900**	NA	NA	17.3	5.89
Chlorpyrifos	131	27.0	**3.56**	**0.730**	**0.890**	**0.180**	NA	NA	NA	NA	17.8	**3.67**
Clothianidin	680	466	129	88.1	NA	NA	NA	NA	NA	NA	NA	NA
Dimethomorph	148	148	**2.46**	**2.46**	13.0	13.8	17.3	17.3	NA	NA	NA	NA
Thiamethoxam	LR	LR	150	71.0	NA	NA	NA	NA	NA	NA	NA	NA
Chlorantraniliprole	LR	146	236	12.8	NA	NA	NA	NA	96.5	5.23	NA	NA
Abamectin	LR	LR	LR	LR	NA	NA	LR	314	NA	NA	13.2	**2.20**
Lufenuron	LR	LR	LR	LR	NA	NA	NA	NA	NA	NA	40.0	21.6
Pymetrozine	LR	LR	NA	NA	NA	NA	12.6	11.0	NA	NA	NA	NA
Carbofuran	LR	LR	76.0	71.4	NA	NA	LR	LR	NA	NA	365	343
Imidacloprid	LR	LR	LR	510	NA	NA	NA	NA	NA	NA	NA	NA
Tebuconazole	LR	LR	323	49.0	NA	NA	741	112	LR	560	117	17.7
Atrazine	LR	LR	30.8	20.0	NA	NA	7.69	5.09	NA	NA	NA	NA

Note.
NA, data not available.
LR means the corresponding TER value above 1000, for which the exposure risk from pesticides could be perceived as low.

were mostly posed by atrazine, while imidacloprid and chlorpyrifos were the major ecological risks contributors to in apple orchards (Fig. 3). In the high-risk locations ($\sum RQ_{site} > 1$), dominant contributors to ecological risk were imidacloprid and lufenuron, as they dominated in 34 and 32 locations, respectively. The contributions to the $\sum RQ_{site}$ ranged from 4 to 99% for imidacloprid and from 3 to 100% for lufenuron.

3.3. Hazard ranking of pesticide residues in soil

In this study, pesticides were ranked according to the hazard they posed to soil biota with the most hazardous pesticides being identified using a Hasse diagram. As shown in Fig. 5, all pesticides were ranked and separated into one of 5 levels following a descending order of hazard from H1 to H5. Abamectin, tebuconazole, chlorantraniliprole and chlorpyrifos, which were ranked at H1 level, were found to be the most hazardous pesticides in this study. In contrast, clothianidin and pymtrozine, at H5, were perceived to cause the least harm as compared to the other pesticides that were detected.

4. Discussion

4.1. Pesticide residues in agricultural soil

This study measured the concentrations of pesticides commonly used in major crop fields in Quzhou, NCP at 0–2 and 2–10 cm depths. The sampling campaign was performed twice, once before pesticide application and once after harvest, to compare the background and accumulation values of pesticides. Carbendazim was found in the highest concentrations in the top soil layer, with 1.85 mg kg^{-1}, while chlorantraniliprole was found in the highest concentrations at the 2–10 cm depth. The positive linkages between pesticide application rates and the measured concentrations confirmed that successive pesticide application is the main cause of pesticide accumulation in soil. Compared to studies performed in other regions, higher accumulation levels of commonly used pesticides including carbendazim, tebuconazole, atrazine and imidacloprid were found in this study (Table S6). In the North China Plain, farmers tend to use pesticides collectively in one spraying event and may even apply them in excessive doses (Zhang et al., 2015). It is reported that surprisingly large amounts of pesticides are used in fields to secure yield, for example, a total of 107 different pesticides

	Wheat maize rotation	Vegetables	Apple orchards	Grape
Carbendazim	0	0	14,15	**40,58**
Chlorpyrifos	0,43	0	**46,35**	0
Clothianidin	0	1,25	0	0
Dimethomorph	0,01	0,30	0	0,95
Thiamethoxam	0,45	0,33	0,08	0,47
Chlorantraniliprole	0	0,01	0	0,02
Abamectin	0,14	13,38	4,75	0,83
Lufenuron	9,98	**84,63**	3,09	11,76
Pymetrozine	0	0,10	0,03	0
Carbofuran	0	0	5,48	2,30
Imidacloprid	4,96	0	22,87	28,24
Tebuconazole	0	0	1,55	1,27
Pendimethalin	0	0,01	0,01	0,01
Atrazine	**84,03**	0	1,63	13,56

Contributions (%) 0 20 40 60 80 100

Fig. 3. Contributions (%) of detected pesticides to the ΣRQ_{site} for samples in different crop type fields.

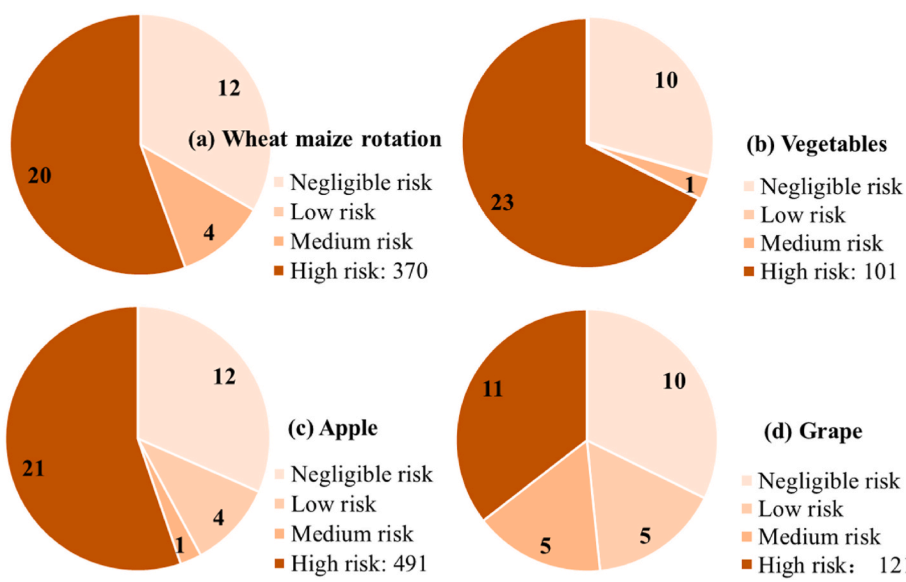

Fig. 4. Percentages (%) of ecological risk levels in samples from (a) wheat maize rotation, (b) vegetable, (c) apple orchards and (d) grape fields, Note: The figures in the high risk categories of legends represent the highest values of the calculated ΣRQ_{site} in the corresponding farming systems.

were used by the interviewed grain crop farmers (Sun et al., 2019). Thus, interviewing farmers from both local and surrounding regions would help to obtain a complete pesticide list to reflect the real combinations of pesticide residues in soil. Besides the pesticide usage patterns, the lower temperature might inhibit the soil dissipation process due to lower pesticide degradation rates by microorganisms in the soil (Li and Niu, 2021), which caused higher pesticide residual levels in the study region.

Fine fractions of surface soil can easily be transported by wind and water erosion (Silva et al., 2018), indicating that attached pesticides could also potentially spread to ambient air and surrounding water streams. In this study, pesticides were more frequently detected, and were present in higher concentrations, in soils close to the surface (Fig. S2 and Table S5), suggesting that the transport of pesticides in this region due to soil erosion should be further studied.

Despite being forbidden or restricted pesticides in China (MOARA, 2021a,b), chlorpyrifos and carbofuran were both detected in the collected samples, with the maximum values exceeding 1.5 and 0.2 mg kg^{-1}, respectively. The presence of these compounds in the soil indicates that there might still be new inputs of these compounds in the fields, which needs to be further verified, possibly by comparing their concentrations with those of their degradation products.

4.2. Ecological risk assessment of pesticides for soil biota

This study includes a comprehensive ecological risk assessment of pesticides based on the application of TERs and RQs. The use of measured concentrations based on a designated sampling scheme, rather than predicted concentrations, better considers the inherent homogeneity of the ecosystem, and presents a more accurate estimation of risk (Bhandari et al., 2021).

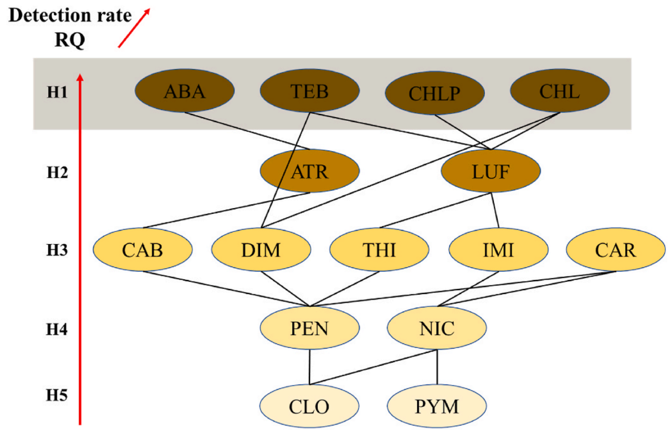

Fig. 5. Hasse diagram for pesticides posing ecological hazards to soil biota in arable soil, Note: ABA, abamectin; TEB, tebuconazole; CHLP, chlorantraniliprole; CHL, chlorpyrifos; ATR, atrazine; LUF, lufenuron; CAB, carbofuran; DIM, dimethomorph; THI, thiamethoxam; IMI, imidacloprid; CAR, carbendazim; PEN, pendimethalin; NIC, nicosulfuron; CLO, clothianidin; PYM, pymtrozine.

The results from the TERs revealed a concerning level of exposure risk from pesticides for N/C mineralization microorganisms (Tables 2 and 3), especially in the 0–2 cm soil depth. The TERs of commonly used pesticides such as abamectin, carbendazim, lufenuron were found to be below the trigger value, indicating that local pesticide application patterns may have caused negative effects on soil microorganism communities, such as a decline in microbial populations. Microorganisms play an essential role in maintaining soil ecosystem functions such as nutrient cycling, deposition of organic compounds (Egbe et al., 2021; Yang et al., 2017), and crop yield. The balance between pesticide application, crop yield and soil quality should be thoroughly considered, and more sustainable crop protection strategies based on local crop types and climactic conditions should be established.

In this study, 47.5% of the locations were assessed as high risk, whereas the proportions from other studies concerning, for example, Nepal and the Czech Republic, were only 16% and 35%, respectively (Bhandari et al., 2021; Vašíčková et al., 2019). The higher ecological risk in Quzhou county is due to the higher pesticide residual levels in soil and the use of pesticides with extremely low LC50 and NOEC. In the soil at both 0–2 and 2–10 cm depths, the accumulated levels of chlorpyrifos and carbendazim threaten multiple soil species (Tables 2 and 3) under both the general scenarios and the worst-case scenarios. Similarly, these compounds were also found to be hazardous to non-target species in Nepalese soils at all depths (Bhandari et al., 2021). Moreover, compared with NCP, the higher temperature in Nepal facilitates soil dissipation of pesticides and thus further lowers their residual levels in the soil. In the present study, insecticides including chlorpyrifos, imidacloprid and lufenuron and the herbicide atrazine were found to have made considerable contributions to the total ecological risks at the studied locations. In Eastern Europe, conazole fungicides and chlorotriazine herbicides contributed most to the eco-risks for soil biota (Vašíčková et al., 2019). The differences in the major risk contributors might be due to the variability in the crop type of sampled fields and the related pesticide application patterns. This study found that the measured concentrations and ecological risks of pesticides in harvested soils were significantly lower, which might be attributed to the pesticide transport from topsoil via water erosion and leaching in the growing season of 2021. Based on the results from the local weather station, heavy rains and downpours were more frequently occurred during summer season of 2021, causing off-site transport of pesticides driven by water erosion and leaching. Besides the measured concentrations of pesticides and their toxicities, the bioavailability of pesticides in soils is a key factor determining its exposure risk to soil biota. The equilibrium of adsorption and desorption of pesticides to soil particles affects their exposure risk to soil biota, which should be considered in future research.

The sampling scheme of this study covers the typical crop types in the NCP; thus, the main findings should bring to attention the negative impact of pesticides on the soil biota under current pesticide application patterns in the whole region. In this study, the ecological risks of pesticide mixtures were assessed using the concentration addition method, which assumes that there are no effects arising from interactions between the analysed pesticides. In field conditions, synergistic and antagonistic effects are likely to exist, especially between insecticides and fungicides. Thus, more holistic risk assessment models taking the synergistic and antagonistic effects into account need to be further developed for pesticide mixtures. The risk assessment was performed based on ecotoxicology tests concerning 5 soil biota species, which may not be representative for all soil species. Future work should focus on ecotoxicology test and comprehensive risk assessment in order to investigate interactions among commonly used pesticides (as shown in Fig. 2) and their effects on more soil biota species.

This study has introduced a novel method for ranking pesticides that are hazardous to soil biota with the help of a Hasse diagram. Based on the diagram, additional attention should be paid to pesticides assigned to the H1 level. As commonly used insecticides, abamectin and chlorantraniliprole can cause negative impacts on non-target soil species as they cause reproductive problems and inhibit growth (Liu et al., 2018; Salman et al., 2022). Similarly, tebuconazole and chlorpyrifos have the potential to cause population declines in ammonia-oxidizing bacteria and archaea (Karas et al., 2018). Given their ubiquitous occurrence and high ecological risk, the use of H1 pesticides should be replaced with low-risk pesticides with similar functions (see Fig. 5), low toxicity pesticides or biopesticides posing less toxicity or being non-toxic on non-target organisms (Hanif et al., 2022). Besides the high-risk pesticides in H1 level, attentions still should be paid on pesticides posing high ecological risks but allocated into lower hazard level, such as carbendazim and carbofuran. For pest control purposes, the use of abamectin and chlorpyrifos can be replaced by clothianidin and pymtrozine; nicosulfuron could be an alternative option to eliminate weeds rather than using atrazine. Moreover, to mitigate the exposure risk of pesticides for non-target soil species and to maintain soil quality, integrated crop protection strategies that rely on multiple field measures, such as introducing natural enemies of pests, setting trap crops and applying mulches in multiple colors (Seidenglanz et al., 2022; Zhu and Zheng, 2022), should be developed based on local cropping patterns.

5. Conclusions

This study investigated the occurrence and distribution of pesticides across soil profiles with various crop types in Quzhou, in the NCP. The ecological risks to soil biota posed by single pesticides and mixtures at sampled locations were assessed using TERs and the RQ method. Based on the RQ_{max} and the detection rates of pesticides, a hazard ranking of the pesticides using a Hasse diagram was proposed.

More pesticide residues were detected in the 0–2 cm layer soil than the 2–10 cm soil layer. The highest concentration was found for carbendazim, followed by chlorpyrifos. Chlorpyrifos, carbendazim and imidacloprid pose chronic exposure risks to soil biota such as *E. fetida*, *F. candida* and *E. crypticus*. *E. fetida* is the species that is the most susceptible to the exposure risks from multiple detected pesticides. The residual levels of pesticide mixtures in most of the collected samples showed potential ecological risks. Specifically, 47.5% of the mixtures were recognized as high risk. Abamectin, tebuconazole, chlorantraniliprole and chlorpyrifos were found to be the most hazardous pesticides for soil biota in the study region.

This work reveals the underlying exposure risk that both individual pesticides and mixtures pose to soil biota under current pesticide application patterns in the NCP. The use of hazardous pesticides, as identified in the hazard ranking, should be replaced by low-risk pesticides with similar functions, or biopesticides.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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