Field and residential exposure of pesticides:

Integrated risk analysis on terrestrial ecosystems and rural residents

Hongyu Mu

Propositions

1. The misuse of pesticides has led to a decline in pollinators and soil biota.
   (this thesis)
2. Most personal exposure to pesticides originates from non-occupational sources.
   (this thesis)
3. Extension services and subsidies are the key drivers of the plant protection transition.
4. Statistics is the bridge from data to conclusion.
5. Playing Texas Hold'em helps improve risk management skills.
6. One who wishes to receive should first give.

Propositions belonging to the thesis, entitled

Field and residential exposure of pesticides: Integrated risk analysis on terrestrial ecosystem and rural residents

Hongyu Mu

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Chapter 1

General introduction

1.1 Global pesticide use

The global population is expected to exceed 9.7 billion by 2050, increasing food demand up to 98% as compared to the beginning of the 21st century (Valin et al., 2014). At the same time, the population explosion will put even more pressure on essential agricultural resources such as water and arable land (Lykogianni et al., 2021; Schneider et al., 2011). To secure crop yield and meet the growing food demand, efforts have been devoted to not only enhancing crop yield, but also preventing yield loss. The global annual yield loss is estimated to range from 20% to 40% as a result of weeds, insects, plant diseases, etc. (CABI, 2019). Weeds, as well as other unwanted plants, are in competition with crops for limited resources including light, nutrients, space and water (Clemens Lamberth, 2013). The decrease in yields is highly associated with insect and plant diseases induced by pathogens (Savary et al., 2019) which are the major threats affecting crop yields. It is estimated that the yield loss from insects could reach up to 20% or even higher as global temperatures continue to increase (Curtis et al., 2018). For grain crops, infections caused by pathogens could result in a yield reduction approaching 9% (Savary et al., 2019). Pesticides have been used since ancient times to cope with weeds, pests, and pathogens.

Pesticides are agrochemicals made from natural or synthetic substances. The initial attempt to use pesticides can be traced back several millennia to the time when farmers applied elemental sulphur to remove pests, quickly followed by the use of Ebers papyrus, primitive sulphides, mercury, and arsenic. During the last century, farmers began to use synthetic pesticides, which were created by modifying organic and inorganic compounds, Dichloro-diphenyl-trichloroethane (DDT) was one of the first synthetic pesticides to be used on a large scale. To date, over 1000 pesticide products have been used by farmers globally (Bhandari, 2021). Synthetic pesticides can be labelled as insecticides, fungicides, herbicides, rodenticides, fumigants, and insect repellents based on the organisms that they target. Pesticides can be further categorized as organochlorines, organophosphates, carbamates, pyrethroids, neonicotinoids and others depending on their chemical groups (Curtis et al., 2018). With such diverse pesticide products available and the increasing pressure on yields, farmers are prone to use multiple pesticides, so-called pesticide cocktails, to protect crops in intensive farming systems. It's reported that farmers in China often use more than 2 active substances per application when spraying staple crops (Zhang et al., 2015). Due to the limited knowledge of pesticides and the risks associated with their use, many farmers apply doses beyond the recommended ranges found on the product labels. Over the past few decades, there has been a strong increase in pesticide use. Global input has reached 2.7 million tonnes **(Fig. 1.1A)**, and the average application rate has increased by 50% compared with the amount used in 1990 **(Fig. 1.1B)**. Admittedly, pesticides have made remarkable contributions to food availability. Unfortunately, being exposed to pesticides threatens human health which has resulted in a death rate between 0.4% and 1.9% and can be directly linked to pesticide-related exposures. These exposures account for the deaths of 200 million people annually. Pesticides can also have negative impacts on biodiversity and ecosystem functions due to their lethal or sublethal effects on non-target species and their disruption of food webs (Chagnon et al., 2015; Tooker et al., 2021). Thus, great concerns have been raised as to the negative impacts of pesticides.

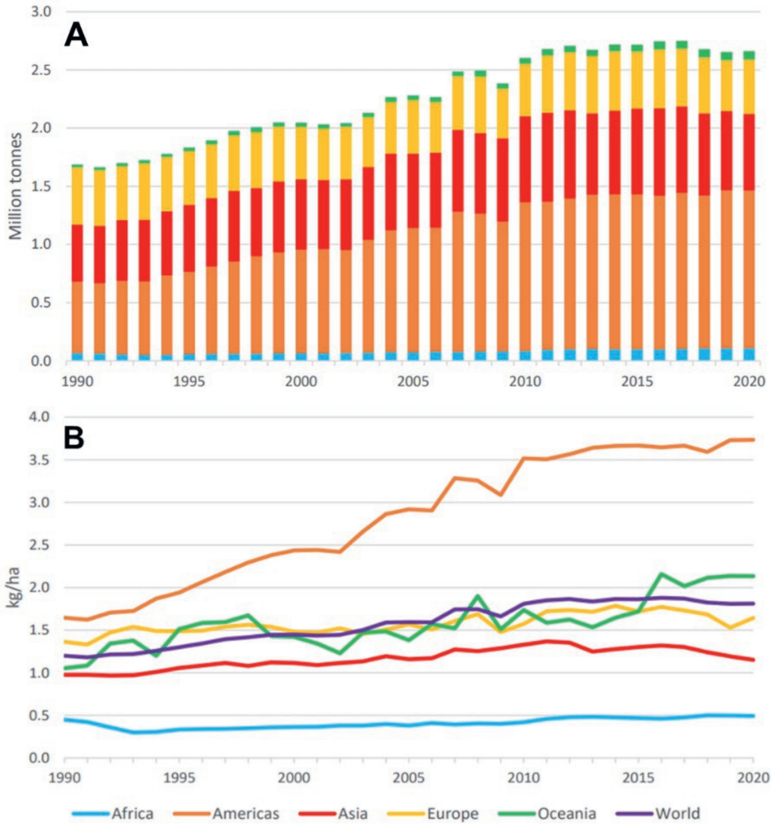

Fig 1.1 Global pesticide use from 1990 to 2020. A: the global annual input of pesticides; B: the average pesticide application rate (modified from: https://www.fao.org/3/cc0918en/cc0918en.pdf).

1.2 Pesticide behaviour in the environment

Synthetic pesticides are often more persistent in the environment than originally predicted and are often toxic to non-target species such as birds, fish, and beneficial insects. Pesticides can accumulate in environmental matrices after continuous field applications and pose further threats to environmental biodiversity and quality. Pesticides applied to fields only partly reach target crops, with the remaining parts dispersed into the air or deposited on the soil surface (Fig. 1.2). As a result of continuous applications, soil is a major collector of pesticide residues, especially the persistent ones. Pesticide residues have been found to be widely spread in agricultural soils, with multiple active ingredients showing up in most of the monitored sites (Riedo et al., 2022). In Europe, pesticides were found to be present in over 83% of soils, while multiple residues were detected in over half of the locations tested (Silva et al., 2019). The pesticides accumulating in topsoil can be absorbed by plant roots and further translocated to the edible parts of plants, resulting in dietary risks to both pollinators and consumers. Pesticide residues in soil can also move downward to deeper soil layers and potentially contaminate ground water via leaching. The leaching process is mainly determined by individual pesticide properties and soil characteristics, such as soil texture, organic matter content and pH. Other than the vertical transport along the soil profile, pesticide residues attached to soil particles can be further transported to the air and adjacent water bodies through wind and water erosion (Haberkon et al., 2021; Reichenberger et al., 2007). Wind-driven particles bound to pesticides are capable of moving long distances, even hundreds of miles (Aparicio et al., 2018b). Thus, under intensive use, pesticide residues can be distributed to multiple surrounding environmental domains and potentially travel to remote areas. For instance, multiple pesticides have been detected in the environmental samples taken from the Tibet plateau, where only limited agricultural activities have ever been carried out (Zhou et al., 2022). The discovery of pesticides that haven't been used in the study region indicates the continuous transport of pesticides from other regions.

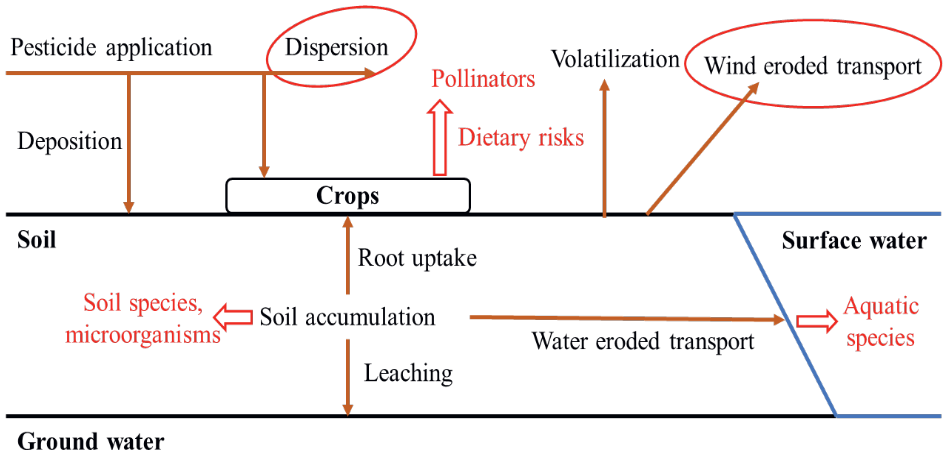

Fig. 1.2 Environmental fate of pesticides.

Pesticide cocktails are widely spread throughout both organically managed and conventionally managed agricultural fields. Based on a global meta, a total of 387 pesticides were observed in monitoring studies, including 106 transformed products (Sabzevari et al., 2022). Herbicides were the most abundant type of pesticides, accounting for over 40% of reported active substances. Concerningly, pesticide mixtures were found in over 70% of sampled sites, indicating potentially elevated ecotoxicity to soil species. Pesticides were also ubiquitous in soils regardless of management patterns and land cover. Despite lower concentrations and detection frequencies, pesticides were found in all sampled organic soils and in some sampled grasslands, with up to 16 residues in fields with no pesticide use for over 20 years (Riedo et al., 2021; Riedo et al., 2022).

As an essential soil degradation process, wind erosion occurs frequently in soils in arid and semiarid areas. During this process, pesticide residues attached to surface soil particles can be picked up by the wind and transported over long distances. Wind-eroded transport mainly occurs in three modes: creep (for particles larger than 500 μm), saltation (for particles ranging from 100 to 500 μm), and suspension (for particles smaller than 100 μm) (Aparicio et al., 2018b). Over 90% of pesticide-contaminated soil particles move via saltation within the first 30 cm of soil. There is increasing evidence that pesticides can be found and are concentrated in wind-eroded soil particles and other related matrices such as settled floor dust. In a field observation in Argentina, glyphosate and its metabolite AMPA were detected in wind-eroded materials at concentrations over 200 μg kg^{-1}, 60 and 3 times the concentration of the original applications of glyphosate and AMPA, respectively (Aparicio et al., 2018b). Pesticides were also found in wind-eroded sediments from loess soil following a wind-tunnel experiment; moreover, pesticides were found to be more concentrated in fine particles (Bento et al., 2017). Other than agricultural fields, pesticides have also been frequently detected in settled dust in residential areas, including indoor dust, outdoor dust on pavement, streets, and concrete exterior surfaces (Aslam et al., 2021; Beranger et al., 2019; Jiang et al., 2016; Jiang et al., 2012; Navarro et al., 2023; Saurat et al., 2023; Shen et al., 2023). As the existence of pesticides in residential areas has been well-studied, concerns have been raised regarding the potential risks posed by the pesticides found in surrounding indoor and outdoor spaces.

1.3 Negative impacts of pesticides on humans and non-target species

1.3.1 Exposure risks of pesticides to human health

Being exposed to pesticides can result in their accumulation in body tissues which can have negative effects on the physical health of exposed individuals. Pesticides can have both acute and chronic poisoning effects on the human body. Acute exposure occurs when individuals suffer high-dose exposure in a short period, causing symptoms such as skin and eye irritation, blisters and rashes, diarrhoea, and vomiting (Sharma et al., 2020). Chronic exposure refers to the negative effects caused by continuous pesticide exposure over months or years, which could induce severe health consequences including functioning system disorders, cancer or even death due to bioaccumulation (Alavanja et al., 2004). Chronic pesticide exposure has elevated the risks of prostate, breast, bladder, lung, and colon cancers. Meanwhile, the rising incidence of diabetes, leukaemia, Parkinson’s disease, Alzheimer’s disease and lung and neurological disorders were found to be correlated with exposure to certain groups of pesticides **(Table 1.1)**.

Efforts have been devoted to estimating pesticide exposures and assessing the associated risks to individuals. A combined field survey-modelling approach has been commonly used to assess the chronic pesticide exposure risk based on the health risk assessment (HRA) model. The health risks of pesticides, including cancer and non-cancer risks, can be attributed to dietary and non-dietary routes. Dietary exposure refers to the intake of pesticide-contaminated food or drinking water, whereas the non-dietary route mainly includes inhalation, ingestion, and dermal contact.

Table 1.1 Health consequences of being exposed to pesticides.

Health issues	Diseases/symptoms	Pesticides	Sources
Cancer	Bladder cancer	Imidazolinone, imazethyper, imazaquin herbicides	(Amr et al., 2015)
	Meningioma	Herbicides	(Samanic et al., 2008)
Diabetes	Type 2 diabetes	Organochlorine pesticides, organophosphate pesticides, DDT and DDE, phenoxy herbicides	(Velmurugan et al., 2017)
	Diabetes and diabetic nephropathy	DDT and heptachlor epoxide	(Everett et al., 2017)
Lung issues	Asthma	Endocrine disruptors, glyphosate and paraquat, α-HCH, DDE, pendimethalin, aldicarb	(Rani et al., 2021)
	Respiratory disorders	Organophosphate pesticides	(Hoppin et al., 2006)
Neuron issues	Parkinson's disease	2, 4-D	(Hoppin et al., 2006)
	Alteration in mental function	Organophosphate pesticides	(Hernandez et al., 2017)
	Alzheimer disease	DDE	(Richardson et al., 2014)
Reproductive problems	Premature abortion	Phenoxyacetic acid, triazines	(Arbuckle et al., 2001)
	Decrease in sperm maturity and motility	Abamectin	(Celik-Ozenci et al., 2012)
	Imperfection of neural tube	Organochlorine pesticides	(Ren et al., 2011)

Table 1.1 (Continued).

Health issues	Diseases/symptoms	Pesticides	Sources
Endocrine disruption	Disrupting the hormone expression in hypothalamus	Acephate	(Guarnotta et al., 2022)
	Androgen inhibition	Atrazine	(Kucka, 2012)

To estimate daily exposure and assess the associated risks, the health risk assessment (HRA) model developed by the EPA has been used for the assessment of both dietary and non-dietary exposures (EPA, 2023). The assessment consists of four steps: 1) hazard identification: ascertain if the studied pesticides can potentially cause harmful effects on the physical health of humans; 2) dose-response assessment: collect toxicology information and verify the numerical relationship between exposure and perceived effects, 3) exposure assessment: measure or estimate the characteristics of the exposure, such as exposure frequency and duration, and 4) risk characterization: determine the degree of harmful effects or health risks (EPA, 2023). Particularly for the exposure assessment, dietary exposures can be assessed by tracing the pesticide levels in food and drinking water and estimating the associated daily intake, which has been extensively investigated in previous studies. Sang et al. (2022) screened pesticide levels in the drinking water of 36 major cities in China and found that chlorpyrifos posed the highest risk (Sang et al., 2022). Residual levels of pesticides in food were examined in countries such as China, Brazil, Germany, Cameroon, Uganda, Poland, and India (Valentim et al., 2023; Galani et al., 2020; Lehmann et al., 2017; Li et al., 2023; Mozzaquatro et al., 2022; Ngabirano et al., 2022; Sharma et al., 2022; Sieke et al., 2018; Szpyrka et al., 2015; Wang et al., 2022) with concentrations exceeding regulated limits and potential dietary risks detected. However, the direct assessment of pesticide exposure from non-dietary sources can be highly challenging to determine due to the complexity of the exposure sources and routes, thus it has been mostly assessed indirectly by measuring pesticide concentrations in the surrounding environmental domains. Due to the fact that soil serves as a primary depository for pesticides, soils have been frequently screened for pesticide residues to assess health risks via ingestion and dermal contact (Hasnake et al., 2023; Li et al., 2021; Yao et al., 2022). These are not the only exposure routes. Distinct exposure risks of pesticides can also be found in different exposure scenarios such as occupational exposures in the fields and non-occupational exposures in the indoor and outdoor spaces. Aerts et al. (2018) found that pesticide levels differed between forest and office environments by using silicone wristbands (Aerts et al., 2018). For example, dust from indoor and outdoor surfaces contained different levels of pesticides due to the differences in environmental settings such as humidity, temperature, and light (Jiang et al., 2016).

Other than the presence of pesticides in environmental matrices, pesticide exposure can be determined by other monitoring approaches, such as biomonitoring and the use of devices made of silicone. Biomonitoring aims to investigate the levels of chemicals in excreted matrices, such as urine, hair, sweat, breast milk, and faeces to reveal the body burden of the chemicals and the potential health impacts (Esteban et al., 2009). A cohort study targeting pregnant women revealed that these women had multiple exposures to pesticides during pregnancy with an average of 22 and 12 residues detected in hair and urine samples, respectively (Hardy et al., 2021). In recent years, numerous studies have investigated pesticide concentrations in biological samples collected from women, children, and adults in order to build links between pesticide levels and health issues (Baumert et al., 2022; Fabbri et al., 2023; Lee et al., 2022) as well as daily habits (Iglesias-Gonzales et al., 2022; Li et al., 2022). Admittedly, biomonitoring provides an overview of personal exposure to various pesticides by integrating the major exposure routes; however, the sample collection procedures can be invasive, especially for children (Samon et al., 2022).

With the ability to absorb volatile or semi-volatile compounds in the air, silicone wristbands have been used to monitor personal exposures for a wide range of organic pollutants (Aerts et al., 2018; O'Connell et al., 2014). The exposome derived from silicone wristbands provides integrative and highly individualized exposure profiles in the daily life by indicating the merged exposure dosages from mainly inhalation and partly dermal contact and dietary (dermal excretion) routes (Samon et al., 2022). As wearable passive sensors, wristbands have been used to measure hundreds of chemicals, including pesticides (Alkon et al., 2022; Arcury et al., 2021; Bergmann et al., 2017; Harley et al., 2019), polychlorinated biphenyls (PCBs) (Vorkamp et al., 2016; Young et al., 2021), polycyclic aromatic hydrocarbons (PAHs) (Andersen et al., 2021; Dixon et al., 2019; Donatuto et al., 2019), flame retardants (Travis et al., 2020), and polybrominated diphenyl ethers (PBDEs) (Wang et al., 2020) normally within a time period of a week. With such a broad scope of monitored chemicals, diverse groups of participants were included in the exposure assessment experiments, such as pregnant women (Mendoza-Sanchez et al., 2022), farmworkers (Donald et al., 2016), children (Hammel et al., 2020), industrial workers (Wang et al., 2020), fishermen (Santiago et al., 2021) and even pets (Dixon et al., 2022), indicating the low invasiveness and high flexibility of utilizing silicone wristbands. In previous studies, silicone wristbands were mostly deployed solely to measure personal exposure levels. However, combined with other monitoring approaches, such as biomonitoring and active sampling, associations, or potential predictive relationships between the analytical results from different matrices can be examined (Dixon et al., 2022; Nhuyen et al., 2022). During the sampling periods, the uptake of chemicals on silicone wristbands consists of three phases: linear, curvilinear, and equilibrium (O'Connell et al., 2022). Thus, the links between direct measurements in wristbands and environmental concentrations were explored by quantifying the uptake processes, which included estimating the sampling rates and calculating silicone-air partitioning coefficients and equivalent air concentrations for a variety of chemicals. Despite the fact that scientists have more insights into the process of the silicone-gas interphase, the links between personal exposure and environmental enrichment of pesticides remain largely unknown.

Regrettably, previous studies assessed pesticide exposure risks indirectly by screening pesticides in environmental matrices or measuring different exposure routes and scenarios. To date, the complete picture of personal exposure to pesticides is still unclear, underlining the need for more precise and comprehensive exposure assessments.

1.3.2 The ecological risks of pesticides

Due to their toxicity, pesticides can have harmful effects on non-target species, such as birds, fish, mammals, and non-target insects, which results in increased mortality or even population decline (Serrao et al., 2022; Sanchez-Bayo et al., 2021; Tudi et al., 2021). Due to the changes in the populations of common food sources, predators and natural enemies might interfere with the biodiversity of local eco-communities and affect ecosystem functioning by decreasing habitats and nutrient cycling (Sim et al., 2022; Rumschlag et al., 2020). Special attention to the exposure risks of pesticides to pollinators and terrestrial species is needed due to the high environmental relevance of these creatures. Pollinators facilitate the reproduction of over 75% of flowering plants, which adds tremendous economic value to global crop productivity and secures nutrient availability (Dicks et al., 2021). Under field conditions, exposure to pesticides mainly occurs via direct contact with pesticide drifts, or indirect contact as a result of foraging attractive pesticide-contaminated crops. It has also been reported that bees might be frequently exposed to complex pesticide cocktails that accumulate in crops which are then transferred to pollen and nectar (David et al., 2016). Thus, exposure to pesticides can cause increased mortality in bees and even lead to population decline, which might result in the loss of wild plant diversity and long-term changes in food web interactions. Soil biota plays an essential role in maintaining soil functions, such as regulating soil nutrient cycling and contributing to soil biodiversity. Pesticide residues can have adverse impacts on soil biota by inhibiting gene expression and interrupting enzyme activities which affect performance, reproduction and growth (Ferreira et al., 2023).

Risk assessment approaches have been developed to better understand and evaluate the potential risks of soil pesticide residues to non-target organisms. The European Food Safety Authority has recommended a set of risk assessment methods, Toxicity Exposure Ratios (TERs) and a Risk Quotient-based approach to evaluate the exposure risk to soil biota posed by single pesticides and mixtures of pesticides (Products et al., 2017). In the assessment, five soil organisms, including *Eisenia fetida*, *Enchytraeus crypticus*, *Folsomia candida*, *Hypoaspis aculifer* and nitrogen mineralizing organisms, were selected as indicative species for pesticide exposure risks. The TER approach was designated to assess the species-specific exposure risk of a single pesticide active substance. As a unitless indicator, TERs were calculated based on the measured pesticide concentrations as well as ecotoxicological parameters such as $NOEC_{species}$ or $LC50_{species}$. Trigger values were set separately for acute (TER=5) and chronic (TER=10) exposure risks to characterize the harmful effects of pesticides, which means that the exposure risks to soil species is acceptable for acute TERs above 5 or chronic TERs above 10. In real exposure scenarios, soil species normally suffer from exposure to multiple residues. The RQ-based method was developed to assess exposure risks to soil species in the sampled locations based on the concentration-addition (CA) approach, assuming that there were no antagonistic or synergistic effects among the existing pesticide combinations. For the assessment, $PNEC_{mss}$ was introduced as the predicted no effect concentration for the most susceptible species among the five soil indicative organisms, which is perceived to be the ratio of the exposure endpoint (*LC50*, *EC50* or *NOEC*) and the assessment factor (AF). Sequentially, the *RQ* for a specific pesticide can be calculated based on the $PNEC_{mss}$ and measured pesticide concentrations. The risk posed by pesticide mixtures ($\sum RQ_{site}$) can be calculated as the sum of all RQs for all separate pesticide residues detected at the sampled location. In previous studies, the detrimental risks under general and worst cases were assessed using the measured mean and maximum concentrations for the calculation of *TERs* and *RQs*. Current studies focus mainly on the toxicity effects and mechanisms of pesticides for soil species under lab conditions, while studies evaluating exposure risks under field conditions are very limited.

1.4 Pesticide use in China: Current status and the underlying risks

To feed the largest population in the world, pesticides have been extensively applied to agricultural fields in China with a steady increase, from 154 kt in 1990 to a peak value of 351 kt in 2013 **(Fig. 1.3A)**. Since the government issued a zero increase of pesticides action plan there has been a large reduction in the field input of pesticides, which was 244 kt in 2021. Similar trends have been observed for the application intensity of pesticides which reached a peak at 2.64 kg ha^{-1} in 2014 and smoothly decreased to 1.9 kg ha^{-1} by 2021. The use of pesticides and chemical fertilizer greatly increase crop yields in China and as a result, pesticides used per value of agricultural product have steadily dropped to 0.25 kg per 1000 $ **(Fig. 1.3B)**. Despite the trend to decrease pesticide inputs, misuse of pesticides has still been frequently observed in field surveys, raising concerns about risks of pesticide use in actual field conditions. Pesticides were overused in over half of pest control cases with overuse rates exceeding 75% for the control of striped stem borer in rice fields and aphids in wheat fields (Zhang et al., 2015). Similarly, based on a nationwide survey, pesticides were misused in most pest control cases, whereas extremely high misuse rates were found for plant disease control in vegetable fields for crops such as tea, cucumber and tomato (Sun et al., 2019). Furthermore, farmers tend to use pesticide cocktails that consist of between 1.7 and 2.6 pesticides on average to handle insects, potentially causing additional damage to soil organisms due to synergistic effects (Zhang et al., 2015). To reduce the inputs of highly hazardous pesticides, the government has issued regulations that classify pesticides into three categories: allowed for use, restricted for use only on certain occasions and forbidden. Until now, a total of fifty pesticides have been forbidden by the government due to their toxicity, including 34 insecticides, 7 herbicides, 6 rodenticides, 2 fungicides, 12 acaricides, and 1 fumigant (MOARA, 2019b).

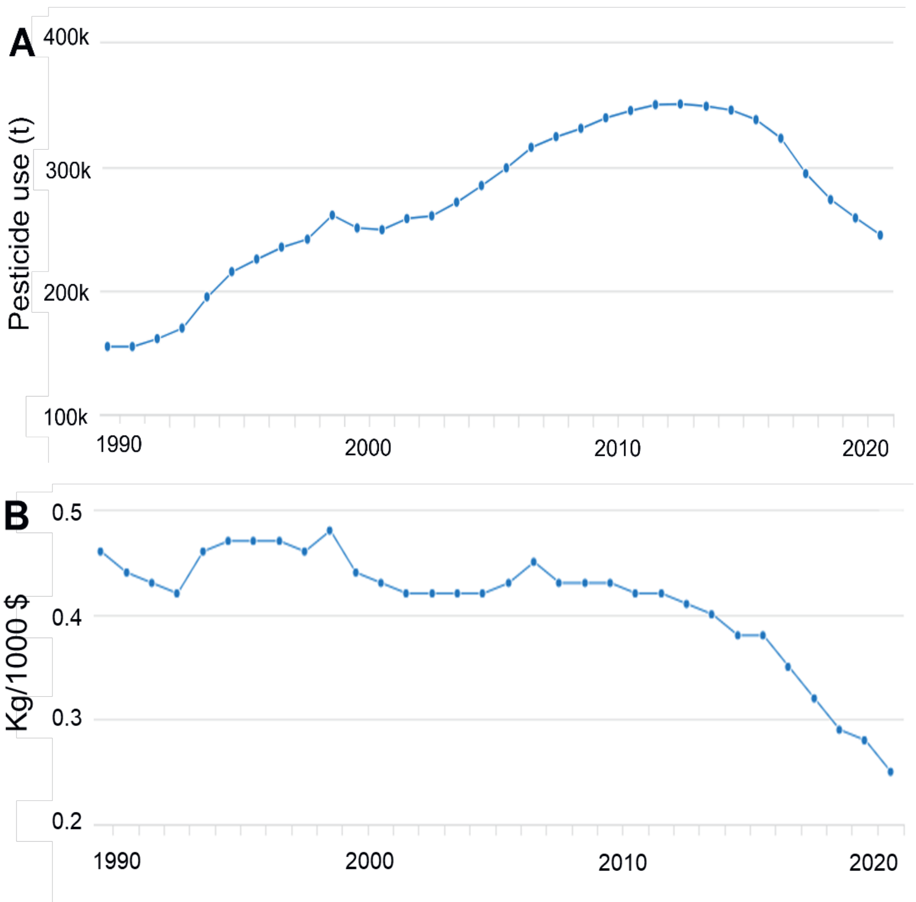

Fig. 1.3 Pesticide use in China from 1990 to 2021. A: the annual pesticide field input, B: annual pesticide usage per value of agricultural production (%).

The extensive misuse of pesticide cocktails in China has resulted in a hefty accumulation in surface soils. Despite the restrictive regulations of highly toxic pesticides, forbidden pesticides have been detected in agricultural soils, such as DDT and its metabolites, highlighting the persistence of pesticides and indicating potentially new inputs (Zuo et al., 2023). Based on a national monitoring study, 20 out of the 107 currently used pesticides (CUPs) that were analysed were insecticides which were detected in more than 60% of the collected soil samples (Zhou et al., 2023). Pesticide mixtures were frequently detected in monitored sites in combinations containing between 21 and 30 pesticide residues in more than three quarters of the samples. After exposure to pesticide mixtures, soil biota, such as *E. fetida*, suffered both acute and chronic effects. In case-specific studies, pesticides posed high ecological risks to soil species in 35% and 11% of monitored sites in the Three Gorges Reservoir Area and northeast China, respectively (Bhandari et al., 2021; Vasickova et al., 2019; Yang et al., 2022; Zhou et al., 2023). For the health risks which were determined using an integrated machine learning algorithm, approximately 3.7% of the soils in China that were determined to be risky where found mainly in the central-southern and northwest areas of China (Wang et al., 2022). Settled dust, especially indoor dust, in residential areas could be more indicative of the potential health risks of pesticides due to the concentrations of pesticides and the higher likelihood of exposures. However, there are only a few studies that have monitored pesticide levels in residential dust analysing only a limited number of pesticides and mainly targeting DDTs and organochlorine pesticides (OCPs) (Li et al., 2012; Shen et al., 2023; Wang et al., 2013; Zhang et al., 2010). Wang et al. (2013) found that the cancer risk from daily contact with OCPs in dust was concerning (RQ $> 10^{-5}$) to 43% of residents, while the exposure risks for other aspects, such as non-cancer risk or a broader range of CUPs, remained largely unknown. In summary, current pesticide level monitoring studies targeting CUPs in dust are inadequate, leading to an overlooked residential exposure risk to residents.

1.5 Study area and the sampling scheme

Pesticides have been applied intensively in the North China Plain (NCP), one of the major crop producing areas in China **(Fig. 1.4A)**. The NCP accounts for 3% of the land area and includes the Shandong province and parts of the Hebei, Henan, Anhui, and Jiangsu provinces; however, the pesticide input in this region constitutes over 30% of the national total input. Staple crops, including wheat, maize, and rice, are the major farming systems in the NCP **(Fig. 1.4B)**. Quzhou is a typical agricultural county, which is located in the central area of the NCP. Quzhou county (36°34′45″ N - 36°57′57″ N, 114°50′30″ E - 115°13′30″ E) has a total area of 667 km^2 with farmland accounting for 82.5% of the area. Located centrally in the North China Plain, the area has a subtropical humid monsoon climate with an annual mean temperature of 13.4 ℃ and an annual average precipitation of 556.2 mm. Grain crops, such as maize and wheat, and vegetables are the predominant crops. Apple orchards also can be found in a few villages. Until now, the state of pesticide uses and the accompanying environmental and health impacts in the NCP remain largely unknown. Thus, we selected Quzhou as the case study region where we performed farmer interviews, systemic monitoring programs and cohort studies related to pesticide usage and exposure risks.

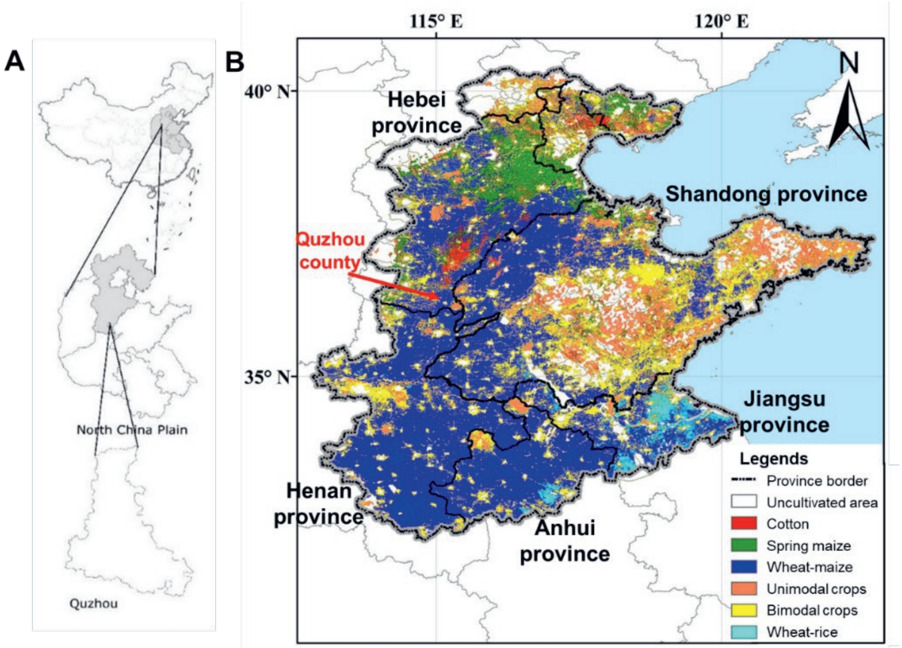

Fig. 1.4 Study area. A: Geographical locations in the North China Plain (NCP) and Quzhou county; B: spatial distribution of farming systems in the NCP (modified from: Distribution maps of crop planting areas in the North China Plain (2001-2018). A Big Earth Data Platform for Three Poles, DOI: 10.1016/j.compag.2021.106222.)

Farmer interviews were conducted prior to sampling to investigate the pesticide use patterns in the study region. Six villages covering the major cropping systems in Quzhou were selected and 197 farmers were randomly interviewed **(Fig. 1.5A)**. Sequentially, a systematic sampling campaign was carried out which included soil, residential dust, and silicone wristbands **(Fig. 1.5B)**. The sampling locations were mainly distributed around four villages to trace the accumulation and transport of pesticides in both particulate and gaseous phases from surrounding fields to the residential areas.

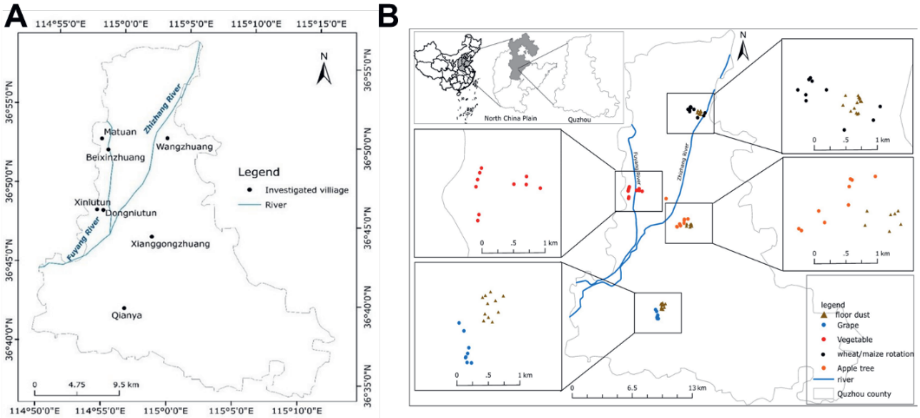

Fig. 1.5 Overview of sampling sites. A: villages selected for farmer interviews; B: distribution of sampling sites in Quzhou county.

1.6 Research gaps and objectives of the thesis

In summary, previous studies have improved our understanding of the presence, and some of the mechanisms, of pesticides in the environment and the toxicity effects of pesticide residues for non-target species and humans. However, the associated exposure risks to residents and non-target species posed by pesticides in the environment, especially when taking various exposure routes into account, remain largely unknown. Lacking risk evaluation and identification of the risk contributors further hinders the development of more sustainable pesticide management strategies that are vital for regions with intensive agricultural farming systems and dense populations such as the NCP.

Given these research gaps, this thesis aims to expand our insights into pesticide use in the NCP and further assess the associated exposure risks for non-target species and local residents. Pollinators and soil biota were selected as indicators to address the ecological impacts of pesticides because of their environmental significance. Multiple monitoring approaches, including screening of residential dust and using silicone wristbands, were used to reveal the actual exposure risks to residents from pesticides in the surrounding environments. Specific research objectives are as follows: 1) Investigate pesticide use patterns of major farming systems in Quzhou and assess the associated exposure risks to pollinators; 2) Determine the presence of pesticides at different depths of agricultural soils and assess the ecological risks to soil biota; 3) Monitor pesticide levels in the particulate and gaseous phases in the indoor-outdoor environments by taking residential dust and stationary wristbands as mediums; 4) Characterize exposure risks of farmers and bystanders to particulate and gaseous pesticides.

1.7 Outline of the thesis

This thesis consists of six chapters with **Chapter 2-5** focusing on the Process-Risk modules **(Fig. 1.6)**. The first chapter gives a general introduction on the use of pesticides in modern farming, the environmental fate of pesticide residues and the associated ecological risks to non-target species, negative impacts of pesticide exposure to physical health, major exposure routes to individuals, and exposure monitoring approaches. Along with the findings previously summarized, research gaps have been stated accordingly.

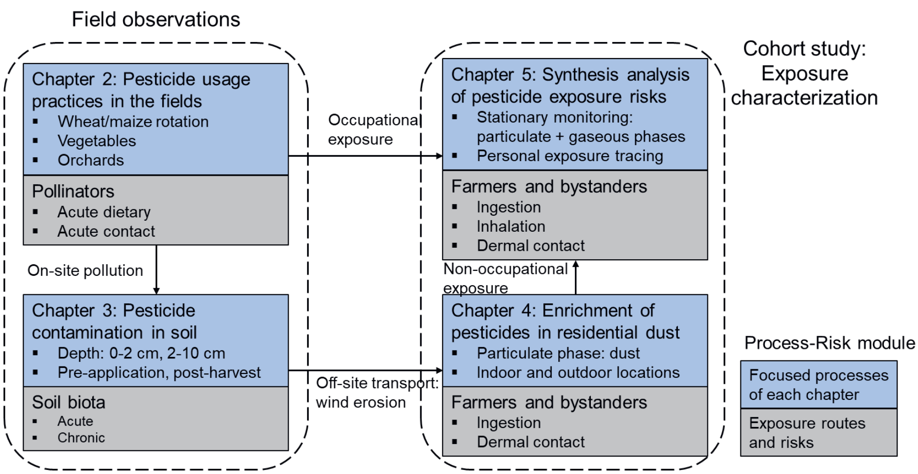

Fig. 1.6 Structural outline of this thesis.

The work found in **Chapters 2-3**, addressing the research objectives 1 and 2, was conducted using an integrated field survey and observation study. An integrated field-modelling approach was used to investigate patterns in pesticide use and residual pesticide levels in soil in order to determine the exposure risks for pollinators and soil biota. With the existence of pesticides in the fields well-studied, a cohort study, the results of which are found in **Chapters 4-5** of this thesis, was carried out to determine the distribution of particulate and gaseous pesticides in the indoor-outdoor nexus of residential areas. Specifically, **Chapter 4** covers the pesticides screened in indoor and outdoor residential dust, while chapter 5 follows a dust-silicone wristband medium approach to characterize personal exposure, and the probabilistic health risks, to particulate and gaseous pesticides in both indoor and outdoor settings.

Chapter 6 summarizes the main findings from **Chapters 2-5** and discusses strengths, limitations and implications for future studies.

Chapter 2
Pesticide usage practices and the exposure risk to pollinators: A case study in the North China Plain

Based on:

Mu, H., Wang, K., Yang, X., Xu, W., Liu, X., Ritsema, C. J., & Geissen, V. (2022). Pesticide usage practices and the exposure risk to pollinators: A case study in the North China Plain. *Ecotoxicology and environmental safety*, *241*, 113713. https://doi.org/10.1016/j.ecoenv.2022.113713.

Abstract

Due to the frequent pesticide applications, bees are suffered from pesticide exposure risks via consumption and direct contact with sprayed drifts. However, if pesticides are misused and the potential exposure risk to bees based on realistic pesticide application data are still little reported. In this study, pesticide application patterns in wheat-maize rotation system, vegetable and apple producing areas, was studied by interviewing farmers in Quzhou County, the North China Plain. The pesticide use status was evaluated by the recommended and actual applied dose and risk quotient (RQ) based Bee-REX model was used to assess the exposure risks of pesticide to bees based on the collected pesticide application data. The results showed that over half (52 %) of farmers in selected sites misused pesticides and orchard owners were frequently misused pesticides. Positive correlations were found between pesticide usage performance and farmers' specialized training experience. Pesticides applied in orchards have caused higher exposure risks to bees with the mean of RQs exceed 120 and 1880 via acute contact and dietary routes, respectively. Pesticide misuse significantly elevates the exposure risk to bees that the mean RQ under misuse scenarios was 5.8 times than that of correct use. Abamectin, fipronil and neonicotinoids contributed most to the pesticide exposure risk to bees. The main findings of this study imply that more sustainable pest and pollinator management strategies, including the moratorium high-risk insecticides and providing diverse flower resources and habitats, are highly needed. Additionally, measures such as implementing farmer educating and training programs should also be put on the agenda.

Chapter 2

2.1 Introduction

Pesticides are used to prevent yield losses caused by pests, weeds and plant diseases and have been widely used worldwide, especially in developing countries (Dobson et al., 2007; Sexton et al., 2007). Due to the limited knowledge and insufficient training of farmers in developing countries, very few are able to follow the instructions printed on pesticide labels allowing them to handle the pesticides properly (Akter et al., 2018; Sharafi et al., 2018). Consequently, pesticides are often misused by farmers in some ways that frequently apply either excessive or insufficient amounts of these compounds or using pesticides have been forbidden / restricted by the government.

Bees such as honeybees play an essential role in maintaining diverse plant species and help to produce valuable products such as jelly, yet the population of bees has been declined over the past decades driven by multiple stressors including pesticides, parasites and limited flowers (Calderone, 2012; Goulson et al., 2015; Jiang et al., 2018). The use of pesticides could cause direct toxic effects on bees. Being exposed to insecticides, such as neonicotinoids, can affect bees' ability of disease tolerance and thus makes bees more susceptible to pathogens and other toxic substances (Boncristiani et al., 2012; Prisco et al., 2013). Additionally, it has been proved that the co-occurrence of multiple pesticides, such as fungicides and neonicotinoids, can synergistically cause greater toxic effects to bees (Sgolastra et al., 2020). Other than the direct exposure toxicity posed by pesticides to bees, the application of herbicides in the fields can reduce the diversity and availability of flowers, leading to monotonous diets of bees that indirectly causing population decline (Goulson et al., 2015). Understandably, the misuse of pesticides might higher level of exposure risks to bees. In this case, systemic risk assessment for bees based on the realistic pesticide field application patterns is highly needed.

Bees can be exposed to pesticides in several ways. Pesticides can be sprayed directly on the pollinators or pesticides can drift to pollinator attractive crops (PAC) during periods when bees are likely foraging. Some persistent pesticides sprayed during the pre-bloom foliar applications on PAC may eventually be transferred to pollen and nectar, thus exposing pollinators (EPA, 2014). The abundance of possible exposure routes makes determining total pesticide exposure very difficult. Attempting to track routes via tracing devices or biomonitoring experiments is far too complex for most studies (Colosio et al., 2012). Hence, predictive and quantitative models have been developed to estimate pesticide exposure. PRIMET is one model used to quantify the exposure risk to bees via in-crop and off-crop exposure prediction (PRIMET-Ethiopia, 2016). This method was updated by the EU and further revised by the European Food Safety Authority (Products et al.) and now provides a cost-effective hazard quotient (HQ) based assessment model for the exposure estimation for honeybees, bumble bees and solitary bees (EFSA, 2013). Another RQ-based model called the Bee REX model estimates exposure through direct contact and dietary processes and was adopted as an exposure risk assessment tool for bees by the Kenyan government and the Environmental Protection Agency (EPA) in the United States (Horst, 2020). In the assessment, honeybees (A. mellifera) are selected as surrogates for *Apis* bees and other pollinating insects. This method does not require a complex set of input parameters and can provide estimated HQs for different ages of honeybees and for different exposure routes.

Recent studies found that pesticide misuse has been common in China, particularly in several provinces in south-eastern and southern China in several cereal, vegetable and fruit producing systems (Sun et al., 2019; Zhang et al., 2015). As a major intensive crop production area in China, it is essential for the government and farmers to understand pesticide usage patterns, including the proper use of pesticides, in the North China Plain (NCP) in order to establish more sustainable plant protection strategies. Considering the fact that multiple pesticides are often mixed and sprayed simultaneously, causing exposure risks to pollinators, a comprehensive risk assessment for pollinators based on actual pesticide field spraying patterns is urgently needed. Thus, the main objectives of this study were to: 1) investigate pesticide usage patterns and examine if pesticides were misused in major cropping systems in Quzhou, NCP; 2) identify the potential driving factors of pesticide misuse and 3) assess the exposure risk of pesticides to pollinators in different cropping systems based on Bee-REX model. Based on the risk assessment results, the exposure risks posed to bees when pesticides were correctly used and misused were compared.

2.2 Materials and methods

2.2.1 Study area

Quzhou county (36°34′45″ N - 36°57′57″ N, 114°50′30″ E - 115°13′30″ E) is a typical agricultural county with a total area of 667 km^2 with farmland accounting for 82.5% of the area. Located centrally in the North China Plain, the area has a subtropical humid monsoon climate with an annual mean temperature of 13.4 ℃ and an annual average precipitation of 556.2 mm. Grain crops, such as maize and wheat, and vegetables are the dominant crop producing systems. Apple orchards also can be found in a few villages.

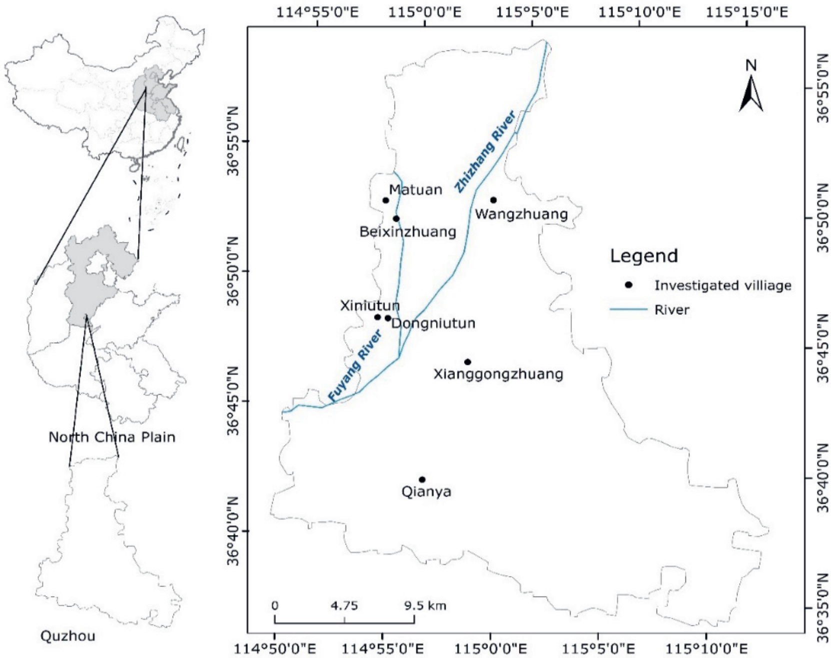

Fig. 2.1 Study area and the locations of investigated villages in Quzhou villages in Quzhou county, Hebei province

2.2.2 Farmer interviews and data collection

In this study, a standardized questionnaire containing questions related to personal data **(Table S2.1)**, cropping system, pesticide application pattern, pesticide storage and disposal was used for data collection. In total, 197 farmers growing grain crops, vegetables and apple orchards in 7 villages in Quzhou **(Fig. 2.1)** were selected and interviewed in December 2019. In the pesticide application pattern section, respondents were asked to name 1-3 most common pests or plant diseases and further describe how pesticides were used to handle these crop protection issues, including applied dose, active substance concentrations of used pesticides, frequency, and application interval. The application rates (AR) were then calculated separately for knapsack spraying farmers and vehicle-mounted pump spraying farmers based on the equations below. To ensure data quality, the application doses were double checked with farmers and incomplete responses were excluded from this study.

$$AR_{Knapsack} = AD_{bottle} \times n \times Fre \times ASC \times 15 \div 1000 \quad (2.1)$$

$$AR_{Vehicle-pump} = AD_{pump} \times Fre \times ASC \times 15 \div 1000 \quad (2.2)$$

Here, AD_{bottle} (g or mL, depending on the formulation type) represents applied dose per bottle (15 L knapsack) per mu (15 mu equals 1 hectare), $AD_{vehicle\text{-}pump}$ (g or mL) represents the applied dose for one application event for the vehicle-mounted pump, *n* means number of bottles of mixed solvents applied to treated crops per mu, *Fre* means the number of times of certain pesticide has been applied in a growing season, *ASC* represents active substance concentration, 15 is the transfer coefficient of treated area from mu to hectare, 1000 is transfer coefficient from g to kg.

2.2.3 Pesticide misuse classification

In this study, a set of completed pesticide application data was defined as a case. If the application rate was larger than or less than the recommended range, or farmers using forbidden pesticides with high toxicity, the case was then defined as misuse. To better address to what extent pesticides were misused in specific cases, four scenarios related to pesticide use behaviors were established: S1, correct use; S2, only one ingredient was misused; S3, more than one ingredient was misused and S4, forbidden or restricted ingredients were used. To minimize the potential systematic errors in further risk assessment results posed by the interference of outliers, only the plant protection purposes (PPPs) with 3 or more cases were included in further exposure analysis.

Calculated ARs were compared with the recommended safe ranges found on the labels of the pesticide products. Label information can be found on the information platform (ICAMA, 2020) powered by the Institute Control of Agrochemicals, Ministry of Agriculture and Rural Affairs, P.R. China.

2.2.4 Bee-REX model

The exposure risk for pollinators was assessed using the USEPA Bee-REX model (USEPA, 2014). In this study, the assessment procedure included 4 steps: 1) problem formulation, 2) exposure analysis (Tier I assessment), 3) risk characterization and 4) assessment of uncertainties, possible risk mitigation strategies and the need for Tier II assessment. In the Tier I assessment, pesticide application rate and toxicity data such as LD_{50} and no-observed allowance effect level (NOAEL) for bees were used in the model. The risk quotients (RQs) were used as quotients for estimated exposure. Among the calculated RQs for bees in different classes and ages, the highest value was chosen to represent the most conservative exposure risk assessment. Detailed descriptions can be found in the supplementary information **(Text S2.1)**. Despite the standardized protocol for pesticide chronic exposure test on bees was developed (OECD, 2017), the chronic exposure parameters such as NOAELs (No Observed Adverse Effect Levels) of commonly used pesticides on bees are limited. Thus, in this study, only acute contact and adult dietary exposure for bees could be calculated and assessed. For cases that multiple pesticides were collectively used, the RQs for each pesticide were summed up follow the concentration-addition method, which has been widely used in the ecological risk assessment for multiple pollutants based on the assumption that all the co-exposure effects among pesticide mixtures were addictive effect (G. Bhandari et al., 2021; Tian et al., 2018). The highest RQs derived from Bee-REX model were then further compared with the level of concern (LOC) value which was 0.4 for acute exposure scenarios. For RQs below the LOC, a minimal exposure risk can be expected (EPA, 2014).

To understand possible pesticide exposure risks to pollinators, the degree of hazard of commonly used pesticides was summarized in **Table S2.4**. All pesticides listed were found to be hazardous to pollinators via acute exposure and dietary routes. Required toxicity parameters such as LD50 (μg a.s./bee) for acute contact and dietary contact derived from the Pesticide Properties Data Base (PPDB) are listed in **Table S2.5**.

The contributions (%) of each pesticide to the exposure risks were further examined to identify the major risk contributors.

$$Contribution\ (\%) = \frac{RQ_{mean,i}}{RQ_{total}} \tag{2.5}$$

Here the $RQ_{mean,i}$ refers to the average RQ for pesticide i, the RQ_{total} refers to the sum of RQs of all involved pesticides.

2.2.5 Statistical analysis

The Kolmogorov-Smirnov test was performed to identify the normality of the data. The Mann-Whitney U test and t test were conducted to compare the means of ARs of pesticides applied in different cropping systems and RQs posed by each pesticide, exposure routes and pesticide usage scenarios and pesticides applied in different cropping systems.

As a useful tool to extract correlations among or common sources of multivariable by dimension reduction method (Barbieri et al., 2021; Zhuang et al., 2020), principal component analysis (PCA) was performed to identify potential driving factors of pesticide misuse in the present study.

2.3 Results

2.3.1 Overview of pesticide usage in Quzhou

In total, 27 insecticides, 8 herbicides and 7 fungicides were used by the interviewed farmers. Spraying a single pesticide to address a specific crop issue was the most common application method used by most farmers in this study. Two or three pesticides were found to be used in cocktails in 35.3 and 6% of the collected pesticide application cases.

The fifteen most-used pesticides in this study are listed in Table 1, which includes 10 insecticides, 2 herbicides and 3 fungicides. Among the applied active substances, dimethoate, omethoate and chlorpyrifos were classified as restricted pesticides by the government (MOARA, 2017, 2019a). The top five commonly used insecticides cypermethrin (pyrethroid), imidacloprid (neonicotinoid), acetamiprid (neonicotinoid), emamectin benzoate (Micro-organism derived compounds) and abamectin (Micro-organism derived compounds) were all used by over 25% of the respondents in all three cropping systems, showing that pest control was the major concern for local farmers in terms of crop protection.

Table 2.1 Application rates of most-used pesticides for major crop systems based on the farmer interview results.

Pesticide	Chemical group	Use frequency (%)	Application rate (kg a.s. /ha/yr)							
			Overall		Wheat/maize rotation		Vegetables		Orchards	
			Misuse rate (%)	Mean (Range)	Mean (Recommended range)	n	Mean (Recommended range)	n	Mean (Recommended range)	n
I: Cypermethrin	Pyrethroid	55.3	35	0.30 (0.01-2.25）	0.16 (0.02-0.16) b	31	0.41 (0.02-0.20) a	16	0.50 (0.07-0.41) a	13
I: Imidacloprid	Neonicotinoid	51.3	59	0.39 (0.01-2.52)	0.12 (0.02-0.12) b	21	0.67 (0.01-0.18) a	31	0.31 (0.12-0.15) b	9
I: Acetamiprid	Neonicotinoid	41.1	89	0.42 (0.01-2.1)	0.30 (0.03-0.07) a	10	0.44 (0.02-0.11) a	18	0.59 (0.02-0.10) a	10
I: Emamectin Benzoate	Micro-organism derived	32.5	34	0.08 (0.01-0.42)	0.06 (0.02-0.1) b	6	0.11 (0.02-0.1) a	31	0.11 (0.02-0.1) a	7
I: Abamectin	Micro-organism derived	27.4	56	0.11 (0.01-0.58	0.18 (0.018-0.023) a	9	0.16 (0.008-0.011) b	21	0.08 (0.02-0.05) b	6
F: Carbendazim	Benzimidazole	15.7	50	6.52 (1.2-24)	-	-	2.18 (2.04-4.5) a	3	7.30 (0.23-9) a	17
F: Mancozeb	Carbamate	13.2	36	13.35 (7.2-43.2)	-	-	13.13 (1.85-7.11) a	4	13.38 (0.45-14.4) a	10

Note: I, H and F represent the type of pesticide, namely insecticide, herbicide and fungicide. *, restricted pesticides that have been banned from being used in vegetable fields. The recommended application range was derived from label information of pesticide products (ICAMA, 2020). NA, data not available.

Table 2.1 (Continued).

Pesticide	Chemical group	Use frequency (%)	Application rate (kg a.s. /ha/yr)							
			Overall		Wheat/maize rotation		Vegetables		Orchards	
			Misuse rate (%)	Mean (Range)	Mean (Recommended range)	n	Mean (Recommended range)	n	Mean (Recommended range)	n
I: Dimethoate	Organophosphate	13.2	32	1.4 (0.3-5.76)	0.65 (0.45-1.8) b	13	3.84 (0.45-1.8) a	4	-	-
I: Omethoate*	Organophosphate	12.7	75	3.54 (0.24-18)	1.53 (0.6-1.35) a	7	5.60 (NA) a	9		
I: Chlorpyrifos*	Organophosphate	10.2	88	3.61 (0.18-7.2)	0.30 (0.54-1.44) b	3	6.00 (NA)	1	4.94 (0.9-1.2) a	4
F: Tebuconazole	Triazole	8.1	69	6.37 (0.06-19.5)	0.06 (0.08-0.30)	1	1.20 (0.11-0.34) a	3	8.79 (0.30-1.13) a	9
H: Nicosulfuron	Sulfonylurea	8.1	58	0.11 (0.01-0.22)	0.14 (0.05-0.06)	11	-	-	0.09 (0.05-0.06)	1
H: Tribenuron-methyl	Sulfonylurea	7.6	63	0.05 (0.01-0.09)	0.05 (0.01-0.02)	8	-	-	-	-
I: Chlorfenapyr	Pyrrole	7.1	50	0.56 (0.01-1.5)	-	-	0.40 (0.14-0.36) a	8	0.98 (0.11-0.14) a	2
I: Thiamethoxam	Neonicotinoid	7.1	83	0.91 (0.01-2.16)	0.64 (0.54-0.72)	2	0.88 (0.01-0.05) a	8	1.64 (0.05-0.28) a	2

2.3.2 Pesticide misuse classification

2.3.2.1 Pesticide misuse in different cropping systems and crop protection purposes

Generally, acetamiprid, omethoate, chlorpyrifos and thiamethoxam were most frequently misused by farmers with misuse rates above 75% **(Table 2.1)**. As shown in **Fig. 2.2**, roughly 50% of farmers growing grain crops and vegetables could spray approved pesticides in a safe range while only 42.9% of orchard owners could do so. When spraying pesticide cocktails to handle crop issues, around 7% of grain farmers and 10% of orchards owners misused all of the ingredients they applied, while the figure for vegetable growers was 15% **(Fig. 2.2)**. Also, forbidden / restricted pesticides were used in 8.3% of the cases of vegetable cultivation. When only one ingredient was used, farmers growing vegetables maintained better habits with regards to pesticide application, using the correct rates, roughly 6 and 11% higher than grain crop farmers and orchard owners, respectively **(Fig. S2.1)**. In cases where two ingredients were used together, nearly half of grain crop growers applied proper doses of pesticide mixtures, with correct use rates 9% and 23% higher than vegetable farmers and orchard owners, respectively **(Fig. S2.1)**. Similarly, compared with vegetable farmers, more grain crop growers could spray appropriate doses when using three ingredients simultaneously.

Omethoate, dimethoate, chlorpyrifos and fipronil were found to be used in grain crop fields, vegetable fields and orchards, although these chemicals have been banned by the government for certain cropping systems (MOARA, 2017). Farmers' pesticide usage strategies for different crop protection purposes were evaluated and summarized **(Table S2.2 and S2.3)**. Cases for eliminating aphids and red spiders accounted for 55.7% and 28.7% of pest control cases, thus aphids and red spiders were recognized as major pests in this study. In the meantime, *Pieris rapae, Helicoverpa armigera* and *Spodoptera exigua* were recognized as secondary pests. As the most handled insect in the study area, aphid was found to be eliminated by farmers via occasionally spraying restricted / forbidden or overdosed pesticides.

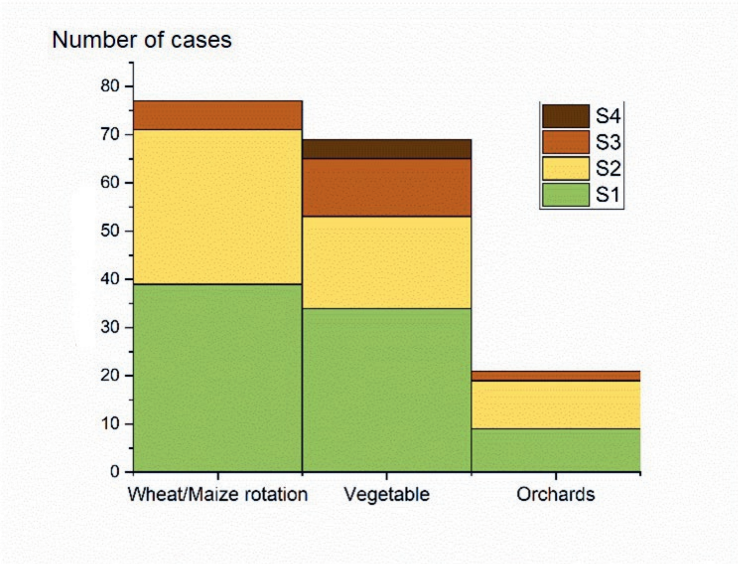

Fig. 2.2 Number of pesticide usage scenario cases in different cropping systems

Note: S1: correct use; S2:one pesticide ingredient was misused; S3: more than one pesticide ingredients were misused; S4: using forbidden / restricted pesticides.

2.3.2.2 Potential driving factors of pesticide misuse

The Bee-REX model assessed the exposure risks of pesticides to bees, addressing a significantly higher level of exposure risk when pesticides were misused. To further explore the potential driving factors of pesticide misuse, principal component analysis (PCA) was performed to extract the correlations between pesticide misuse and farmers' socioeconomic indicators **(Table S2.1)**. The results showed that 79.9% of the total variance could be explained by the four extracted principal components (PCs). Pesticide usage (misuse) was found to be highly correlated with farmers' pesticide specialized training experience due to the similar loading patterns of PC1, 2 and 3 on these two variables **(Fig. 2.3 and Fig. S2.2)**. Additionally, female farmers tend to spray pesticides correctly in agricultural practices, which may need to be further verified due to limited sample size for female respondents.

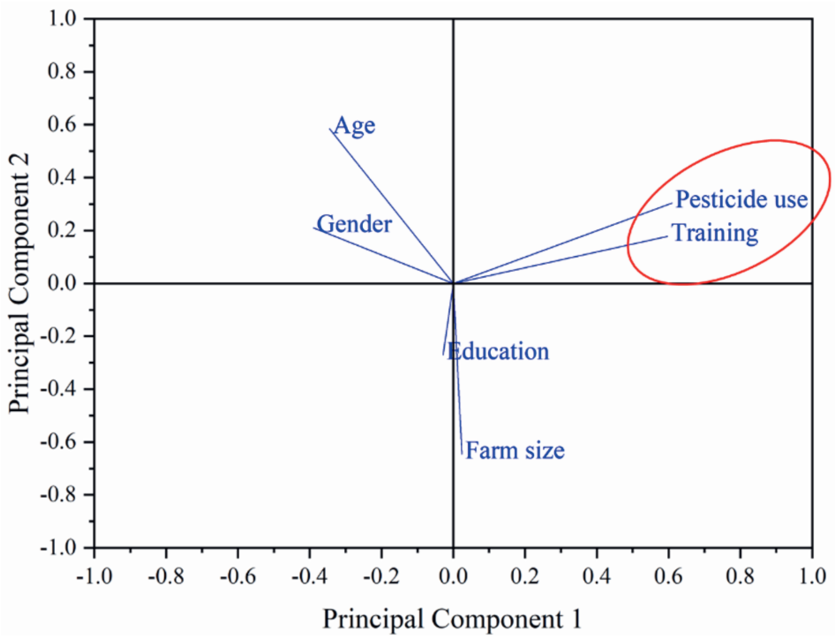

Fig. 2.3 Biplot of the Principal Component Analysis (PCA) referring pesticide use and the sociological determinants.

Note: Age: 1, under 50 years old; 2, 31—45 years old; 3, 46—60 years old; 61—70 years old; 5, older than 70 years old. Education: 1, illiterate; 2, primary school; 3, middle school; 4, high school; 5, higher educated experience. Farm size: 1, less than 2 mu; 2, 2.1—3 mu; 3, 3.1—5 mu; 4, 5.1—8 mu; 5, larger than 8 mu. Gender: 0, female; 1, male. Training: 0, never has received pesticide related specialized training; 1, has received specialized training. Pesticide use: 0, misuse; 1, correct use.
15 mu=1 ha.

2.3.3 Exposure risks of pesticides to pollinators

2.3.3.1 Calculated risk quotients (RQs) based on the Bee-REX model

To address the exposure risks by pesticides through acute contact and dietary routes, the Tier I assessment based on collected cases was examined using the Bee-REX model. Because toxicity data could be obtained for only a limited range of pesticides, and to cover more cases and provide a more general assessment, the ETEs for pesticides lacking solid toxicity data were simplified to 0 in further analysis.

The RQs for each pesticide being used in more than three cases were extracted and examined. The results showed that extreme high RQs were found for abamectin with the median value over 300 and 3900 for acute contact and dietary routes

(Table 2.2), followed by cypermethrin and thiamethoxam. The RQs for herbicides and fungicides were relatively low, with mean value of RQs all below the LOC. For imidacloprid and omethoate that also being widely used by local farmers, high RQs were also frequently found especially refers to the acute dietary route with the median RQs all exceeds 2000.

Table 2.2 Calculated RQs for commonly used pesticides based on the realistic pesticide application data and recommended doses.

Pesticides	Acute contact			Acute dietary		
	RQ (mean)	RQ (median)	RQ range (RD)	RQ (mean)	RQ (median)	RQ range (RD)
Abamectin	601.52	327.27	8.73-54.55	7174.11	3902.73	104.07-650.45
Imidacloprid	9.76	8.89	0.30-4.44	2547.95	2320.54	77.35-1160.27
Thiamethoxam	37.5	30	1-72	2146.4	1717.2	57.24-4121.28
Omethoate	11.96	9.9	NA	142.59	118.06	357.75-804.94
Dimethoate	11.03	9.45	10.8-43.2	131.5925	112.69	128.79-515.16
Chlorfenapyr	4.5	5.4	1.32-4.32	53.67	64.4	15.74-51.52
Indoxacarb	8.28	6.75	2.1-3.6	34.05	27.76	8.64-14.8
Acetamiprid	0.13	0.13	0.006-0.03	69.33	62.4	0.04-0.22
Cypermethrin	43.47	39.13	2.09-42.78	0.89	0.89	3.33-68.22
Tebuconazole	0.04	0.03	0.001-0.014	1.16	0.91	0.03-0.39
Nicosulfuron	0.06	0.05	0.0016-0.0019	9.88	9.2	0.27-0.33
Atrazine	0.07	0.07	0.05-0.07	0.87	0.87	0.64-0.86

Note: RD, recommended dose. NA, data not applicable.

Generally, pesticide applications in orchards have caused highest exposure risks to bees whereas the least risk was found for grain producing cases for both acute dietary exposure and direct contact routes **(Fig. 2.4A** and **Table S2.6)**. The mean of RQs in vegetable fields were found from 1.2 to 1.5 times than those of grain crop and vegetable cases. There was no significant difference in the RQs for grain and vegetable crop cases when looking at acute contact route. The acute risk posed by dietary exposure was found to be much higher than for direct contact exposure

(Table S2.7). It should also be noted that all calculated RQs through acute dietary route exceed the LOC, while roughly 3 out of 4 RQs in contact route exceed the LOC **(Table S2.7)**. For different pest control purposes, such as dealing with secondary insects in the vegetable fields, the exposure risk was much lower than in other scenarios **(Fig. S2.3)**. For both acute dietary and dietary routes, red spider related cases exhibited highest RQs with the mean RQ 1.5-17.6 times than those for other PPPs.

Additionally, the assessment results indicated that pesticide misuse has caused elevated exposure risks to bees **(Fig. 2.5B)**. The ratio of mean RQs under misuse and correct use was 5.8. It is worth noting that the RQs calculated based on the recommended doses of each pesticide mostly exceeded the LOC, with extreme high values were found for insecticides such as abamectin, imidacloprid, dimethoate and thiamethoxam **(Table 2.2)**. The results indicated that the exposure risk to bees was dominated by the toxicity of pesticides. Furthermore, the exposure risk can be significantly elevated when misusing pesticides.

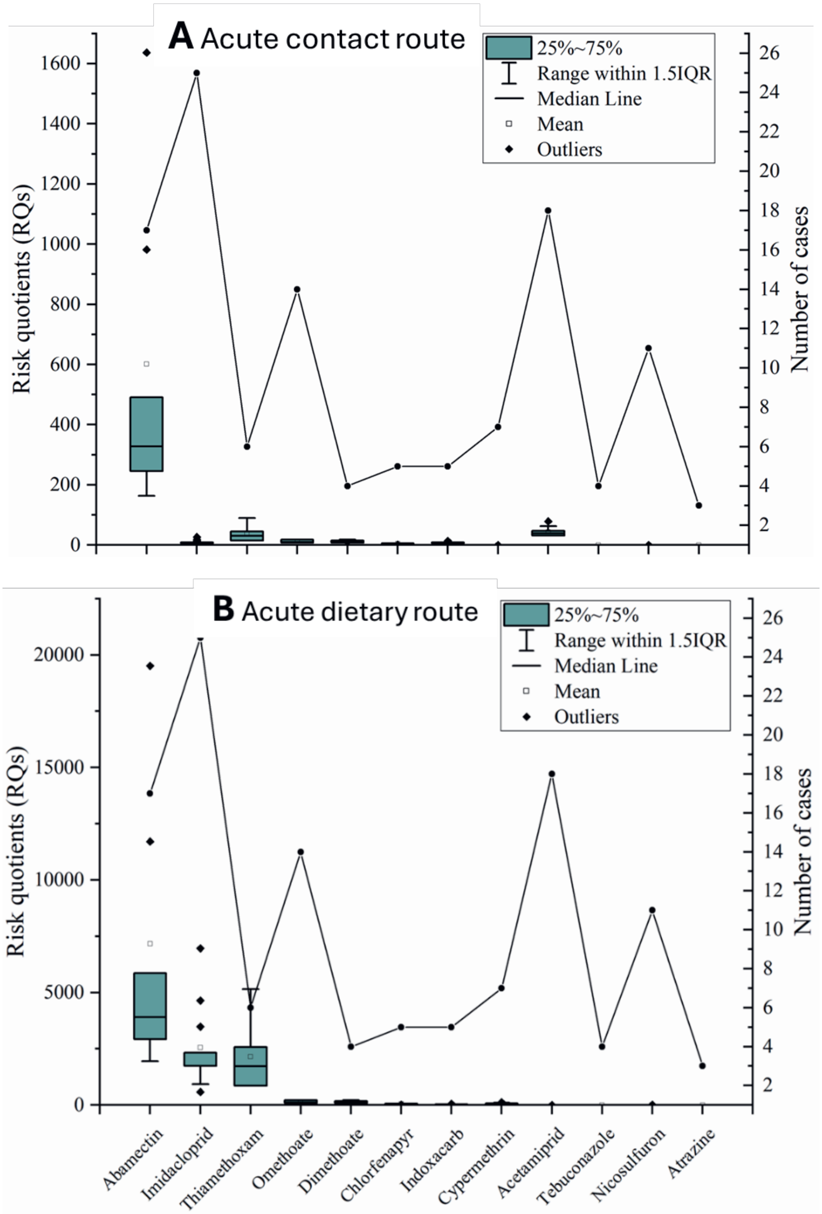

Fig. 2.4 Calculated risk quotients (RQs) of pesticides based on the Bee-REX model. Notes: Only pesticides with usage cases more than three were included in the graph. IRQ, interquartile range.

2.3.3.2 Contributions of pesticides to the exposure risk

For both acute contact and dietary exposure routes, abamectin was the biggest contributor to the exposure risk, followed by fipronil and neonicotinoids **(Fig. 2.5)**. As a broad-spectrum insecticide, abamectin has been widely used by local farmers to handle multiple pests such as red spiders and aphids. Similarly, fipronil and imidacloprid also play an important role in pest control in the case study area.

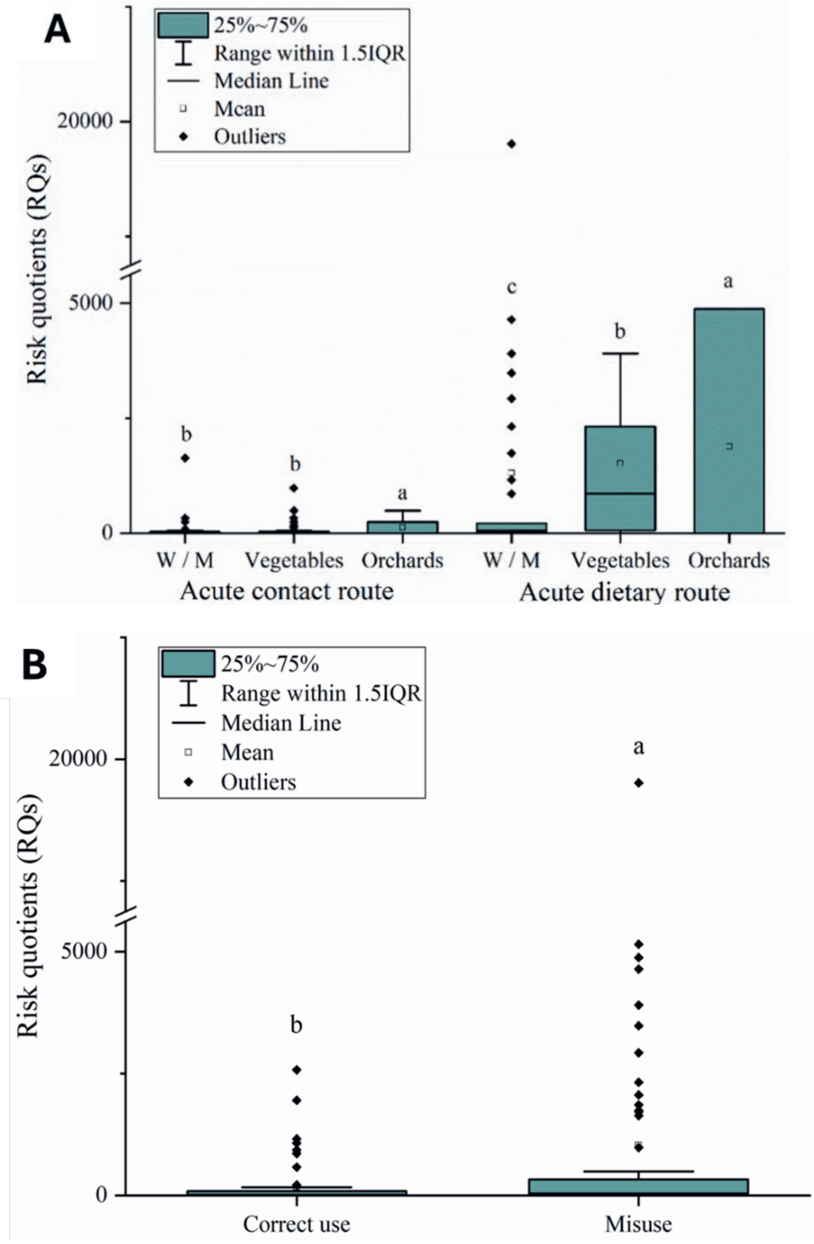

Fig. 2.5 Risk quotients (RQs) of cases in A: different cropping systems, and B: under correct use and misuse scenarios.

Note: Correct use refers to S1. Misuse includes S2, 3, and 4. W / M, wheat / maize rotation; IQR, interquartile range.

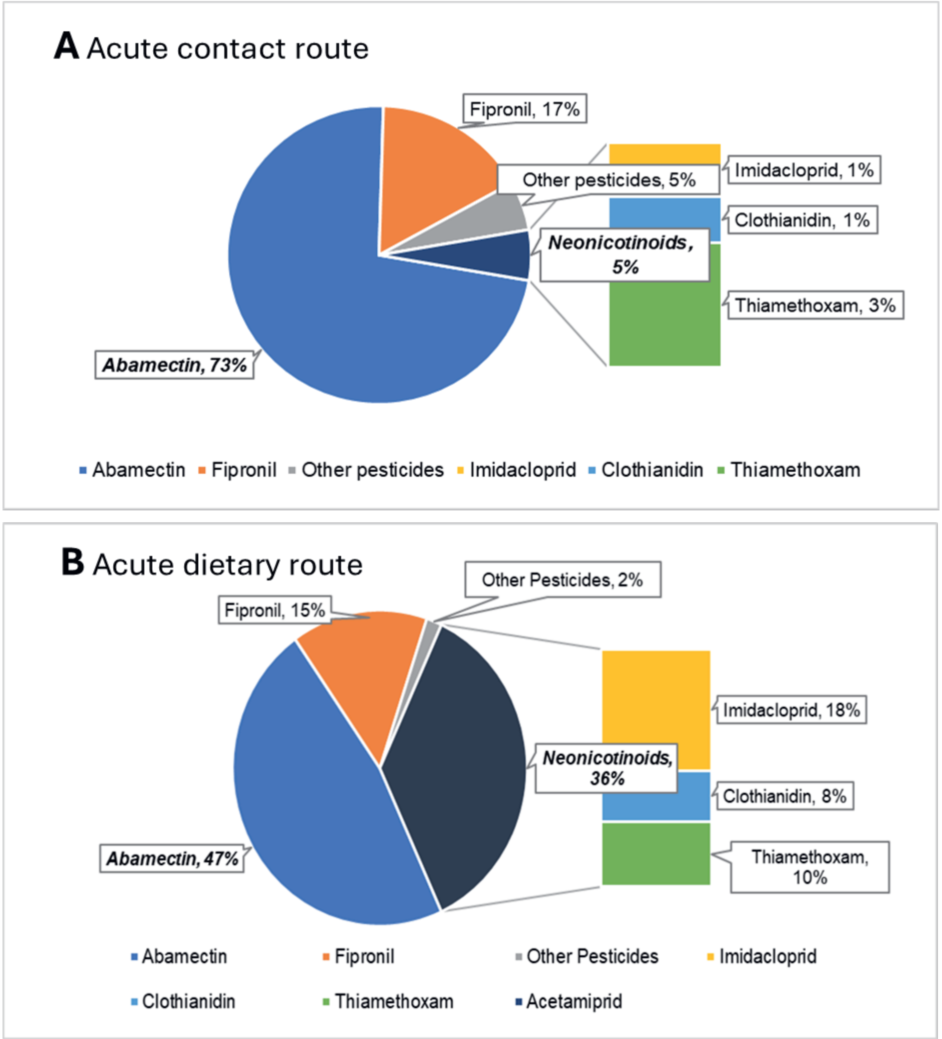

Fig. 2.6 Contributions (%) of each pesticide to the exposure risk to bees by A: acute contact route and B: acute dietary route.

2.4 Discussion

This study investigated the pesticide application patterns in Quzhou, NCP based on field survey and farmer interview. To what extent pesticides were misused by farmers growing different crops and the resulting exposure risk to bees were further examined. The risk assessment results from Bee-REX model revealed that high level of exposure risks posed by insecticides such as abamectin, fipronil and neonicotinoids, furthermore, pesticide misuse has caused elevated exposure risk to bees.

2.4.1 Pesticide misuse in different cropping systems

Despite studies examined pesticide misuse in certain area are limited, unfortunately, the misuse of pesticides occurs in major crop production systems in China and other countries (Panuwet et al., 2012; Strid et al., 2021; Zhang et al., 2015). In one study, the misuse rates of pesticide cocktails on pests in grain crop fields in south and north China were found to over 52%, with the misuse rate reaching 90% when against wheat aphid (Zhang et al., 2015). Same trends were also exhibited by another field survey study that only 54.4% of observed pesticide application cases can be recognized as correct use. Specifically, when dealing with aphid in tea, cucumber, tomato and apple orchard fields, the misuse rates were all exceeded 75% (Sun et al., 2019). Much lower misuse frequencies were found in American in terms of red bug control, and the professional farmers showed better performance in pesticide correct use (Strid et al., 2021), which is coherent with the positive correlations between pesticide correct use and training experience in our study. Except training experience, farmers' education levels were found negatively associated with their pesticide application performance **(Fig. 2.3)**. The reason could be explained that farmers with lower educational levels were well connected with the scientific and technology backyards (STBs) in the village and more willing to receive new crop management technologies and sustainable farming perceptions. STBs are non-profit demonstration farming stations focusing on transforming knowledge from the laboratory to the field that could provide farmer educating programs or field sessions related to pesticide use (Zhang et al., 2016). In this case, training and educating sessions from agriculture extension services or other farmer supporting agencies are highly needed to improve the pest management performance and reduce the load of agrochemicals to the environment.

2.4.2 Implications for systemic risk assessment to bees

Exposure levels for pollinators in actual field conditions were determined in this study despite the fact that the assessment was performed in a most conservative way. The lack of toxicity data on pesticides, especially insecticides, limited the study and may have been attributed to uncertainties in the assessment. Field measurements can be carried out to determine residual levels of pesticides in the matrix, such as pollen and nectar, which can reflect the exposure level of bees (Gierer et al., 2019; Jiang et al., 2018). In this case, Tier II assessment based on field sampling and lab measurements was highly needed. With completed assessments, further risk remediation measures can be determined based on local agricultural characteristics.

In realistic field conditions, bees are exposed to multiple pesticides due to the frequent application of pesticide cocktails. Except addictive effects, synergistic effects have been found also existed among commonly used pesticides such as combinations of insecticides and fungicides (Brigante et al., 2021; Christen et al., 2017; Wang et al., 2020). The existence of synergistic effects among field sprayed pesticides could cause greater exposure effects on bees, which should be considered in the development of further risk assessment methods. Bee-REX model takes honeybee *A. mellifera* as a surrogate for other pollinator species, yet the sensitivities to pesticides differ among different species (Sarto et al., 2014; Sgolastra et al., 2020). For instance, non-*Apis* bees are more susceptible to neonicotinoids, one of the major risk contributors in the present study, than honey bees (Arena et al., 2014), which potentially adds uncertainties to the risk assessment results. Additionally, it is reported that bumblebees suffered higher dose of pesticide exposure through diet and contact route, indicating that the risk assessment results for honeybees might not protective enough for bumblebees and more systematic risk assessment models that provide most conservative results covering more species are required (Gradish et al., 2019). This study addresses the acute exposure risks of pesticides to bees, while the assessment for chronic exposure scenarios should also be performed once the test data is available to present more comprehensive first Tier assessment results (Thompson et al., 2019). Given that some pesticides can potentially cause sublethal effects such as impaired performance in learning, orientation and reproduction, multi-dimensional criteria including essential sublethal consequences should also be considered in the future risk assessment (Sgolastra et al., 2020). Generally, toxicology tests for sublethal effects and synergistic effects among commonly used pesticide combinations for different bee species are highly needed, more systemic risk assessment methods needed to be developed to address the exposure risk under realistic exposure scenarios in the fields to different bees.

2.4.3 Implications for more sustainable management for pests and bees

The findings of this study indicated that the toxicity of pesticides to bees is the dominant factor in the exposures, while the pesticide misuse could significantly elevate the exposure level. Broad spectrum insecticides such as abamectin and neonicotinoids have been commonly used by local farmers, yet extreme high levels of exposure risks were caused even if the applied doses were complied with the label instructions **(Fig. 2.5 and Table 2.2)**. As the biggest risk contributor in the present study, abamectin was recognized as highly hazardous to bee populations with high mortalities via oral route exposure (Li et al., 2022). As major risk contributors, neonicotinoids were known that capable to hinder colony growth and queen production, causing reduction of bees population (Gill et al., 2012), for which the outdoor spray of these chemicals were banned by the EFSA (EFSA, 2018). In field condition, the co-existence of neonicotinoids and fungicides might pose synergistic effects enlarging the hazard to bees. In another study, imidacloprid and thiamethoxam were also assessed to impair honeybees based on measured concentrations in pollen, nectar and leaves (Jiang et al., 2018). In the present study, these high toxic pesticides were also frequently misused by farmers causing significantly higher RQs compared with RQs under correct use scenarios. Due to the high toxicity to bees, the use of these compounds in field spray should be banned and replaced by alternatives such as low-toxic insecticides or biopesticides.

Other than the moratorium of the high-risk insecticides in the outdoor spray, field measures should also be implemented to maintain the growing and diversity of bee population. Additional habitats along with a diverse planting of flowers or pollinator attractive crops should better be provided around the edge of orchards or farms in order to effectively facilitate the abundance of bee species (Biddlinger et al., 2015).

2.5 Conclusions

This study investigated pesticide usage patterns and evaluated pesticides status by farmers in three cropping systems (i.e., wheat / maize, vegetable and apple) via farmer interviews in Quzhou county, the North China Plain. Based on the collected data, the exposure risk to bees from pesticide mixtures was further assessed based on the Bee-REX model. The main findings and conclusions are as following:

- Over 50% of the farmers misused pesticides in Quzhou, NCP. Pesticides were more frequently misused by orchard owners.
- Farmers' pesticide usage performance is positively associated with the specialized training experience.
- Pesticides applied in orchards have caused higher exposure risks to bees with the mean of RQs exceeding 120 and 1880 via acute contact and dietary routes, respectively. Pesticide misuse significantly elevates the exposure risk to bees that the mean RQ under misuse scenarios was 5.8 times than that of correct use. Abamectin, fipronil and neonicotinoids contributed most to the pesticide exposure risk to bees.

Based on the findings, we suggest that more sustainable pest and pollinator management strategies should be developed through moratorium high-risk insecticides and providing diverse habitats and flowers for bees along the fields.

Specialized training and field school sessions are highly needed from both the government and agricultural extension services, especially for orchard owners. Additionally, more systemic risk assessment methods integrating the synergistic effects of pesticides, sublethal effects and susceptibilities of different groups of bees are highly needed to address the realistic pesticide co-exposure risks to bees under field conditions.

Acknowledgement

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Supplementary materials

Text S2.1 Description of the assessment procedure using Bee-REX model.

1. Problem formulation
This step aims to evaluate if the perceived pesticide spraying has the potential to cause acute or chronic exposure to pollinators, with the pesticide properties and potential exposure routes being considered.

2. Exposure analysis based on Tier I assessment
Analysis in this section was performed based on the provided exposure screening model Bee-REX (EPA, 2014) by inputting pesticide application rates and toxicity data such as LD_{50} for bees and no-observed allowance effect level (NOAEL) derived from laboratory-based studies. The model can present calculated risk quotients (RQs) for different ages and classes of honeybees for exposure via direct contact and diet and further provides the most conservative RQs (highest RQs) for larva and adult bees for three exposure scenarios: acute contact, acute dietary and chronic dietary. Currently, there is no standardized guideline for lab-based chronic tests of bees, thus in this study, only acute contact and dietary exposure for adult bees could be calculated and assessed.

3. Risk characterization
If the highest RQs were below LOC, a minimal risk could be expected since the assessment was made in a conservative, worst-case scenario way. If RQs exceeding the LOC were found, the exposure risks could not be neglected.

4. Consider uncertainties, risk mitigation options and the need for Tier II assessment
Uncertainties caused by inputting data such as application rates, application methods or toxicity parameters need to be taken into consideration after the exposure analysis. If a potential exposure risk is revealed via the Tier I assessment, possible mitigation options should be further explored based on the specific situation and should include things such as crop type, climate conditions or pest distribution. Tier II assessment based on estimating residue levels in nectar and pollen can give more insight into the exposure assessment, thus the necessity of a Tier II study should be considered.

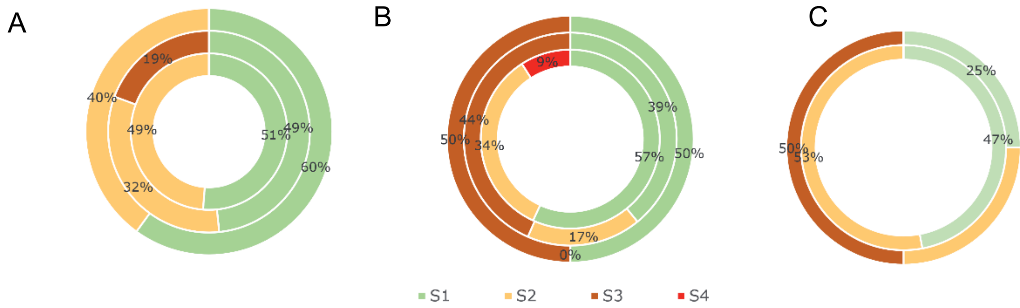
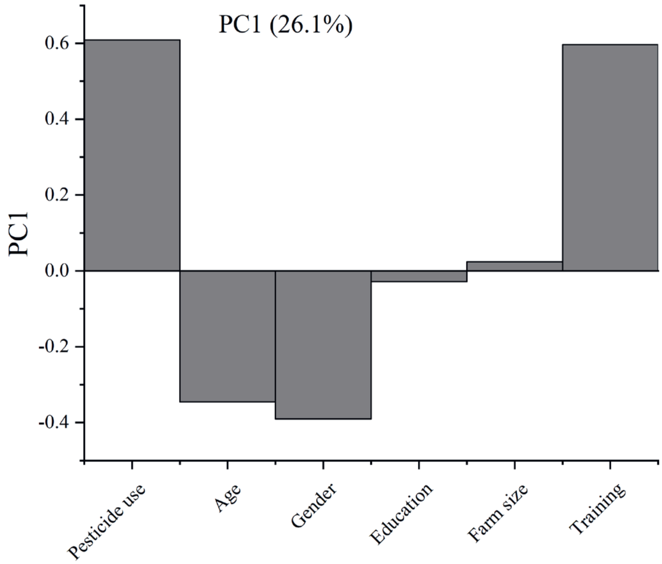


Fig. S2.1 Percentages of pesticide usage scenarios in different cropping systems. (a), wheat/maize rotation system; (b), vegetable cultivation system; (c) orchards. The three circles from the inner circle to the outer one represent cases when farmers spray 1, 2 and 3 pesticides. Referring to the inner circle, only S1, 2 and 4 are included.

Note: S1, correct use; S2, one pesticide ingredient was misused; S3, more than one pesticide ingredients were misused; S4, using forbidden / restricted pesticides.



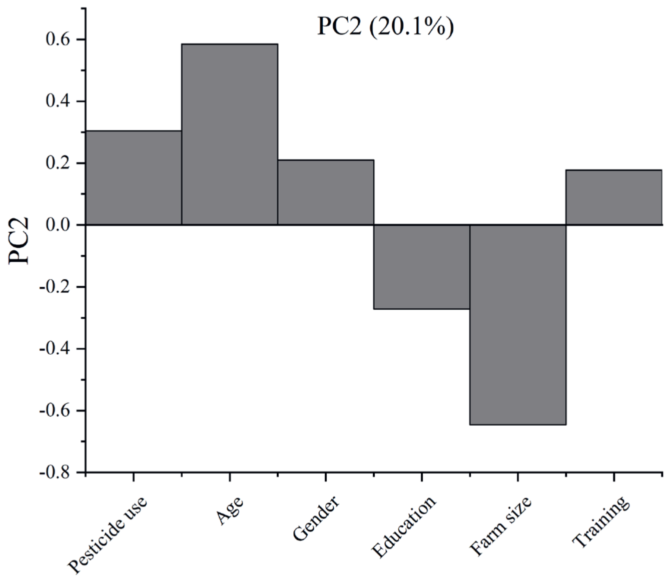
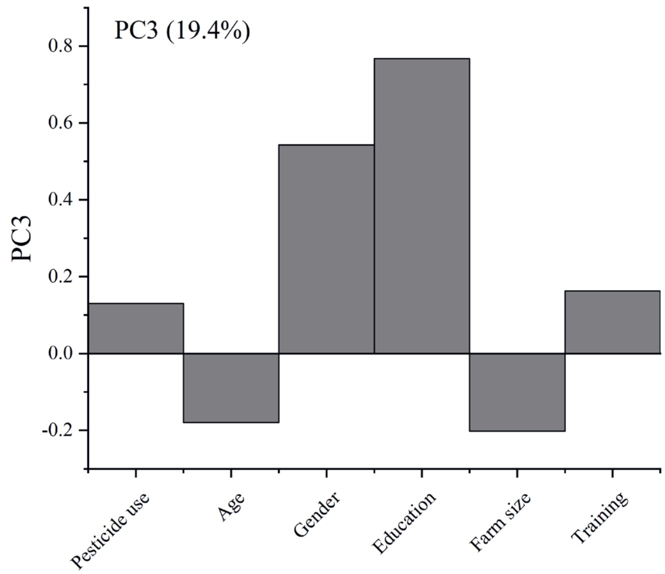


Fig. S2.2 Variances explained by each extracted principal components (PCs) and the loading plots.



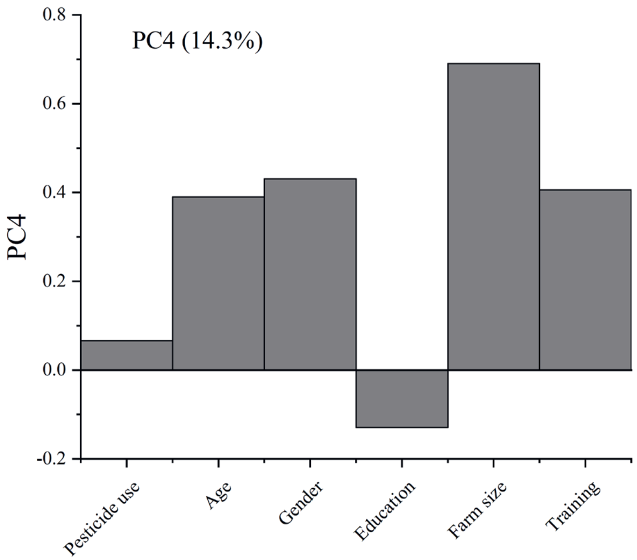


Fig. S2.2 (Continued).

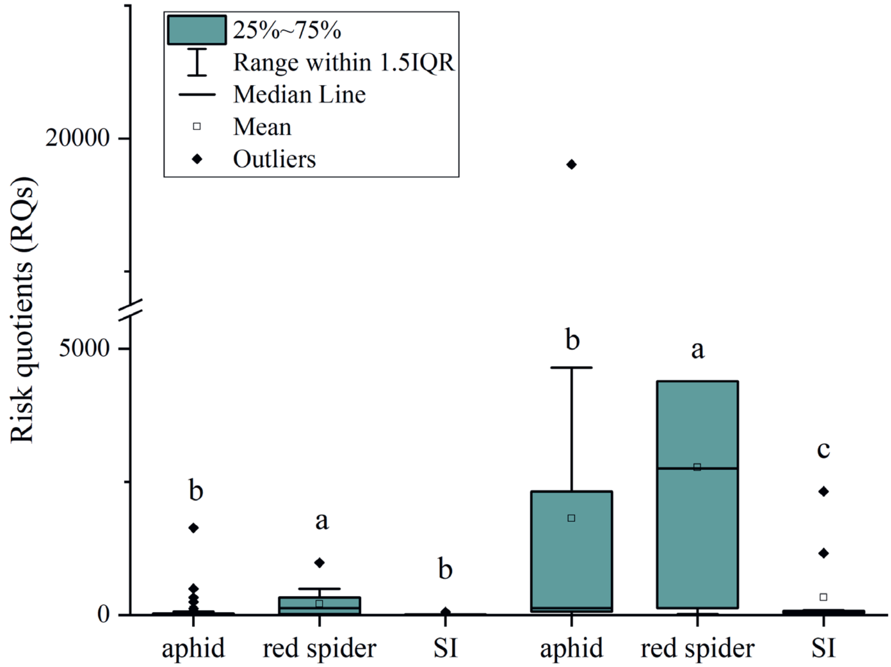


Fig. S2.3 Risk quotients (RQs) of cases for different plant protection purposes (PPPs). Note: SI, secondary insects.

Table S2.1 Personal information and socioeconomic indicators of respondents.

Indicators	Frequency	Percentage (%)	Mean	STD
Age				
< 40	32	16.2		
41-60	95	48.2		
> 61	70	35.5		
Gender				
Male	135	68.5		
Female	62	31.5		
Education				
Illiterate	29	14.7		
Primary school	38	19.3		
Middle school	97	49.2		
High school	33	16.8		
Farm size (mu)			6.08	6.67
< 3	76	38.6		
3-5	54	27.4		
5-8	29	14.7		
> 8	38	19.3		
Training experience				
No	145	73.6		
From the government	7	3.6		
From scientific and technology backyards (STBs) / field school	39	19.8		
From companies	5	2.5		
From retailors	4	2.0		

Table S2.2 Number of cases for different PPPs in different cropping systems.

	Number of cases for W/M rotation	number of cases for vegetables	number of cases for orchards	In total
Aphid	41	32	0	73
Red spider	11	15	9	35
Pieris rapae	0	8	0	8
Helicoverpa armigera	0	5	0	5
Spodoptera exigua	0	6	0	6
Powdery mildew	0	3	0	3
Brown spot	0	0	5	5
Mycosis	0	0	7	7
Weeds	25	3	0	28
In total	47	72	21	170

Table S2.3 Pesticide usage practices regarding certain PPP.

Name	Number	Pesticides (combinations)	n_{S1}	n_{S2}	n_{S3}	n_{S4}
Wheat/maize rotation						
Red spider	1	Abamectin，malathion，Omethoate，Dimethoate，Thiamethoxam	5	4	0	0
	2	Emamectin benzoate+Abamectin ；Omethoate+chlorpyrifos	1	0	1	0
Aphid	1	Imidacloprid 、Dimethoate 、lambda-cyhalothrin、chlorpyrifos、Abamectin	5	5	0	0
	2	Imidacloprid+acetamiprid ；Cypermethrin+Imidacloprid ；Cypermethrin+Abamectin ；Cypermethrin+acetamiprid ；Omethoate+Cypermethrin ；chlorpyrifos+Imidacloprid ；Imidacloprid+Dimethoate ；Imidacloprid+monosultap ；Dimethoate+Cypermethrin ；Dimethoate+Thiamethoxam；lambda-cyhalothrin+Emamectin benzoate ；Cypermethrin+Abamectin；Emamectin benzoate+acetamiprid	11	10	5	0
	3	acetamiprid+Omethoate+Cypermethrin ；Imidacloprid+Cypermethrin+Emamectin benzoate ；Imidacloprid+Abamectin+Cypermethrin ；Cypermethrin+Dimethoate+Thiamethoxam ；Imidacloprid+acetamiprid+Cypermethrin	3	2	0	0
Weeds	1	MCPA-Na, Tribenuron-methyl, atrazine, mesotrione	11	11	0	0
	2	Tribenuron-methyl+ nicosulfuron; MCPA-Na+ Tribenuron-methyl; atrazine+ nicosulfuron	3	0	0	0

Table S2.3 (Continued).

Name	Number	Pesticides (combinations)	n_{S1}	n_{S2}	n_{S3}	n_{S4}
Vegetables						
Powdery mildew	1	Chlorothalonil	1	0	0	0
	2	Trifloxystrobin+tebuconazole ; Boscalid+ Kresoxim-methyl	1	1	0	0
Pieris rapae	1	Emamectin benzoate; indoxacarb; chlorfenapyr; Abamectin	5	0	0	0
	2	chlorfenapyr+indoxacarb ; Emamectin benzoate+indoxacarb	1	0	2	0
Red spider	1	Abamectin ; bifenazate ; Azocyclotin; Phoxim	5	4	0	0
	2	pyridaben+Abamectin ; spirodiclofen+Abamectin	1	0	4	0
	3	Abamectin+spirodiclofen+Azocyclotin	0	0	1	0
Helicoverpa armigera	1	Imidacloprid; Chlorantraniliprole; Dimethoate	2	1	0	1
	2	Emamectin benzoate+chlorfenapyr	0	0	1	0
Weeds	1	Pendimethalin	1	1	0	0
	2	Diquat+Fluoroglycofen	1	0	0	0
Spodoptera exigua	1	Lufenuron	1	1	0	0
	2	Emamectin benzoate+chlorfenapyr	2	0	1	0
	3	Lufenuron+Bifenthrin+acetamiprid	0	1	0	0
Aphid	1	Imidacloprid ; acetamiprid ; Thiamethoxam; Beta cypermethrin; carbosulfan; Dimethoate; Abamectin	9	8	0	3
	2	Emamectin benzoate+indoxacarb; Imidacloprid+acetamiprid ; Imidacloprid+Fipronil ; Imidacloprid+lambda-cyhalothrin; acetamiprid+Thiamethoxam ; cyhalothrin+Imidacloprid ; Abamectin+Imidacloprid ; Imidacloprid+Emamectin benzoate	4	3	2	0

Table S2.3 (Continued).

Name	Number	Pesticides (combinations)	n_{S1}	n_{S2}	n_{S3}	n_{S4}
	3	Bifenthrin+clothianidin+Pymetrozine ; Imidacloprid+Beta cypermethrin+Emamectin benzoate	2	0	1	0
Orchards						
Red spider	1	Spirodiclofen ; chlorfenapyr ; Abamectin; Azocyclotin	3	2	0	0
	2	Abamectin+Azocyclotin ; Acetamiprid+spirodiclofen ; Thiamethoxam+chlorfenapyr ; chlorpyrifos+Thiamethoxam	1	1	2	0
Brown spot	1	Mancozeb	3	2	0	0
Mycosis	1	Carbendazim, Tebuconazole	2	5	0	0

Table S2.4 Risk indicators of most used pesticides for bees.

Pesticides	Honeybees		
	Contact acute LD50	Oral acute LD50	Unknown mode acute LD50
Cypermethrin	H	H	DU
Imidacloprid	H	H	DU
Acetamiprid	M	M	DU
Emamectin Benzoate	H		
Abamectin	H		
carbendazim	M	L	DU
Mancozeb	M	L	DU
Dimethoate	H	H	H
Omethoate	DU	H	DU
Chlorpyrifos	H	H	DU
Tebuconazole	L	M	DU
Nicosulfuron	M	M	DU
Tribenuron-methyl	DU	M	M
Chlorfenapyr	DU	DU	H
Thiamethoxam	H	H	DU

Note: L=Low; M=Moderate; H=High.Data source: PPDB database, IUPAC pesticide properties database and PAN pesticide database.

Table S2.5 Parameters regarding toxicity data for the Bee-REX model.

Pesticide	Adult contact LD50 (μg a.s./bee)	Adult oral LD50 (μg a.s./bee)
Cypermethrin	0.023	0.172
Imidacloprid	0.081	0.0037
Acetamiprid	8.09	14.53
Emamectin Benzoate	NA	NA
Abamectin	0.0022	0.0022
Carbendazim	> 50	> 756
Mancozeb	141	162
Dimethoate	0.1	0.1
Omethoate	NA	0.048
Chlorpyrifos	0.059	0.25
Tebuconazole	> 200	> 83.05
Nicosulfuron	76	5.24
Tribenuron-methyl	NA	> 9.1
Thiamethoxam	0.024	0.005
Malathion	NA	NA
Lambda-cyhalothrin	NA	NA
Boscalid	> 200	> 166
Kresoxim-methyl	> 20	14
Indoxacarb	0.08	0.232
Chlorfenapyr	0.2	0.2
Phoxim	NA	NA
Pyridaben	0.024	0.535
Spirodiclofen	> 200	> 196
Chlorantraniliprole	> 100	> 104.1
Lufenuron	> 200	> 197
Bifenthrin	0.016	0.1
Carbosulfan	0.18	1.04
Fipronil	0.0059	0.00417
Cyhalothrin	0.027	0.27
Clothianidin	0.044	0.004
Pymetrozine	> 200	> 117
Thiophanate-Methyl	> 100	> 114.7
Chlorothalonil	> 40	> 40

Note: For a limit data reported as a "greater than" value, that given value was used in the calculations; NA, not available.

Table S2.5 (Continued).

Pesticide	Adult contact LD50 (μg a.s./bee)	Adult oral LD50 (μg a.s./bee)
Bifenazate	8.5	> 100
Trifloxystrobin	> 100	> 110
Tebuconazole	> 200	> 83.05
Azocyclotin	> 100	> 100
Tribenuron-methyl	NA	> 9.1
Atrazine	> 100	> 100
Mesotrione	> 100	> 11
Pendimethalin	> 100	> 101.2
Diquat	60	13
Fluoroglycofen	> 100	NA
Nicosulfuron	76	5.24

Table S2.6 Descriptive statistics of RQs in different cropping systems.

Cropping systems	Exposure route	Mean value	Median	Maximum value	Minimum value	% of exceeding LOC
Wheat/ maize rotation	Acute contact	87.53 b	8.89	1636.36	0	68
Vegetables		80.34 b	9.9	981.82	0.01	88.9
Orchards		123.42 a	0.06	490	0.02	40
Wheat/ maize rotation	Acute dietary	1308.15 b	62.4	19513.65	0.42	100
Vegetables		1516.06b	858.6	11708.19	0.46	100
Orchards		1881.55 a	1.68	5854	0.40	80

Note: Mean values of RQs in different cropping systems were compared via Mann-Whitney U test.

Table S2.7 Descriptive statistics of risk quotients (RQs) derived from the Bee-REX assessment.

	Mean value	Median	Maximum value	Minimum value	% Of exceeding LOC
Acute contact, n=152	87.32 b	8.89	1636.36	0.001	74.8
Acute dietary, n=163	1432. a	85.86	19513.65	0.40	100
Correct use, n=118	176.92 b	15.00	2575.80	0.001	89.41
Misuse, n=197	1033.06 a	37.01	19513.65	0.02	85.30

Chapter 3
Ecological risk assessment of pesticides on soil biota: An integrated field-modelling approach

Based on:

Mu, H., Yang, X., Wang, K., Tang, D., Xu, W., Liu, X., Ritsema, C. J., & Geissen, V. (2023). Ecological risk assessment of pesticides on soil biota: An integrated field-modelling approach. Chemosphere, 326, 138428. https://doi.org/10.1016/j.chemosphere.2023.138428

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 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.

3.1 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, 2022). 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 (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 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 have been well studied. However, information concerning the risks to soil biota is limited. Jana et al., (2019) and Govinda 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, 2022). 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, 2021), 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). 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.

3.2 Materials and methods

3.2.1 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 ℃ 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.

3.2.2 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 S3.1)**. 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 6-8 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℃ until the chemical analyses were performed.

3.2.3 Pesticide determination

3.2.3.1 Chemicals and solvents

Prior to the chemical analyses, farmers were interviewed and asked to list the pesticides that they commonly used in 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.

3.2.3.2 Extraction and clean-up

The pre-treatment procedure was modified from our previous study (Mu et al., 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 vertexing for 15 minutes 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 C_{18}, 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 10000 rpm. The upper layer supernatants were passed through 0.45 μm filters and stored in glass vials at -20℃ for further instrumental analysis.

3.2.3.3 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. Analyzed 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 analyzed chemicals was 0.01 mg kg^{-1}.

3.2.3.4 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 analyzed pesticides for fortified blank samples and calibration curve solutions were both acquired within a range of 70 % to 110 %. Also, the calibration curves were fairly linear, with linear correlation coefficients over 0.99.

3.2.4 Ecological risk assessment

3.2.4.1 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 3.1)**. 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).

$$TER_{species} = \frac{NOEC_{species}\ or\ LC50_{species}}{MC_{mean\ or\ max}} \tag{3.1}$$

$NOEC_{species}$ 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.) 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 (2022) 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.

3.2.4.2 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 3.2 and 3.3)**.

$$RQ_i = \frac{MC_{soil}}{PNEC_{mss}} \tag{3.2}$$

$$\sum RQ_{site} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MC_i}{PNEC_i} \tag{3.3}$$

$$Contribution\ \% = \frac{RQ_i}{\sum RQ_{site}} \tag{3.4}$$

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 (Vasickova 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 S3.3)**. $\sum RQ_{site}$ 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 ($\sum RQ_{site} > 1$).

3.2.5 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 order and visualizes the connections between these objects (Brüggemann and Ganapati, 2011). The ecological risk indictor and detection rates of pesticides in soil samples were ranked using the Hasse diagram **(Fig. 3.1)**. 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.

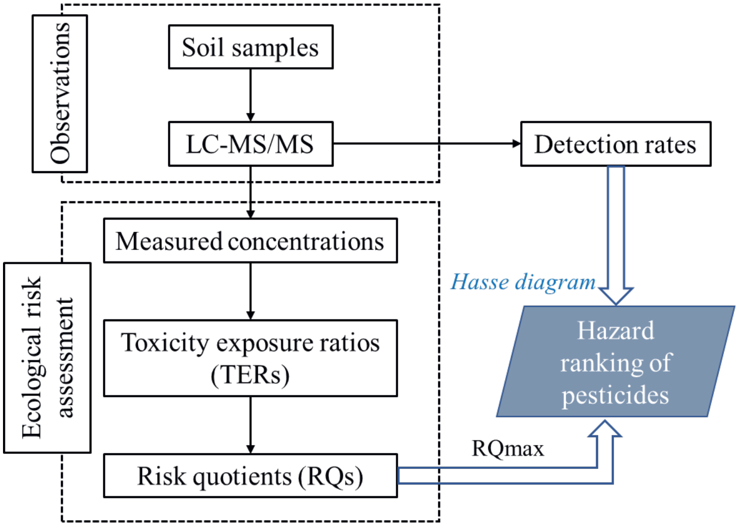


Fig. 3.1 The framework of the pesticide hazard ranking model.

3.2.6 Statistical analysis

Only concentrations above the LOQ were included in 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.

3.3 Results

3.3.1 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 residues **(Fig. 3.2)**. Chlorantraniliprole and tebuconazole were the most widely detected pesticides in the soil, with the detection rates exceeding 35% **(Table 3.1)**. 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. S3.1)**. More residues (2.7 residues on average) were found in the topsoil than from deeper layers (2.3 residues on average) **(Fig. S3.1)**. Pesticide concentrations were widely distributed ranging from 0.01 to 1.85 mg kg^{-1} **(Table 3.1)**. Among all collected samples, the highest concentration was found for carbendazim, followed by chlorantraniliprole and chlorpyrifos at roughly 1.50 mg kg^{-1} **(Fig. 3.2** and **Table 3.1)**. No significant differences were found in pesticide concentrations in samples taken from different crops, depths and times **(Fig. S3.2)**. The application rates of the analysed pesticides (displayed in **Table S3.4**) were obtained via farmer interviews in the study region that were carried out prior to the field sampling (Mu et al., 2022). The measured pesticide concentrations were found to be positively correlated with the pesticide application rates in the field **(Fig. S3.3)**.

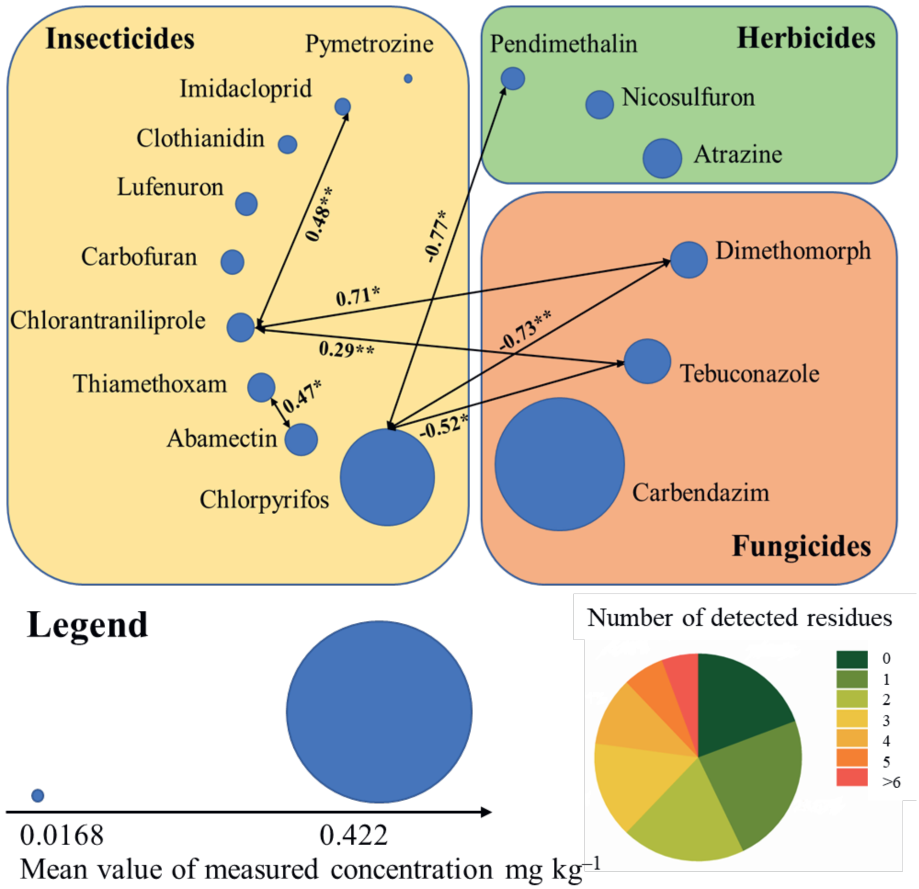


Fig. 3.2 Measured pesticide concentrations in soil samples and the internal correlations between paired pesticides.

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

Pesticide	Type	Class	Overall				0-2 cm depths			2-10 cm depths		
			DR (%)	C_{mean}	Median	C_{max}	DR (%)	C_{mean}	C_{max}	DR (%)	C_{mean}	C_{max}
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:

DR, detection rate. nd, not detected.

3.3.2 Ecological risk assessment

3.3.2.1 Risk assessment of single pesticide 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 **(Table 3.2** and **3.3)**. 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.

Table 3.2 TER_{max} and TER_{mean} calculated based on the selected species and single pesticides in the 0-2 cm soil depth.

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 3.3 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.

3.3.2.2 Risk assessment of pesticide mixtures by RQs

As shown in **Fig. 3.3**, 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. 3.3)**. 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. S3.4)**.

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. 3.4** and **Fig. S3.5)**. The major risk contributors varied due to different pesticide accumulation patterns across the sampled fields. For the wheat / maize rotation fields, the ecological risks were mostly posed by atrazine, while imidacloprid and chlorpyrifos were the major ecological risks contributors to 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.

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

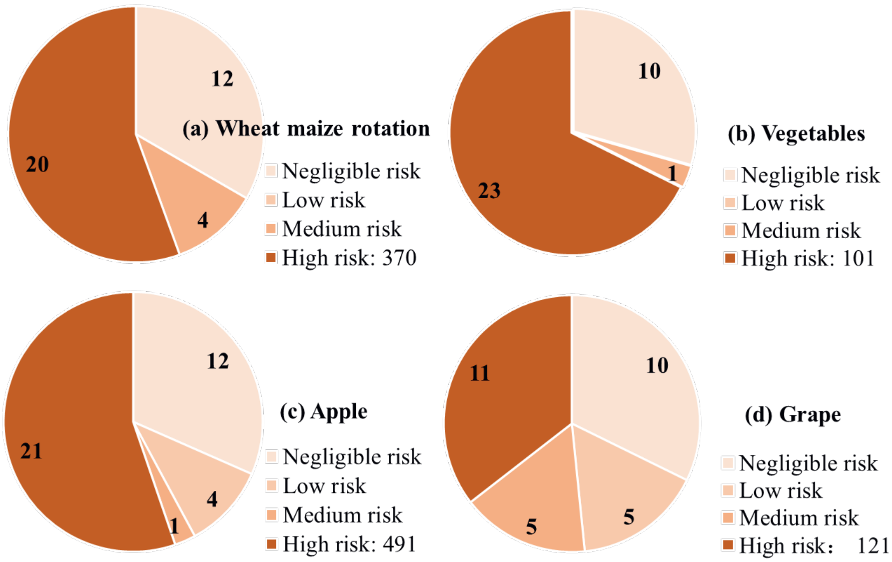


Fig. 3.4 Percentages (%) of ecological risk levels in samples from (a) wheat maize rotation, (b) vegetable, (c) apple orchards and (d) grape fields.

Note: The figures in the high-risk categories of legends represent the highest values of the calculated $\sum RQ_{site}$ in the corresponding farming systems.

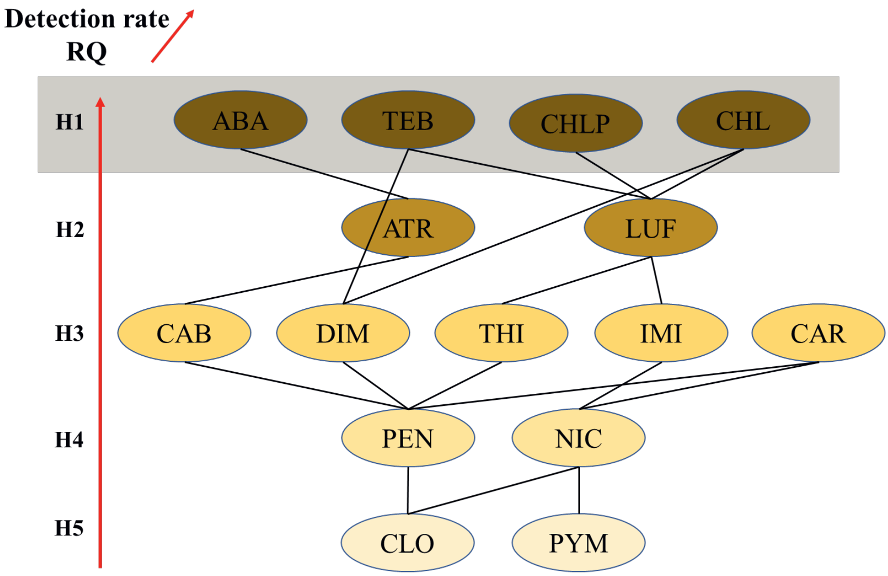


Fig. 3.5 Hasse diagram for pesticides posing ecological hazards to soil biota in arable soil.

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.

3.3.3 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. 3.5**, 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.

3.4 Discussion

3.4.1 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 topsoil 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 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 et al., 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. S3.2** and **Table S3.5)**, 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, 2021), 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 need to be further verified, possibly by comparing their concentrations with those of their degradation products.

3.4.2 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).

The results from the TERs revealed a concerning level of exposure risk from pesticides for N/C mineralization microorganisms **(Table 3.2** and **3.3)**, 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; Vasickova 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 **(Table 3.3** and **3.4)** 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 (Vasickova 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 analyzed 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 tests and comprehensive risk assessment in order to investigate interactions among commonly used pesticides (as shown in **Fig 3.2**) 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, attention still should be paid to 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 et al., 2022), should be developed based on local cropping patterns.

3.5 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 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.

Acknowledgement

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Supplementary information

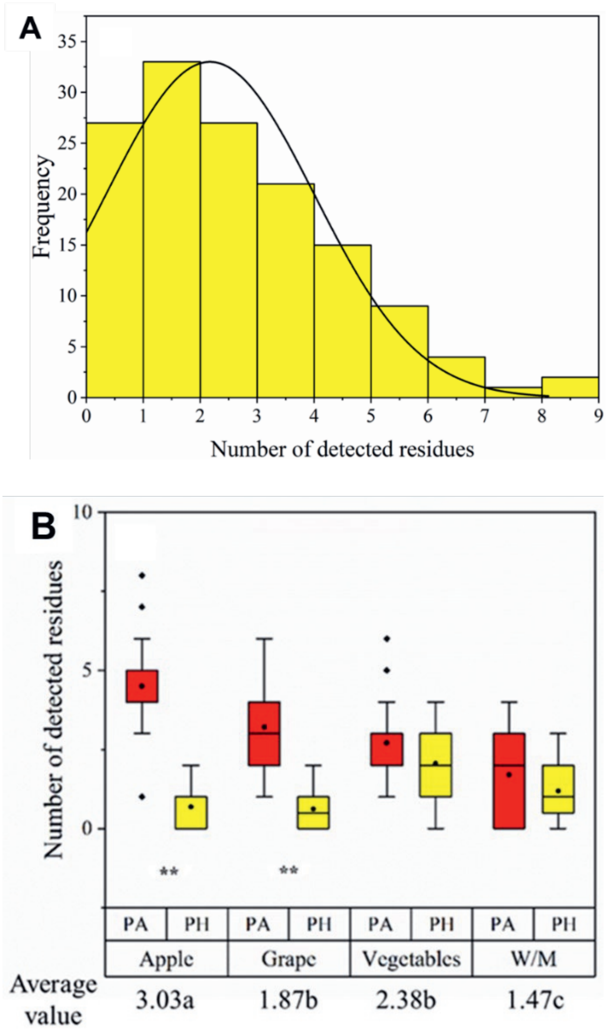


Fig. S3.1 Number of detected pesticide residues in A collected soil samples, B soils taken the two sampling events from different crop fields and C from different layer soils in Quzhou county.

Note: PA, pre-application sampling; PH, post-harvest sampling. ** Significant at $p < 0.01$.

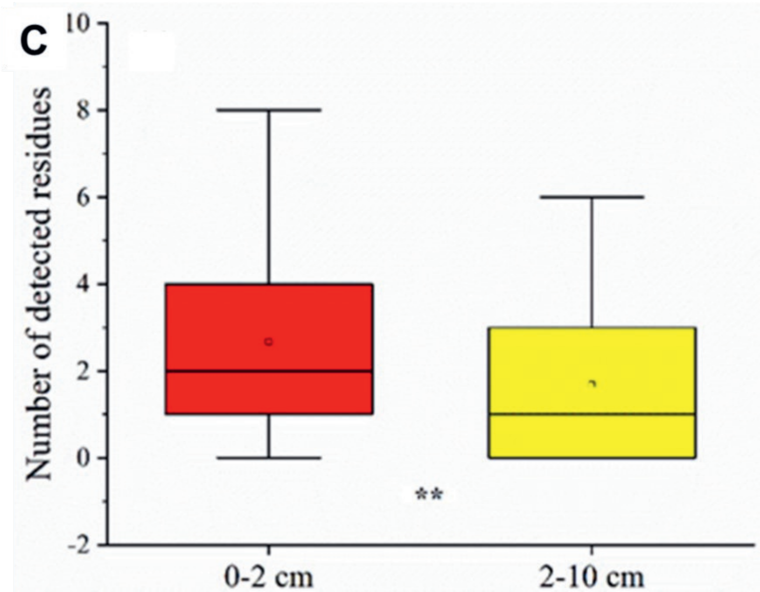


Fig. S3.1 (Continued).

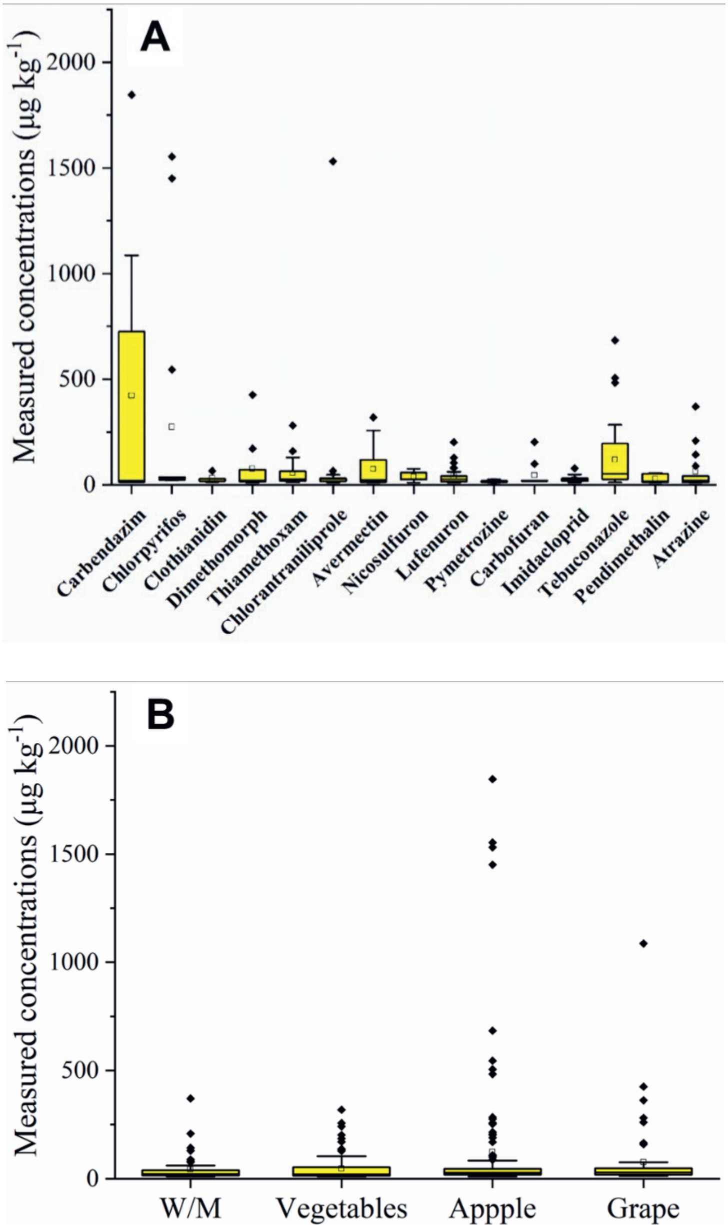


Fig. S3.2 Distribution of measured pesticide concentrations in A: all collected soil samples, B: different crop field samples, C: different soil depth samples, and D: samples taken in different times.

Note: W/M, wheat maize rotation fields.

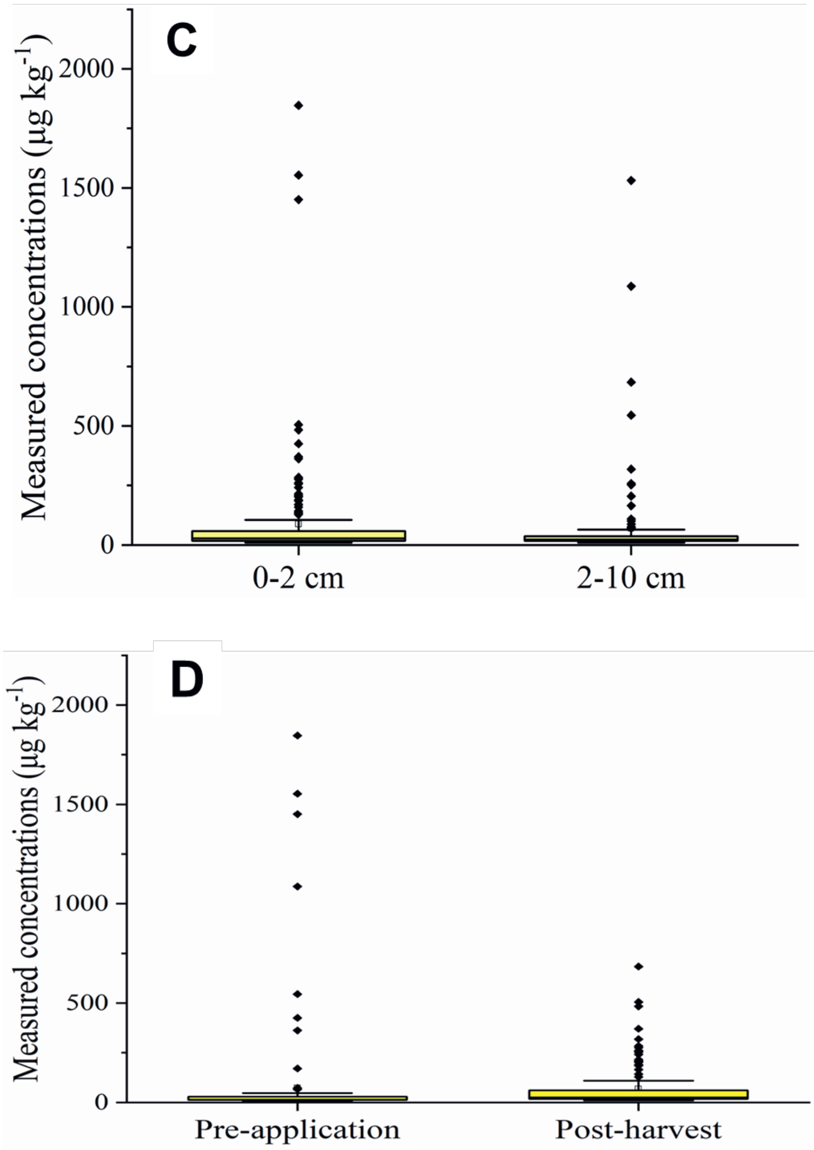


Fig. S3.2 (Continued).

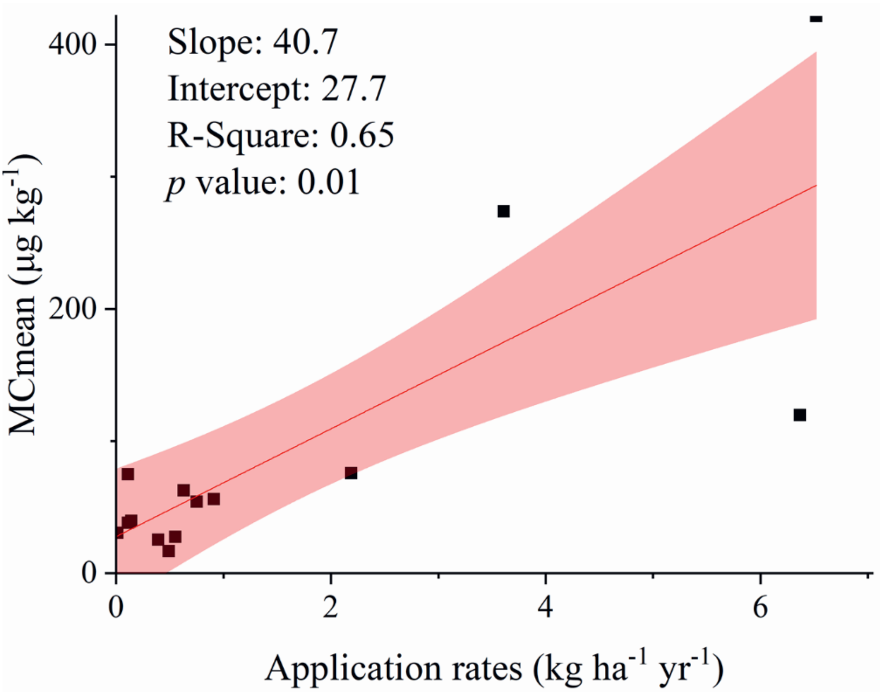


Fig. S3.3 The linear fitting curve between pesticide application rates and the mean measured concentrations.

Note: The red shade represents the 95% confidential interval. Pesticide application rates were derived from previous study in Quzhou county (Mu et al. 2022a).

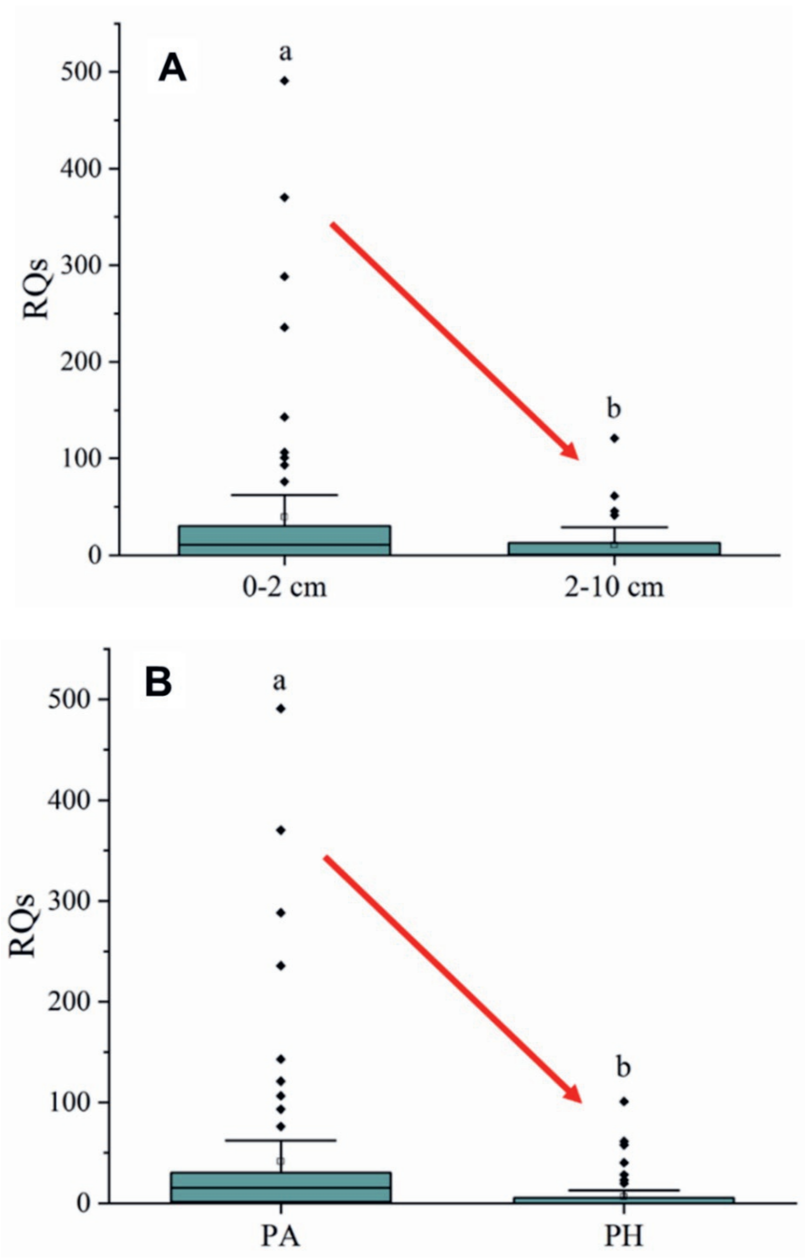


Fig. S3.4 Calculated RQs of samples taken from A different soil depth and B sampling times.
Note: PA, pre-application; PH, post-harvest.

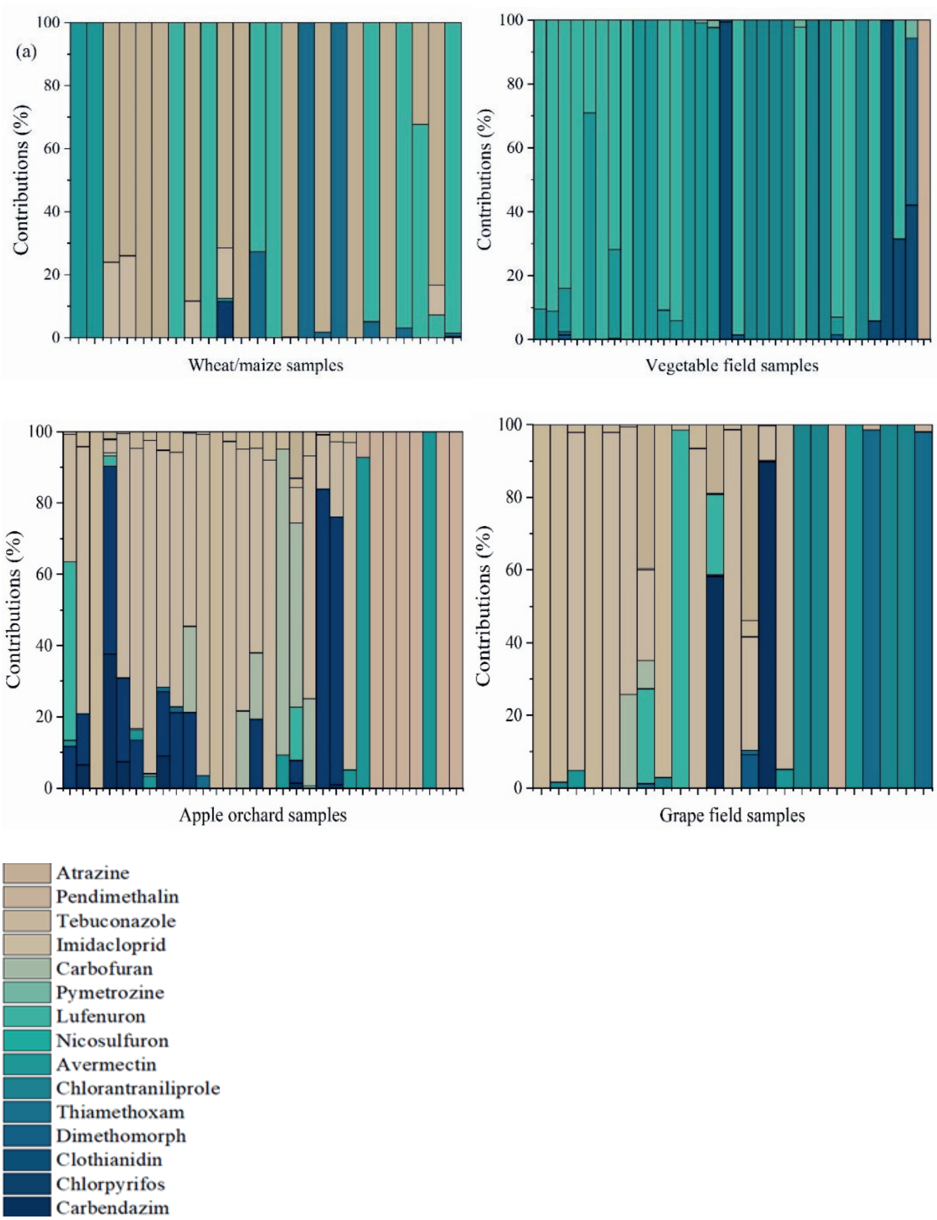


Fig. S3.5 Contributions (%) of pesticides to the $\sum RQ_{site}$ in different crop field samples.

Table S3.1 Sampling time for different crop fields.

Crop type	2020							2021										
	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11
Wheat maize rotation	√											√						
Vegetables	√		√															
Apple										√								√
Grape										√						√		

Note: √ represents sampling events.

Table S3.2 Instrumental conditions in the lab analysis.

Pesticides	Precursor Ion	Product Ion	Dwell (msec)	Q1 Pre Bias(V) 1	CE	Q3 Pre Bias(V) 1	RT (min)	Mode
Chlorpyrifos	351.90	199.90	30	-27	-18	-21	6.408	ESI+
Carbendazim	192.05	160.05	30	-30	-17	-30	0.374	ESI+
Thiamethoxam	292.00	211.10	30	-30	-11	-22	1.466	ESI+
Dimethomorph	388.10	301.00	30	-19	-20	-21	3.761	ESI+
Clothianidin	250.00	169.10	30	-29	-12	-17	1.966	ESI+
Chlorantraniliprole	484.00	452.90	30	-24	-19	-30	3.726	ESI+
Abamectin B1a	886.60	158.15	30	-24	-40	-28	7.190	ESI+
Nicosulfuron	411.10	182.10	30	-21	-20	-19	2.804	ESI+
Lufenuron	509.00	326.00	30	24	19	15	6.135	ESI+
Fipronil	435.00	330.00	30	10	16	21	4.726	ESI-
Pymetrozine	218.10	105.05	30	-26	-20	-20	0.519	ESI+
Imidacloprid	256.05	175.10	30	-29	-17	-18	2.087	ESI+
Pendimethalin	282.20	212.05	30	-30	-10	-23	6.236	ESI+
Emamectin benzoate	895.50	449.30	30	-32	-46	-32	3.362	ESI+
Carbosulfan	381.20	118.10	30	-30	-19	-22	3.181	ESI+
Tebuconazole	308.10	70.10	30	-22	-22	-27	4.145	ESI+
Atrazine	216.10	174.05	30	-30	-17	-18	3.352	ESI+
Indoxacarb	528.10	249.10	30	-26	-17	-27	5.286	ESI+

Table S3.3 Toxicity parameters (mg kg^{-1}) of detected residues in soil for the ecological risk assessment

Pesticides	E.fetida LC50	E.fetida NOEC	E. crypticus NOEC	F. candida NOEC	H. aculeifer NOEC	NSDE for N Mineralization microorganisms	PNEC AF	PNECmss
Chlorpyrifos	143.4	4		0.1		6.4	10	0.006
Carbendazim	14.7	0.4	0.1			2	10	0.01
Clothianidin	13.21	2.5					100	0.025
Imidacloprid	10.7	0.178	1	1.25	⩾2.67		10	0.0178
Thiamethoxam	1000	5.34					100	0.0534
Dimethomorph	223	19.6			8		50	0.16
Chlorantraniliprole	1000	350		100		0.7	10	10
Abamectin	28	0.25	10	0.25			10	0.025
Nicosulfuron	1000	1000				0.8	10	100
Lufenuron	500			0.2			100	0.002
Pymetrozine	1098	1.386		1000		6.66	10	0.1386
Pyraclostrobin	567	23.1					100	0.231
Pendimethalin	1000	33.5		76.8	383.2	12.1	10	3.34
Atrazine	79		1.0				100	0.001
Carbofuran	224	0.84		0.21			50	0.0042
Tebuconazole	1381	10		250			50	0.2

Note: NSDE, No significant adverse effect. The toxicity data was derived from PPDB database and literature. No toxicity data for Emamectin Benzoate. Sources: PPDB database.

Table S3.4 Application rates of most-used pesticides in major crop systems based on the farmer interview results.

Pesticides	Use frequency (%)	Misuse rate (%)	Annual application rate (kg ha yr^{-1})
Imidacloprid	51.3	59	0.01-2.52
Acetamiprid	41.1	26	0.01-2.1
Abamectin	27.4	31	0.01-0.58
Carbendazim	15.7	50	1.2-24
Chlorpyrifos	10.2	88	0.18-7.2
Tebuconazole	8.1	69	0.06-19.5
Nicosulfuron	8.1	17	0.01-0.22
Thiamethoxam	7.1	31	0.01-2.16

Table S3.5 Measured concentrations (μg kg^{-1}) of pesticides in different layer soil.

Pesticides	Measured concentration (μg kg^{-1})			
	Mean value 0-2	Mean value 2-10	Maximum value 0-2	Maximum value 2-10
Carbendazim	452.28	370.64	1846.41	1087.02
Chlorpyrifos	395.14	112.37	1553.70	545.11
Clothianidin	46.84	19.43	66.05	28.38
Dimethomorph	76.12	72.32	425.57	72.32
Thiamethoxam	70.60	35.69	280.81	75.23
Chlorantraniliprole	25.24	82.90	66.08	1531.00
Avermectin	96.75	53.17	257.20	318.58
Nicosulfuron	38.12	ND	75.91	ND
Lufenuron	46.25	20.06	201.58	36.97
Pymetrozine	17.50	15.84	24.34	18.27
Carbofuran	62.29	18.25	202.76	19.42
Imidacloprid	27.61	23.00	78.15	45.33
Tebuconazole	128.75	103.62	505.76	683.77
Pendimethalin	27.51	ND	55.59	ND
Atrazine	73.58	27.31	370.28	41.26

Note: ND, not detected.

Table S3.6 Pesticide concentrations in agricultural soils in other study areas.

Pesticides	Study area	Average concentration (μg kg^{-1})	Sources
Chlorpyrifos	Okara, Pakistan	1393	(Rafique et al., 2016)
	Nepal	40.8	(Bhandari et al., 2020)
	China	17.15	(Liu et al., 2016)
	China	42.2	(Han et al., 2017)
	Europe	30 (median)	(Silva et al., 2019)
	Czech	21	(Hvezdova et al., 2018)
	Quzhou, China	273.95	The present study
Carbendazim	Nepal	2.12	(Bhandari et al., 2020)
	Czech	8	(Hvezdova et al., 2018)
	Beijing, China	10.3	(Tao et al., 2021)
	Quzhou, China	421.67	The present study
Imidacloprid	Beijing, China	24.3	(Tao et al., 2021)
	Europe	20 (median)	(Silva et al., 2019)
	Quzhou, China	25.44	The present study
Tebuconazole	Beijing, China	36.8	(Tao et al., 2021)
	Czech	10	(Hvezdova et al., 2018)
	Europe	20 (median)	(Silva et al., 2019)
	Quzhou, China	119.59	The present study
Pendimethalin	Czech	62	(Hvezdova et al., 2018)
	Quzhou, China	27.51	The present study
Atrazine	Europe	10 (median)	(Silva et al., 2019)
	Quzhou, China	62.69	The present study

Chapter 4
Pesticide screening and health risk assessment of residential dust in a rural region of the North China Plain

Based on:

Mu, H., Zhang, J., Yang, X., Wang, K., Xu, W., Zhang, H., Liu, X., Ritsema, C. J., & Geissen, V. (2022). Pesticide screening and health risk assessment of residential dust in a rural region of the North China Plain. *Chemosphere*, *303*(Pt 2), 135115. https://doi.org/10.1016/j.chemosphere.2022.135115.

Abstract

Pesticides that have accumulated in arable soil could be easily transported by wind erosion, thereby potentially threating air quality and human health in surrounding areas. The risks this poses to farmers exposed to pesticide-associated dust is still unknown, especially in rural areas of China. In this study, we screened pesticide residues in dust (indoor and outdoor) collected from the homes and yards of farmers (21 participants) and bystanderss (14 participants) living in Quzhou County located in the North China Plain to assess health risks by exposed to pesticide-contaminated dust. The results showed that multiple pesticide residues were detected in the dust samples and more than 90% of the samples contained over 10 pesticide residues. The maximum detected number of residues was 23, out of the 25 pesticides currently used in the farming area. There was a wide range of pesticide concentrations with the geometric mean values measuring between 0.03 and 0.86 mg kg^{-1}. More residues and higher concentrations of pesticides were detected in indoor dust compared to outdoor dust. Over the monitoring period, the pesticide application has not caused significant pesticide accumulation in dust. The measured concentrations of carbendazim, dimethomorph, dimethomorph and pendimethalin paired indoor-outdoor dust samples were significantly correlated ($p < 0.05$). The health risks were assessed using the hazard index (HI) and highest HI was found for children under indoor exposure (HI = 0.82). In addition, based on the survey and statistics, pesticide preparation in the home was significantly correlated with the pesticide indoor exposure level. Therefore, farmers should take measures, such as preparing pesticides outside of the house or in the open fields with protection, in order to avoid the exposure risk of pesticides associated with dust.

4.1 Introduction

Pesticides are known to have multiple negative effects on the human body, and interfere with body functioning systems, such as neurological and reproductive systems (Akter et al., 2018; Rani et al., 2017). Once applied, pesticides can accumulate in soil, binding to surface soil particles which can then be transferred by the wind over long distances (Aparicio et al., 2018a). Fine soil particles enriched with pesticide residues erode from fields are transported to surrounding neighborhoods, which could potentially cause exposure risks to residents. The wind-borne particles have the potential to deposit on hard surfaces in outdoor environments such as pavements and gutters and then be easily picked up again by the wind and transported further into the air or indoor environments (Jiang et al., 2016). Previous studies have proved that pesticides are ubiquitous in both indoor and outdoor residential environments with maximum values measuring over 2000 μg kg^{-1} dust (Hwang et al., 2008; Waheed et al., 2017; Jiang et al., 2016). Considering the different environmental conditions of indoor and outdoor spaces, such as temperature, humidity and light intensity, the degradation rates of pesticides, and thus their accumulation characteristics in the dust on interior and exterior surfaces, might be different (Mahler et al., 2009). Residences can be exposed to pesticides via both dietary and non-dietary routes. The intake of pesticide-contaminated food and drinking water is the main route for dietary exposure (Nougadere et al., 2012), while the main routes for non-dietary exposure to pesticide-contaminated soil and dust are ingestion, inhalation, and dermal contact (Bhandari et al., 2020). This would include ingestion of soil or dust mainly through the mouth via dirty hands (mainly for children) or eating foods that have come into direct contact with dust. The inhalation route refers to the inhalation of respirable particles with a size less than 2.5 μm ($PM_{2.5}$) which have the potential to reach alveoli, including chemicals in the gas phase (USEPA, 2017). Larger particles of dust are most likely removed by the cilia in the lungs and swallowed, where the particles then enter the digestive system (USEPA, 2011). Thus, people can be exposed to pesticide-contaminated dust via both ingestion and dermal contact.

Pesticides were intensively sprayed by farmers in China with an increasing annual input till the launch of Zero-Growth Action Plan for Pesticides from 0.8 in 1990 to 1.8 million tons in 2019 (FAO, 2021; NBSC, 2021). As a major crop producing area in China, large pesticide, especially insecticides inputs and a wide usage of insecticides can be found in the North China Plain (NCP) (Aparicio et al., 2018a; Zhang et al., 2015). Quzhou is a typical agricultural county centrally located in the NCP where pesticides are intensively used. Additionally, particulate pollution events, such as haze and smog, occasionally occur in Quzhou during the winter season, elevating the exposure risk of pesticides in the airborne dust. For this study, Quzhou was selected as the study area to 1) investigate the occurrence and distribution of pesticides in indoor and outdoor dust, 2) assess the non-dietary exposure risks posed by pesticide mixtures in residential dust, and 3) explore key factors influencing the exposure risk to pesticides in dust. To the best of our knowledge, this study is the first to investigate the extent to which residents were exposed to pesticides in indoor and outdoor dust and to assess the related health risks that this exposure poses in the NCP. The results of this study could reflect the health risks that rural residents face due to daily contact with pesticide-contaminated dust and provide guidance for farmers to mitigate their exposure risk.

4.2 Materials and methods

4.2.1 Study area

Quzhou county (36°34′45″ N - 36°57′57″ N, 114°50′30″ E - 115°13′30″ E) is a typical agricultural county encompassing a total area of 667 km^2 with farmland accounting for 82.5% of that area. Located in the central area of the NCP, Quzhou has a subtropical humid monsoon climate with an annual mean temperature of 13.4 ℃ and an annual average precipitation of 556.2 mm. Grain crops, such as maize and wheat, and vegetables are the dominant crops.

4.2.2 Sampling scheme

In this study, three villages (Qianya, Wangzhuang and Xianggongzhuang, see **Fig. 4.1**) in Quzhou county were selected for participant recruitment and dust sampling that was conducted during the growing season **(Table S4.1)**. During May and June (around Grain in Ear of the solar terms and drop of apple), normally local farmers would apply pesticides in maize and vegetable fields and apple orchards. In this case, indoor and outdoor dust samples from the homes of the participants were collected twice, in May and June 2020. 35 people were recruited and divided into two groups: farmers and bystanders. After the dust collection, questionnaires regarding pesticide management (PM) and domestic habits (DH) (see **Table 4.1**) were distributed to farmers to explore possible factors influencing pesticide accumulation in the residential space. Each participant was also required to update the pesticide application details via WeChat. Each participant received a financial reward and gift for their participation, and they were free to exit the project at any time.

For each participant’s residence, indoor and outdoor dust samples were taken on two occasions at the starting and ending dates of the experiment to analyze the temporal variance over the peak season of pesticide application and agricultural activities in the summer. The indoor dust was taken from the floor of the living room, while the outdoor dust was collected from a hard surface in the courtyard or pavement adjacent to the front door.

Indoor and outdoor dust samples were collected from the sampled surfaces using a vacuum cleaner (T10 mix, Puppy Electronic Appliances Internet Technology Beijing Co.， Ltd.) following a Z-shaped movement. After sampling, dust and any other garbage were transferred from the dust collector to a prepared self-sealing bag and transported to the lab. In the lab, each collected sample was first passed through a 0.15 mm sieve to separate surface dust, the contents again placed in a self-sealing bag and then stored at -20℃ until analysis.

Table 4.1 Questionnaire description and farmers' choices.

Questions	Choices and percentages (%)
Group 1: Domestic habits (DH)	
Q1: Floor type	Cement floor (70) Wooden floor (0) Tile floor (30)
Q2: How often do you clean the floor ?	Once every few months. (10) Once every month. (0) Once every 10-15 days. (30) Once a week. (30) Every 1-3 days. (30)
Q3: In the summer season, how long do you ventilate your room per day?	Less than 3 hours. (0) Roughly half a day. (20) All day. (80)
Group 2: Pesticide management (PM)	
Q4: Do you wear special boots when applying pesticides in the field?	No. (50) Yes, the boot was stored in the home. (30) Yes, the boot was stored in the field / tool house adjacent to the field. (20)
Q5: How often do you spray pesticides in your home?	Never. (100) Less than once a month. (0) Once a month. (0) Once in 10-15 days. (0) Once in a few days. (0)
Q6: Do you prepare pesticides in your home rather than in the field?	In the field every time. (30) Occasionally in the home. (30) Irregularly in the home. (30) Most of the time in the home. (30) Yes, every time. (10)
Q7： Where do you store pesticide bottles?	Randomly in the home. (0) In the home, stored in a special corner. (60) Stored in the tool house or do not store pesticides at all. (40)

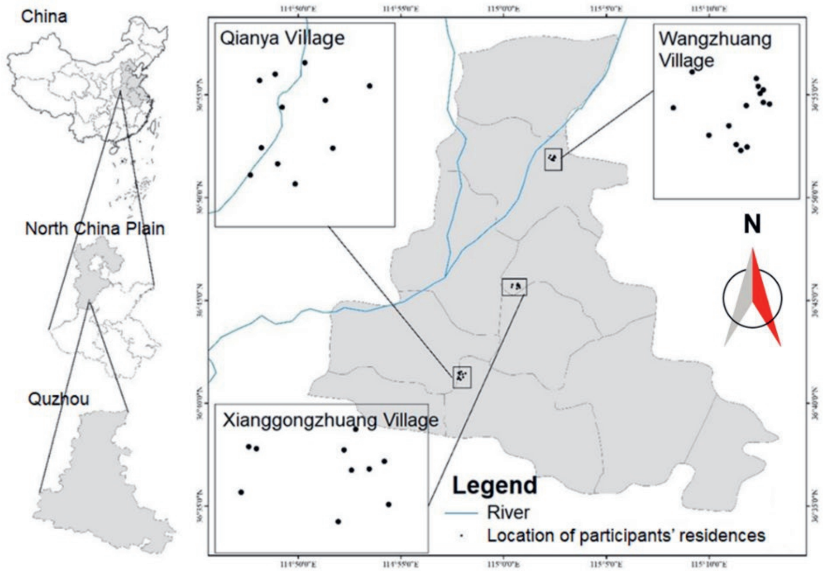


Fig. 4.1 Map of sampling locations for dust sampling (n = 35).

4.2.3 Pesticide screening

4.2.3.1 Chemicals and solvents

Prior to the experiment, a field survey was conducted to interview farmers and collected information related to pesticide usage in the fields. Based on the field survey results **(Table S4.2)** and participants' pesticide application data, in total 25 pesticides were selected for further chemical analysis.

The analytical reference standards for 25 analyzed pesticides 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 to reach the concentrations of 0.01, 0.05, 0.1, 0.5, 1 and 2 mg L^{-1} in acetonitrile. All the solutions were stored in a refrigerator at –20 °C until use.

Untreated bare soil samples were taken in Quzhou and passed through a 0.15 mm sieve as 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.

4.2.3.2 Extraction and clean-up

The pretreatment method was modified based on the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method (Anastassiades et al., 2003). Briefly, 1.0 ± 0.01 g of a dust sample was weighed and placed in a centrifuge tube along with 1.0 mL water, 2.5 mL of acetonitrile and 0.5 g NaCl and then placed on a vortex for 15 min at a rotation rate of 2500 rpm. Tubes were then centrifuged for 5 min at a rotation rate of 3800 rpm. 1 mL of the remaining supernatant was transferred into 2 mL centrifuge tubes for further treatment.

100 mg of $MgSO_4$ and 50 mg of C_{18} were added to each centrifuge tube with the extracts. The tubes were placed on a vortex for 30 s and then centrifuged in a high-speed centrifuge at a speed of 10000 rpm. The upper layer supernatants were passed through 0.45 μm filters and stored in glass vials at −20℃ for tandem mass spectrometry (LC-MS/MS) based instrumental analysis.

4.2.3.3 LC-MS/MS

All measurements were performed by using liquid chromatography coupled with LC-MS/MS with a triple quadrupole mass spectrometer (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. The analyzed compounds were separated in the mobile phase, consisting of eluent A (100% acetonitrile) and B (ultrapure water with 0.1% formic acid). The dry gas (N_2) had a temperature of 300 °C at a flow rate of 11.0 L min^{-1}. The nebulizer pressure was 15.0 psi and the electrospray voltage was + 4000 V. The precursor and corresponding product ions for the multi-reaction monitoring detection of each target compound are presented in Table S3. Gradient elution was optimized at a flow rate of 0.25 mL min^{-1} 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, and 6.5–7.5 min 20% A. List of analyzed pesticides (see Table 2) were selected based on interview results from farmers in Quzhou county. The injection volume was 2 μL at the first-time of analysis and 0.2 μL for samples with concentrations exceeding the maximum addition concentration (2 mg L^{-1}) of the calibration curve. The limit of qualification (LOQ) for analyzed chemicals is 0.01 mg kg^{-1}.

4.2.3.4 Quality assurance and quality control

In order to avoid possible interferences between samples during the dust sampling process, the electronic motor of the vacuum cleaner was removed, and the remaining parts of the vacuum cleaner were thoroughly washed by hand with soap and water between each interval of dust collection.

The calibration curve solutions were injected three times at the beginning, middle and end of the sample sequences. Recovery efficiencies of analyzed pesticides for fortified blank samples and calibration curve solutions were both acquired within a range between 70 % to 110 %. The calibration curves obtained good linearity with the correlation coefficients over 0.99.

4.2.4 Health risk assessment

Health risk assessments were performed based on the exposure assessment model presented by USEPA (2019), which aims to evaluate the potential risk posed by multiple exposure routes. In this study, only ingestion and dermal contact routes for dust were applicable for the assessment. Firstly, the average daily doses (ADI) via ingestion and dermal contact were estimated based on equations (Heather M. Stapleton) and (Heather M. Stapleton). C_{dust} represents measured pesticide concentrations in dust. Details of the explanations and values for other parameters from equations (Heather M. Stapleton) to (Heather M. Stapleton) are listed in Tables S3 and S4. Secondly, the health risks were characterized based on the hazard quotient (HQ) and the hazard index (HI) following equations (Heather M. Stapleton) and (Heather M. Stapleton). Here, a reference dose (RfD) was introduced as the threshold of daily exposure dose. If HQ or HI $>$ 1, possible health risks were posed by the pollutant studied. If the HQ or HI $\leqslant$ 1, then the health risks could be negligible.

$$ADI_{ing} = \frac{C_{dust} \times EF \times ED \times IR_{ing}}{AT \times BW} \times CF \tag{4.1}$$

$$ADI_{der} = \frac{C_{dust} \times SA \times SAF \times ABS \times EF \times ED}{AT \times BW} \times CF \tag{4.2}$$

$$HQ = \frac{ADI}{RfD} \tag{4.3}$$

$$HI = \sum_{k=1}^{n} HQ_i \tag{4.4}$$

Here, i refers to different exposure pathways. The RfD (mg kg^{-1} day^{-1}) represents the daily maximum permissible concentration of pesticide, including RfD_{ing} and RfD_{der} in the ingestion and dermal contact assessment, respectively. $RfD_{de} = RfD_{ing} \times ABS_{GI}$, where ABS_{GI} represents a dimensionless parameter, the gastrointestinal absorption factor (see **Table S4.4**). Metabolites and chlorobenzuron were excluded from the risk assessment due to the lack of solid reference values. The values for all constant parameters and the related data sources are listed in **Tables S4.3** and **S4.4**. The concentration-addition (CA) method was performed to address the health risks of multiple pesticides by assuming that there were no collective interactions between detected compounds, which has been widely accepted in regional risk assessment studies (Bhandari et al., 2021). In this case, the cumulative HI was calculated as the sum of the HIs of a single detected residue in certain sampled locations based on the CA method.

4.2.5 Statistical analysis

In the present study, concentrations below LOQ were excluded from further statistical analysis and counted as half of the LOQ in the risk assessment to reduce risk of these values interfering with the results. The Kolmogorov-Smirnov test was performed to identify the normality of the data. One-way ANOVA was conducted to compare the significant differences in pesticide concentration in dust samples collected from different time and locations. The t-test was performed to compare the differences in the hazardous indices for farmers in Qianya and Xianggongzhuang villages. Mann-Whitney U test, t test and one-way ANOVA were used to compare the differences in measured pesticide concentrations in paired indoor-outdoor dust samples Pearson's correlation test was performed to investigate correlations and to reveal whether there were shared sources among detected pesticides in the indoor and outdoor dust from the houses of farmers. Pesticides with a detection rate below 50% were excluded from the correlation analysis. Multiple linear regression analysis was performed to examine the significant factors affecting the pesticide levels of the indoor dust. In the regression analysis, the variance inflation factor (VIF) was calculated for all considered questionnaire indicators for the collinearity diagnosis.

4.3 Results

4.3.1 Number of residues detected in the residential dust

All analyzed pesticides were detected in the indoor and outdoor dust samples, with detection rates between 10 and 99%. The number of residues in the dust samples were normally distributed with a mean value of 15 (**Fig. 4.2** and **Fig. S4.1**). More than 10 residues were detected in 93% of the samples, while more than 20 residues were detected in 4.4% of the samples. The number (mean value of 17.1) of detected residues in the indoor dust samples were significantly higher compared to 13.2 in the outdoor samples. The number of residues differed significantly between indoor and outdoor dust, with no significant differences found between the samples taken during the first and second sampling events (**Fig. 4.3** and **Fig. S4.3**). Similarly, there were no significant differences between the number of detected residues in samples taken from the houses of bystanders as compared to those taken from the houses of farmers.

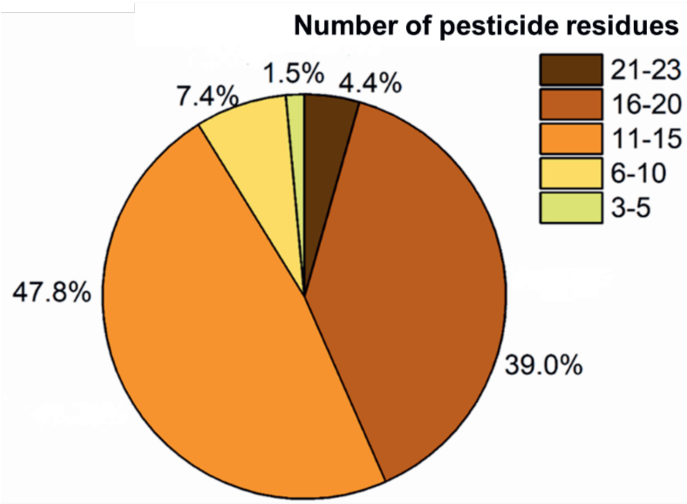


Fig. 4.2 Distribution of number of the detected pesticide residues per sample.

All pesticides were approved for use in the study area, except chlorpyrifos. The Chinese government banned the use of chlorpyrifos as a spray for vegetable fields because of its high toxicity (MOARA, 2017). In the present study, chlorpyrifos was detected in 93% of the samples with a geomean of 0.2 mg kg^{-1}. Given the fact that chlorpyrifos is recognized as a non-persistent chemical under field conditions (PPDB, 2021), the high detection rate indicates a new input of this compound in the area directly surrounding the dwellings or further away.

Table 4.2 Descriptive statistics of pesticide concentrations in all indoor and outdoor collected dust samples.

Pesticides	Chemical group	Detection rate (%)	Geomean (mg kg^{-1})	Median (mg kg^{-1})	75^{th} percentile (mg kg^{-1})	95% percentile (mg kg^{-1})
Carbendazim	Benzimidazole	99	0.86	0.77	3.59	19.32
Carbofuran	Carbamate	69	0.06	0.05	0.10	0.39
Carbofuran-3-Hydroxy	Degradation product	10	0.03	0.02	0.05	NA
Chlorpyrifos	Organophosphate	93	0.20	0.12	0.38	4.80
Clothianidin	Neonicotinoid	87	0.18	0.07	0.84	11.19
Dimethomorph	Morpholine	54	0.08	0.08	0.13	0.30
Thiamethoxam	Neonicotinoid	93	0.27	0.20	0.82	10.36
Chlorantraniliprole	Anthranilic diamide	34	0.09	0.08	0.20	0.72
Abamectin B1a	Micro-organism derived	49	0.15	0.16	0.26	1.50
Nicosulfuron	Sulfonylurea	77	0.05	0.04	0.09	0.74
Lufenuron	Benzoylurea	39	0.04	0.04	0.06	0.24
Pymetrozine	Pyridine	32	0.15	0.09	0.03	4.78
Imidacloprid	Neonicotinoid	95	0.49	0.07	3.0	9.49
Tebuconazole	Triazole	57	0.41	0.04	1.93	9.12
Difenoconazole	Triazole	57	0.20	0.10	0.63	17.28
Pendimethalin	Dinitroaniline	82	0.06	0.06	0.10	0.26

Note:
NA, not applicable.

Table 4.2 (Continued).

Pesticides	Chemical group	Detection rate (%)	Geomean	Pesticides	Chemical group	Detection rate (%)
Atrazine	Triazine	73	0.36	0.33	0.93	22.36
Prochloraz	Imidazole	49	0.13	0.09	0.25	4.22
Pyridaben	Pyridazinone	32	0.14	0.10	0.26	2.13
Acetamiprid	Neonicotinoid	93	0.46	0.41	1.76	11.73
Propamocarb	Carbamate	16	0.17	0.07	1.46	6.10
Thiophanate-Methyl	Benzimidazole	89	0.42	0.35	1.78	29.27
Fipronil	Phenylpyrazole	19	0.09	0.10	0.24	1.56
Fipronil sulfone	Degradation products	28	0.06	0.05	0.11	0.71
Chlorobenzuron	Undefined	89	0.49	0.04	1.43	16.27

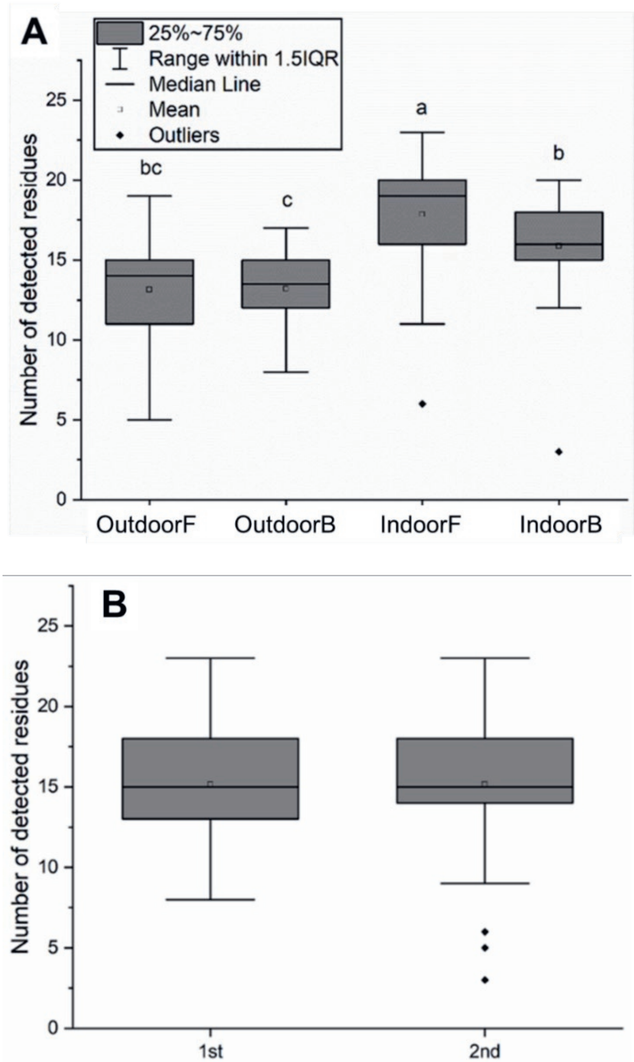


Fig. 4.3 Box chart of number of the detected pesticide residues in A: indoor and outdoor dust and B: the two sampling events.

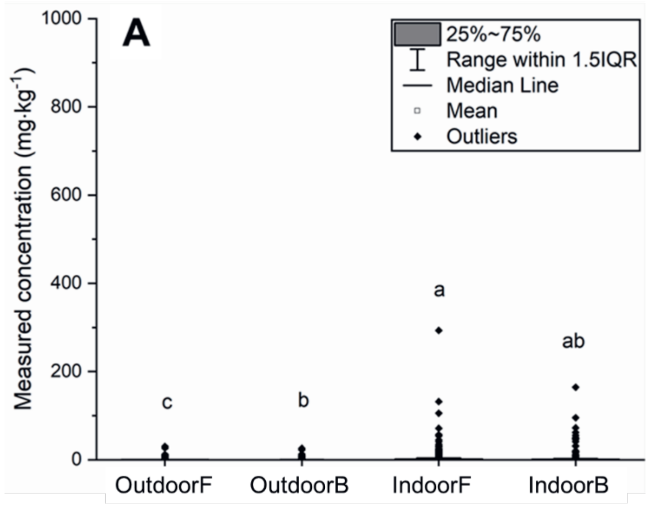
Note: OutdoorF: outdoodust samples taken from farmers' houses, OutdoorB, outdoor dust samples taken from bystanders' houses, IndoorF: indoor dust taken from farmers' houses, IndoorB: indoor dust samples taken from bystanders' houses, 1st, samples taken in the first sampling event; 2nd, samples taken in the second sampling event. a, b and c represent the significant differences between compared groups of data. IQR, interquartile range.

4.3.2 The accumulation levels of pesticides in residential dust

4.3.2.1 Pesticide concentrations in indoor and outdoor dust

There was a wide range of concentrations from below the LOQ (0.01 mg kg^{-1}) to 860 mg kg^{-1} (for thiamethoxam) in collected indoor and outdoor dust samples. The geometric mean of pesticide concentrations ranged from 0.04 to 0.86 mg kg^{-1}. Higher concentrations were found in the indoor dust as well as the samples taken from the houses of farmers **(Fig. 4.4)**. The geomean concentrations of imidacloprid and difenoconazole in the indoor dust reached 2.0 and 2.1 mg kg^{-1}, respectively, which were 20 times more than the geomeans for the outdoor dust. Except for chlorantraniliprole and lufenuron, the geomeans of pesticide concentrations in indoor dust were higher than those of outdoor dust. Despite this, there were no significant differences in the number of detected residues, although significantly higher concentrations of pesticides were detected in samples taken from farmers' houses as compared to bystanders' houses. The geomeans of dimethomorph and tebuconazole from farmers' dwellings were 0.41 and 0.60 mg kg^{-1}, respectively. This was 9.5 and 6.9 times the values for samples taken from bystanders' houses. The variation trends in pesticide concentrations also indicate that farmers may suffer higher health risks as compared to bystanders due to their daily residential contact with pesticide-contaminated dust.

Elevating trends could be observed for the measured concentrations of carbofuran-3-hydroxy, nicosulfuron, propamocarb and chlorobenzuron in samples collected during the two sampling events. The higher concentrations in samples taken in the second sampling event might indicate that these pesticides were continuously sprayed over the monitoring period. Much lower concentrationsnewungicides carbendazim and dimethomorph were found in samples taken in the second round, which could be attributed to the little newly input in the surrounding fields. Generally, the accumulation trends for most pesticides were steady over the monitoring period.



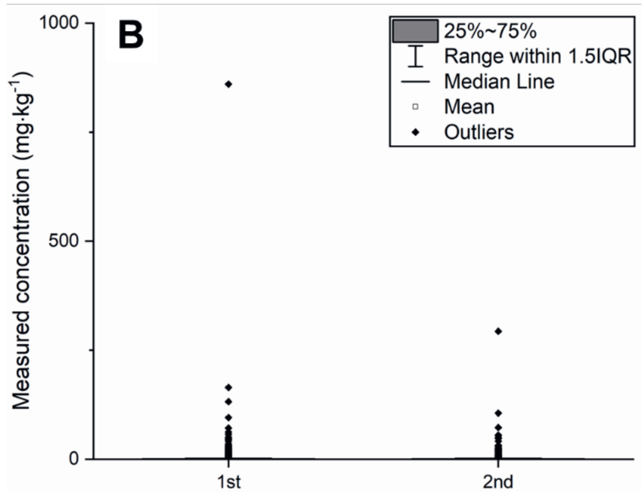


Fig. 4.4 Box chart of the distribution of measured pesticide concentrations in A: indoor and outdoor dust and B: two sampling events.

Note: OutdoorF: outdoodust samples taken from farmers' houses, OutdoorB, outdoor dust samples taken from bystanders' houses, IndoorF: indoor dust taken from farmers' houses, IndoorB: indoor dust samples taken from bystanders' houses, 1^{st}, samples taken in the first sampling event; 2^{nd}, samples taken in the second sampling event. a, b and c represent the significant differences between compared groups of data. IQR, interquartile range.

4.3.2.2 Correlations of pesticide concentrations in the indoor and outdoor dust

The correlations of pesticide concentrations in indoor and outdoor dust were separately analyzed based on Spearman's correlation test **(Fig. 4.5)**. The correlations of measured pesticide concentrations between paired indoor and outdoor dust samples were examined as well **(Table 4.3)**.

Considering the dissipation of pesticide drifts and the wind-facilitated particulate transport in the field, pesticides in the outdoor dust may have originated from the wind-eroded pesticides from surrounding fields or remote areas. Since most pesticides in the paired indoor and outdoor samples were not significantly correlated **(Table 4.3)** and the domestic pesticide preparation contributes to the indoor pesticide accumulation and exposure, indicating that the pesticides in the indoor dust mainly originated from the frequent pesticide preparation behaviors within the home. In this case, the correlations of pesticide concentrations in indoor dust could reflect residents' pesticide choices, while the correlations among pesticide residues in outdoor dust could provide insight into pesticide application patterns and common pesticide cocktail combinations in a larger area.

Regarding the indoor correlations, the results indicate that carbendazim, tebuconazole and difenoconazole were positively correlated, possibly because of their frequent combined use for plant disease control. Significant positive correlations were also found among chlorpyrifos, imidacloprid and chlorobenzuron in indoor dust, which might reflect their frequent selection for pest control purposes by local farmers. Positive correlations were also found within the same type of pesticides such as nicosulfuron and atrazine, indicating frequently pair-wised use by farmers for plant protection purposes. For the correlations in outdoor dust, significant positive correlations were found among carbofuran and chlorobenzuron, indicating the frequent collective use of these two insecticides on a larger scale. Additionally, thiamethoxam and its metabolite clothianidin were highly correlated in the outdoor dust, which illustrates that the predominant source for clothianidin was the degradation of thiamethoxam.

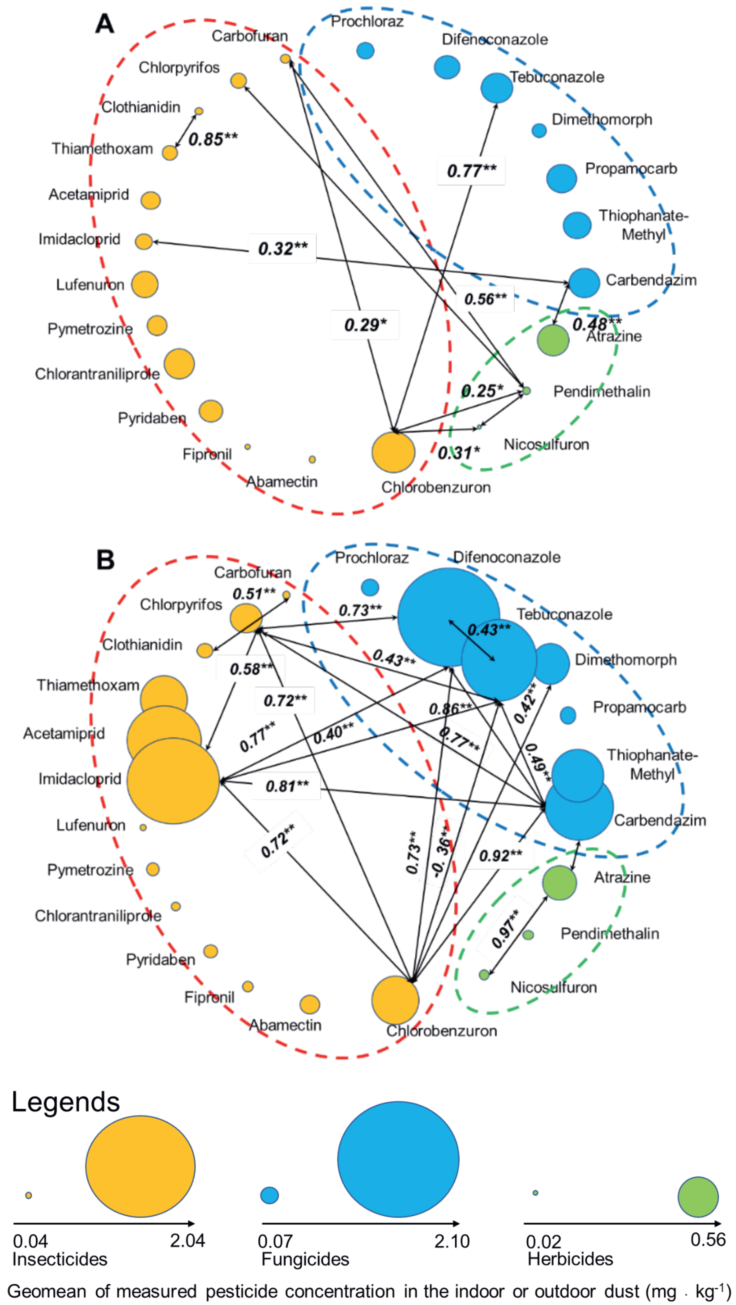


Fig. 4.5 Network graph of the correlations and accumulation characters of pesticides in A: outdoor dust and B: indoor dust.

Note: Only significant correlations were displayed on the network graph.

Table 4.3 Correlations of pesticide concentrations between the indoor and outdoor dust based on Spearman's correlation test.

Pesticides	Correlation coefficient
Carbendazim	0.27*
Carbofuran	-0.30*
Chlorpyrifos	0.04
Dimethomorph	0.30*
Clothianidin	0.23
Thiamethoxam	-0.13
Nicosulfuron	0.09
Imidacloprid	-0.16
Tebuconazole	-0.25
Diefenoconazole	-0.10
Pendimethalin	0.28*
Atrazine	0.02
Acetamiprid	0.06
Thiophanate-Methyl	0.07
Chlorobenzuron	0.10

Note: * Significant at $p < 0.05$.

4.3.3 Health risk assessment

4.3.3.1 The health risks by pesticide mixture in dust to adults and children

The health risks posed by a single pesticide were calculated in a conservative way based on the maximum values of measured concentrations **(Table S4.6)**. There was no hazard index (HI) exceeding 1.0, indicating that the exposure to a single pesticide was not likely to pose a potential health risk to residents. To better address the potential health risks by the exposure of pesticide mixtures, the cumulative HIs for pesticide mixtures in sampled locations via ingestion and dermal contact were further calculated based on the concentration-addition method. For both children and adults, the HIs were all below the threshold, indicating that the current accumulation levels of pesticides in residential dust tend not to pose chronic lifetime exposure health risks. Despite the fact that no exceedances appear, attention should be paid to the health risks posed to children when the maximum HI value (0.82) approaches the threshold. Due to higher concentrations and residue numbers of the indoor dust, the exposure level and HIs related to indoor dust were found to be significantly higher than those of outdoor dust **(Fig. 4.6)**. The results of the assessment indicate the possibility that under the successive pesticide application during the peak summer season, the HI posed by the daily contact with pesticide-contaminated dust might exceed the threshold level.

Taking the measured concentrations and toxicity (RfDs) into account, the cumulative load of detected residues was further calculated to identify high-risk pesticides to the HI. Insecticides contributed 67% of the health risks posed by pesticide mixtures, and thiamethoxam, chlorpyrifos, acetamiprid and fipronil were the major contributors. Other than insecticides, attention needs to be paid to carbendazim and difenoconazole that accounted for nearly 20% of the cumulative HI. These two fungicides were also found to be used frequently in a pair-wise fashion by local farmers, which means that alternatives for plant disease control and reduced application doses are highly needed.

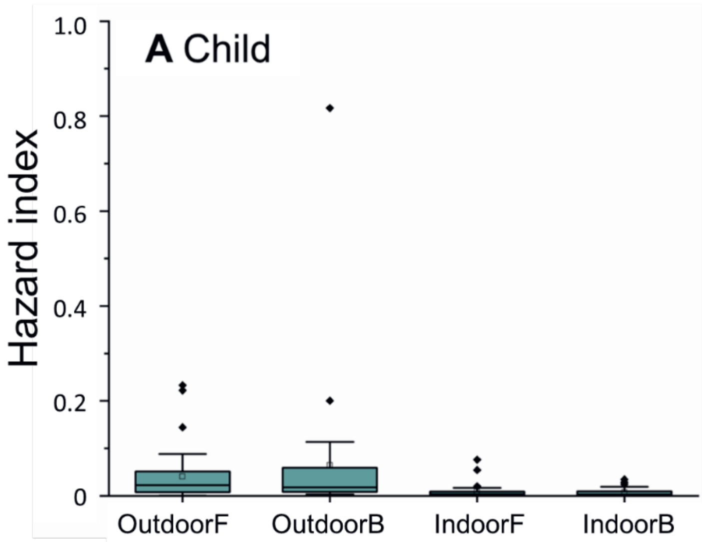


Fig. 4.6 Distribution boxplot of the hazard index for A: child and B: adult, and C: contributions (%) of pesticides to the cumulative health risks.

Note: OutdoorF: outdoodust samples taken from farmers' houses, OutdoorB, outdoor dust samples taken from bystanders' houses, IndoorF: indoor dust taken from farmers' houses, IndoorB: indoor dust samples taken from bystanders' houses. In Fig. 4.6C, other insecticides include carbofuran, chlorantraniliprole, abamectin, lufenuron, pymetrozine, pyridaben, clothianidin and imidacloprid. Other fungicides include prochloraz, propamocarb, dimethomorph, dimethomorph, tebuconazole and thiophanate-methyl. Herbicides include nicosulfuron, pendimethalin and atrazine.

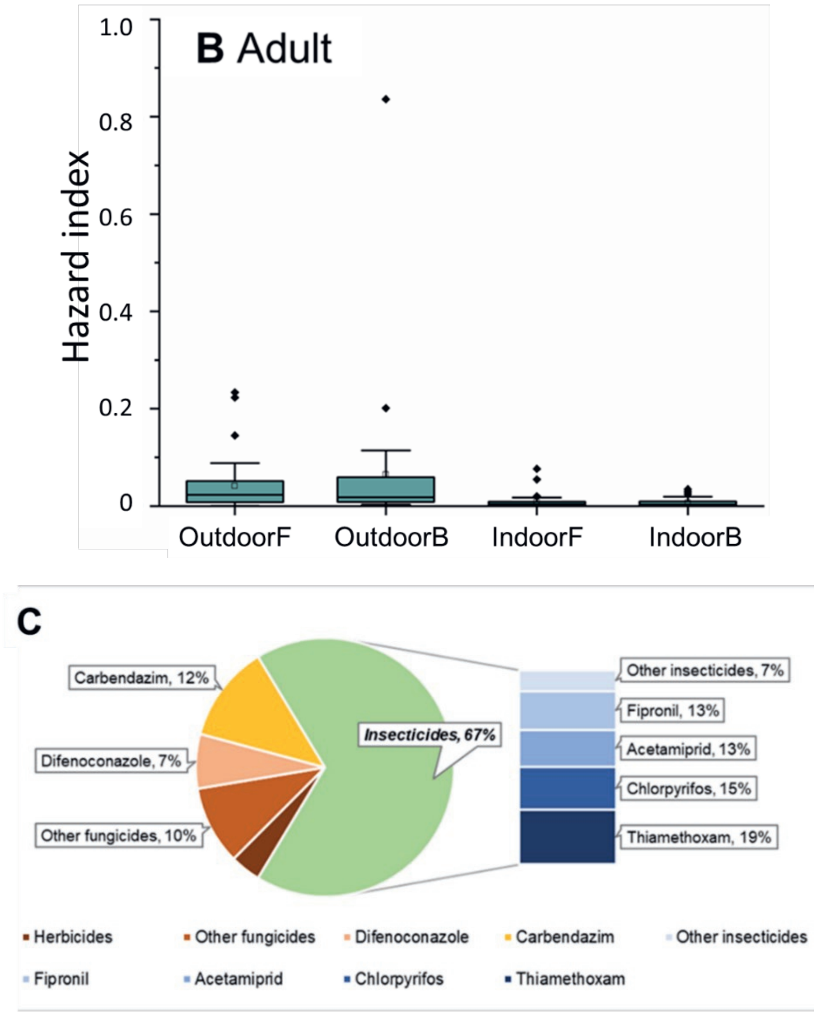


Fig. 4.6 (Continued).

4.3.3.2 Factors influencing indoor pesticide exposure risks

Due to higher concentrations and exposure risks in indoor space, an additional questionnaire was given to farmers to explore possible influencing factors, as well as the major sources of pesticides in the indoor dust. Factors including the home use of pesticides, ventilation practices, pesticide preparation, pesticide storage and dust cleaning behaviors, along with contaminated soil fractions attached to the threads of working boots after pesticide application, were considered as possible sources of pesticides in the indoor dust. Given that all respondents claimed that pesticides had not been used in home, the Q5 (see **Table 4.1**) was excluded for further statistical analysis.

To extract significant determinants of pesticide enrichment in the indoor dust, multiple linear regression analysis was carried out. For each indoor sampling location, the measured pesticide concentrations were summed up (sum conc.) as a dependent variable affected by questionnaire indicators. The hazardous index (for adults) was also set as a dependent variable to separately conduct the regression analysis. The result indicates that the pesticide preparation inside home was significantly associated with the dependent variables **(Table 4.4)**. The correlations between dependent variables and other questionnaire indicators were not significant.

Table 4.4 Multiple linear regression analysis with respect to the possible factors affecting indoor pesticide exposure.

Dependent variable	Independent variable	Standardized coefficient	Adjusted R^2	Partial correlation	VIF
Sum conc. (indoor)	Q1: Floor type	-0.08	0.31	-0.07	1.3
	Q2: Dust cleaning frequency	-0.35		-0.28	1.5
	Q3: Ventilation	0.17		0.15	1.3
	Q5: Special boots when spray pesticides	0.11		0.10	1.4
	Q6: Domestic pesticide preparation	0.45*		0.40	1.3
	Q7: Pesticide storage	0.20		0.17	1.4

Note: Sum conc. (indoor) represents the sum of pesticide concentrations of indoor dust samples. * Significant at $p < 0.05$, ** Significant at $p < 0.01$.

4.4 Discussion

4.4.1 Hazard characteristics and the accumulation of currently used pesticides in residential dust

This study screened the accumulation levels of 25 of the pesticides most-commonly used by local farmers in the residential dust which included restricted pesticides (chlorpyrifos and fipronil) and Ib class pesticides (highly hazardous pesticide, carbofuran). Even though local farmers mainly used approved pesticides to spray their fields, multiple negative health consequences could be potentially caused by the pesticides analyzed **(Table S4.5)**, including cancer, body functioning system disorders and acute poisoning symptoms. For analyzed pesticides in this study, three pesticides have been confirmed to cause disorders in the body's reproductive and nervous systems, and another three pesticides have also been proven to cause acute symptoms such as skin irritation and eye problems **(Fig. S4.5)**. Although it is difficult to build direct links between measured concentrations and the listed health consequences, the hazard screening results indicate that the potential health consequences posed by currently used pesticides cannot be neglected.

Since related studies conducted in other regions have mostly focused on the concentrations of organochlorine pesticides, such as DDTs (Chandra Yadav et al., 2020; Liu et al., 2019; Wang et al., 2013) which have been banned by the government for a long time, the present study adds new knowledge to the occurrence of currently used pesticides on residential surfaces. Compared to the studies conducted in other regions, higher fipronil and chlorpyrifos concentrations were found in the present study **(Table 4.5)**, which may reflect the higher pesticide application doses in the fields around the case study region. It should be noted that this study only analyzed pesticides commonly used by local farmers, and preferably the monitoring list of pesticides should include pesticides that are being used in the surrounding region as well.

Table 4.5 Comparisons of pesticide concentrations in the indoor and outdoor dust.

Locations	Measured concentrations (mg kg^{-1})				Sources
	Fipronil	Fipronil sulfone	Chlorpyrifos	Carbofuran	
Indoor dust					
Austin, Texas	9.8, maximum				(Mahler et al., 2009)
Taiwan, China			0.11, maximum		(C. C. Hung et al., 2018)
California			9.81, maximum		(Harnly et al., 2009)
Outdoor dust					
Austin, Texas	0.3, maximum				(Mahler et al., 2009)
Southern California	0.06, maximum	0.18, maximum	0.06, maximum		(W. Jiang et al., 2016)
Taiwan, China			0.14, maximum	0.24, maximum	(C. C. Hung et al., 2018)
Quzhou, China	0.1, median	0.05, median	0.12, median	0.05, median	The present study

4.4.2 Potential factors associated with the pesticide exposure in households

The accumulation levels of pesticides in the indoor dust were subjected to multiple factors. Residents who applied pesticides in the home, had a carpet in front of the door or lived close to agricultural fields tended to suffer higher personal exposure to pesticides (Glorennec et al., 2017; Harley et al., 2019). Apart from the home use of pesticides, pesticide applications in the fields were also reported to be largely correlated with the personal pesticide exposure levels and the pesticide concentrations in carpet and indoor dust (Teysseire et al., 2020; Trunnelle et al., 2013). In the present study, field facilities such as tool sheds were built and widely distributed throughout the surrounding fields in the Qianya village, providing extra space for pesticide storage and preparation, which allows local farmers in Qianya village to prepare pesticides outside rather than inside their homes **(Table S4.7)**. Consequently, the differences in the location of pesticide preparation can further lead to higher pesticide accumulation levels in indoor dust and even higher health risks for farmers in Xianggongzhuang village. Compared to the open field conditions, the indoor environment can be seen as a confined space despite the ventilation, which makes it difficult for pollutants attached to dust to be further transported to the exterior environment. In this case, the indoor cleaning activities were also found to effectively mitigate the exposure level of pollutants in the indoor environment (Liang et al., 2019).

Admittedly, this study screened the concentrations and the potential health risks for currently used pesticides in dust on both indoor and outdoor surfaces, yet several limitations still exist. The analytical list for this study only includes pesticides commonly used by local farmers, while monitoring programs screening more currently used pesticides in the region could provide more comprehensive risk evaluation (Bhandari et al., 2021). Furthermore, the number of sampled households, sampling locations for each participant and the monitoring period were all limited due to corona restrictions. Studies covering different ages of exposed people with prolonged monitoring periods could provide more representative results regarding the pesticide exposure to residents. In addition, we found that chronic lifetime health risks from pesticides were all below the threshold, yet the health consequences and resulting symptoms for vulnerable people in the real situation are still unknown. During the growing season, pesticides tend to be more concentrated in the residential dust due to successive pesticide applications, thus the health risks could also be elevated with longer monitoring periods. Multi-sectional studies covering more participants and longer time periods are needed to link the environmental fate of pesticides with residents' health issues. Interestingly, higher exposure risk in the indoor environment was found in this study as compared to the outdoor environment. Considering the fact that most residents have spent a lifetime in the indoor environment and the fact that there are differences in air exchange rates among different rooms (López et al., 2021; Shen et al., 2021), more attention needs to be given to the pesticide exposure in the indoor microenvironment, such as the occurrence, fate and degradation of pesticide residues in the different functioning zones.

In the present study, the inhalation routes were not included in the health risk assessment because data concerning pesticide concentrations in the gas phase and fine particulate matter with the sample size less than 2.5 μm ($PM_{2.5}$) were missing. The inhalation pesticide exposure risks were reported by studies conducted in both farming (Pivato et al., 2015) and non-farming areas (Jaipieam et al., 2009) and non-negligible health risks were found for the inhalation of highly toxic pesticides in the gas phase (Petchuay et al., 2017). For the $PM_{2.5}$ inhalation route, the health risk was mostly assessed as negligible to the exposure populations (Liu et al., 2019; Zhou et al., 2020), but the research related to the region of the NCP is limited due to the absence of field monitoring data. In this case, as an essential route for exposure assessment, the inhalation risks via both gas phase and $PM_{2.5}$ should also be considered in further assessment studies. Also, the dietary health risks by food / water intake should also be examined collectively to address the actual exposure level and health risks of rural residences to pesticides.

4.5 Conclusion

In this study, multiple pesticide residues were detected in the indoor and outdoor dust samples and the concentrations varied in a wide range. Carbendazim exhibited the highest geomean concentration, followed by imidacloprid and chlorobenzuron. Higher pesticide concentrations were detected in indoor and outdoor dust from farmers. Pesticide residues and concentrations detected in indoor dust were significantly higher than those in outdoor dust. Attention should be paid to the health risks posed by pesticide mixtures, especially for children in the indoor environment. Pesticide preparation was significantly correlated with the pesticide indoor exposure level. Additionally, pesticides in the indoor dust mainly originated from the successive pesticide preparation carried out in the home.

Based on the findings, we suggest that pesticide selection and usage choices should be adjusted, and the use of major risk contributors should be replaced by reduced-risk pesticides or biopesticides. A field farming facility, such as a shelter with water availability, should be provided for farmers to prepare pesticides outside their homes. Meanwhile, local people should clean their homes frequently and increase ventilation, thereby mitigating exposure risks to indoor pesticides.

Acknowledgement

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Supplementary information

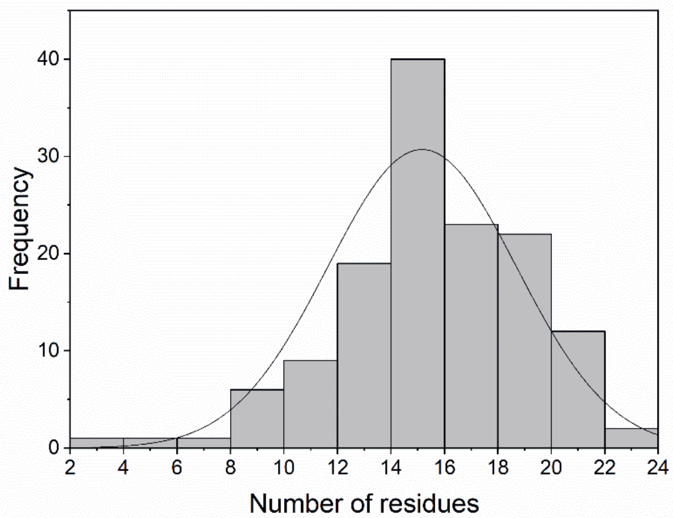

Fig. S4.1 The distribution of the number of residues detected in dust samples.

Pesticides	Detection rate (%)	Concentration (mg/kg)					
		IndoorF	IndoorB	OutdoorF	OutdoorB	1st	2nd
Carbendazim	99	1,38	1,93	0,34	0,73	1,13	0,64
Carbofuran	69	0,10	0,06	0,05	0,05	0,06	0,06
Carbofuran-3-Hydroxy	10	0,05	0,03	0,01	0,02	0,02	0,09
Chlorpyrifos	93	0,41	0,39	0,11	0,08	0,21	0,20
Dimethomorph	54	1,19	0,06	0,12	0,03	0,22	0,14
Clothianidin	87	0,10	0,09	0,04	0,01	0,07	0,09
Thiamethoxam	93	0,63	1,33	0,09	0,09	0,23	0,34
Chlorantraniliprole	34	0,05	0,12	0,28	0,06	0,08	0,10
Abamectin	49	0,27	0,17	0,05	0,03	0,14	0,15
Nicosulfuron	77	0,08	0,07	0,03	0,02	0,03	0,07
Lufenuron	39	0,04	0,05	0,16	0,16	0,05	0,04
Pymetrozine	32	0,09	0,34	0,14	0,10	0,16	0,14
Imidacloprid	95	2,18	1,84	0,10	0,10	0,51	0,47
Tebuconazole	57	1,51	9,50	0,24	0,04	0,47	0,35
Difenoconazole	57	2,26	1,66	0,14	0,07	0,20	0,19
Pendimethalin	82	0,07	0,09	0,05	0,05	0,06	0,07
Atrazine	73	0,34	1,13	0,12	0,21	0,30	0,43
Prochloraz	49	0,08	0,43	0,02	0,14	0,17	0,09
Pyridaben	32	0,14	0,28	0,12	0,17	0,13	0,17
Acetamiprid	93	2,13	0,97	0,18	0,06	0,31	0,70
Propamocarb	16	0,16	NA	0,17	0,1	0,12	0,21
Thiophanate-Methyl	89	1,41	0,77	0,24	0,06	0,39	0,47
Fipronil	19	0,10	0,03	0,04	NA	0,10	0,08
Fipronil sulfone	28	0,08	0,02	0,04	0,02	0,06	0,07
Chlorobenzuron	89	1,54	0,36	0,46	0,14	0,39	0,64

Minimum value　　Median　　Maximum value

Fig. S4.2 Color scale diagram of geometric means of pesticides in residential dust.

Note: OutdoorF: outdoodust samples taken from farmers' houses, OutdoorB, outdoor dust samples taken from bystanders' houses, IndoorF: indoor dust taken from farmers' houses, IndoorB: indoor dust samples taken from bystanders' houses. 1st, first sampling; 2nd, second sampling. NA, not applicable.

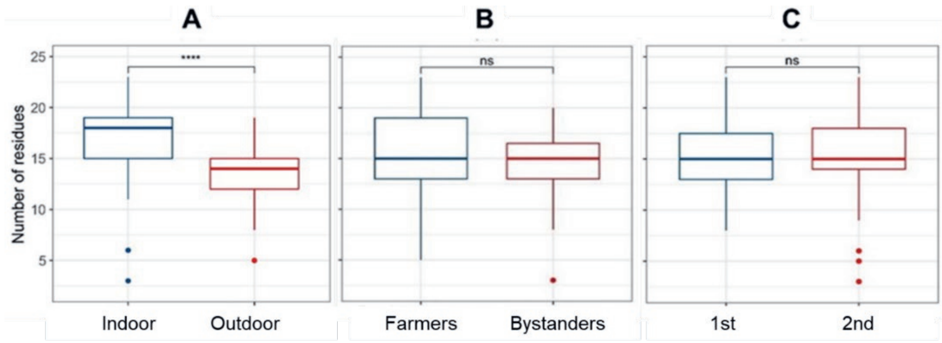

Fig. S4.3 Distribution of the number of detected residues in residential dust from A different sampling locations, B different groups of participants and C different sampling times.

Note: ns, not significant, **** Significant at $p < 0.001$, 1st and 2nd represent the first and second dust sampling.

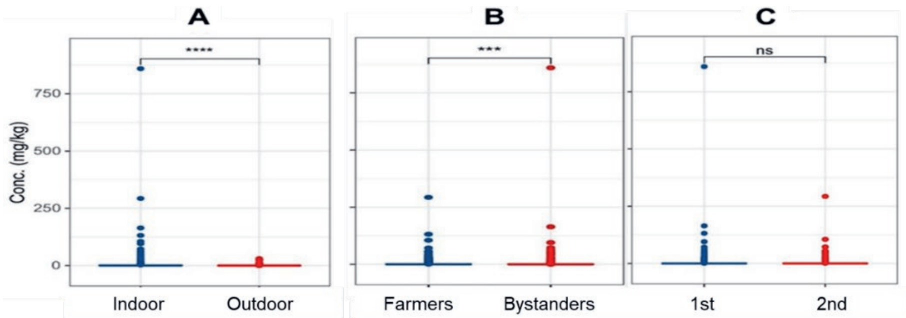

Fig. S4.4 Distribution of pesticide concentrations in residential dust from A different sampling locations, B different groups of participants and C different sampling times. Note: ns, not significant, ** Significant at $p < 0.01$; **** Significant at $p < 0.001$, 1st and 2nd represent the first and second dust sampling.

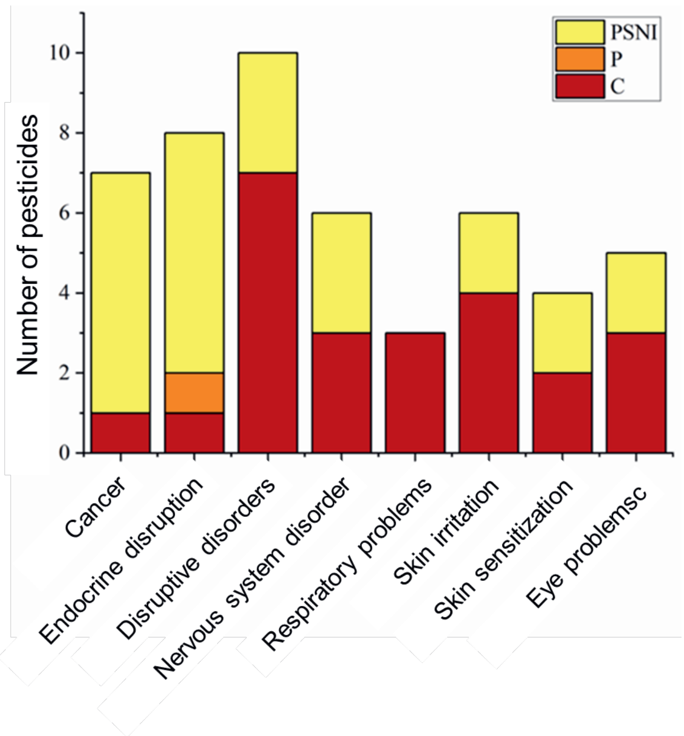

Fig. S4.5 Number of pesticides that can lead to different health consequences
Note: C: Known to cause health consequences, NC: Known not to cause health consequences, P: Possibly, PSNI: Possibly, status has not been identified. Data source: PPDB database

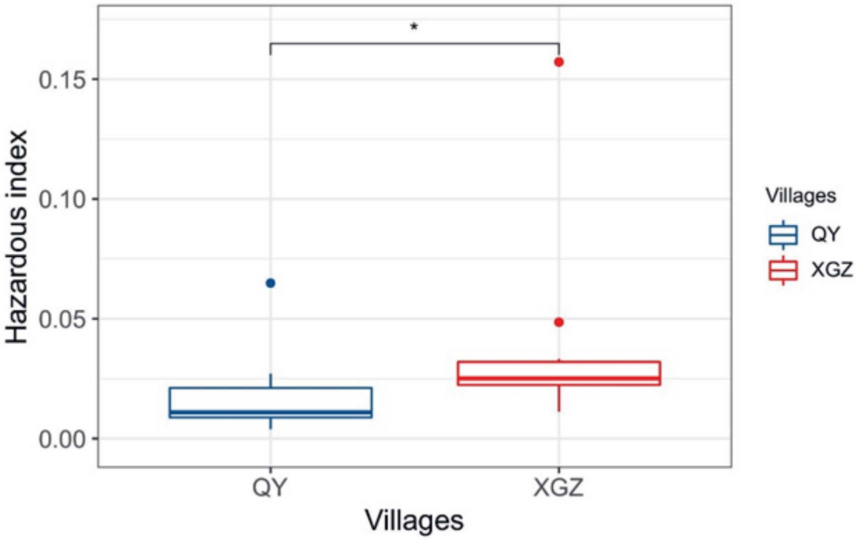

Fig. S4.6 Distribution of the hazard index for farmers in Qianya (QY) and Xianggongzhuang (XGZ).
Note:
* Significant at $p < 0.05$.

Table S4.1 Detailed list of selected villages and the participants.

Selected villages	Major crop	Participants	Starting date	Ending date
Qianya	Grape	11 farmers	19 May, 2020	16 June, 2020
Wangzhuang	Wheat, maize	14 bystanders	20 May, 2020	17 June, 2020
Xianggongzhuang	Apple	10 farmers	1 June, 2020	29 June, 2020

Table S4.2 Estimated application rates of commonly used pesticides in Quzhou county based on field survey.

Name	Frequency	% of use	EAR (kg/ha/yr)		
			N	Mean	SD
Imidacloprid	101	51.3	61	0.39	0.52
Acetamiprid	81	41.1	38	0.42	0.32
Abamectin	54	27.4	36	0.11	0.14
Carbendazim	31	15.7	20	6.52	5.47
Chlorpyrifos	20	10.2	8	3.61	3.18
Tebuconazole	16	8.1	13	6.37	6.28
Nicosulfuron	16	8.1	12	0.11	0.7
Tribenuron-methyl	15	7.6	8	0.55	0.2
Thiamethoxam	14	7.1	12	0.91	0.66

Table S4.3 Instrumental conditions and LOD for chemical analysis.

Compound name	Precursor Ion	Product Ion	Retention time (min)	Q1 Pre Bias (V)	Q3 Pre Bias (V)	CE	Mode	LOD (mg kg^{-1})
Carbendazim	192.05	160.05	0.593	-30	-30	-17	ESI+	0.0002
Carbofuran-3-Hydroxy	238.1	163.1	2.679	-27	-17	-14	ESI+	0.040
Chlorpyrifos	351.9	199.9	6.369	-27	-21	-18	ESI+	0.002
Clothianidin	250	169.1	2.009	-29	-17	-12	ESI+	0.0004
Dimethomorph	388.1	301	3.725	-19	-21	-20	ESI+	0.0005
Thiamethoxam	292	211.1	1.69	-30	-22	-11	ESI+	0.005
Chlorantraniliprole	484	452.9	3.743	-24	-30	-19	ESI+	0.005
Abamectin B1a	895.5	449.3	7.336	-32	-32	-46	ESI+	0.029
Nicosulfuron	411.1	182.1	3.008	-21	-19	-20	ESI+	0.0013
Lufenuron	509	326	6.088	24	15	19	ESI+	0.0004
Pymetrozine	218.1	105.05	0.541	-26	-20	-20	ESI+	0.005
Carbofuran	222.1	165.1	3.364	-25	-17	-11	ESI+	0.0007
Imidacloprid	256.05	175.1	2.596	-29	-17	-18	ESI+	0.004
Tebuconazole	308.1	70.1	4.457	-22	-27	-22	ESI+	0.0001
Difenoconazole	406.1	251.1	5.003	-30	-27	-25	ESI+	0.0002
Pendimethalin	282.2	212.05	6.543	-30	-23	-10	ESI+	0.007
Atrazine	216.1	174.05	3.722	-30	-17	-18	ESI+	0.0005
Prochloraz	376	308	4.14	-19	-21	-11	ESI+	0.00007
Pyridaben	365.1	309.05	7.348	-18	-22	-12	ESI+	0.001
Acetamiprid	223.1	126.05	2.668	-30	-30	-22	ESI+	0.004
Propamocarb	189.2	102.05	0.68	-30	-23	-20	ESI+	0.00008
Metalaxyl	280.1	220.2	3.568	-30	-24	-13	ESI+	0.0003
Thiophanate-Methyl	343.05	151.15	3.248	-17	-16	-20	ESI+	0.0002
Fipronil	435	330	4.887	10	21	16	ESI-	0.00004
Chlorobenzuron	307	154.15	4.695	21	29	11	ESI-	0.0002

Table S4.4 Values for constant exposure factors in the health risk assessment (Bhandari et al., 2020; USEPA, 2017, 2019; NBSC, 2020).

Exposure factor	Values	
	Children	Adult
Exposure frequency (EF, days/yr)	350	350
Exposure duration (ED, years)	14	30
Ingestion rate (IR_{ing}, mg/day)	200	100
Lifetime (LT, years)	76.7	76.7
Average life span (AT, days)	LT×365	LT×365
Body weight (BW, kg)	32	62
Conversion factor (CF, kg/mg)	10^{-6}	10^{-6}
Surface area* (SA, cm^2)	5803	6501
Dermal adherence factor (SAF, mg/cm^2)	0.2	0.07
Dermal absorption factor (ABS)	0.13	0.13

Note: * Surface area (cm^2) = skin surface area (cm^2; 15900 cm^2 for children, 19700 cm^2 for adult) × estimated skin surface exposed during outdoor activities in warm months (%; 36.5 % for children, 33% for adult).

Table S4.5 Reference values and the gastrointestinal absorption factor (ABS_{GI}) of analyzed pesticides.

Pesticides	RfD_{ing} (mg · kg^{-1}/day)	ABS_{GI}
Carbendazim	2.0E-02	1
Carbofuran	5.0E-03	1
Chlorpyrifos	3.0E-03	1
Clothianidin	9.7E-02	1
Dimethomorph	5.0E-02	1
Thiamethoxam	2.6E-02	1
Chlorantraniliprole	1.56	1
Abamectin B1a	1E-02	1
Nicosulfuron	2.0	1
Lufenuron	1.5E-02	1
Pymetrozine	3E-02	1
Imidacloprid	6.0E-02	1
Tebuconazole	3E-02	1
Difenoconazole	1E-02	1
Pendimethalin	4.0E-02	1
Atrazine	3.5E-02	1
Prochloraz	9.0E-03	1
Pyridaben	1E-02	1
Acetamiprid	2.5E-02	1
Propamocarb	0.29	1
Thiophanate-Methyl	8.0E-02	1
Fipronil	2E-04	1

Note: The RfDs were derived from USEPA (2018) and the acceptable daily intake (mg · kg^{-1}/day) in the PPDB (Pesticide Properties DataBase). ABS_{GI} values were derived from USEPA (2018). Default value (1) was assigned for the pesticides not appearing in the list. The RfD_{ing} and ABS_{GI} were not available for degradation products, such as carbofuran-3-Hydroxy and fipronil sulfone.

Table S4.6 Human health consequences of detected pesticides.

Pesticides	WHO class	Cancer	Genotoxicity	ED	RD	CI	ND	RP	SI	SS	EP	Phototoxicity
Carbendazim	U	PSNI	A2; B3; C3; D0; E1	PSNI	C	NC	NC	NC	NC	DU	NC	DU
Carbofuran	Ib	NC	A2; D2; C3; D3; E3	C	C	PSNI	PSNI	NC	NC	DU	NC	DU
Chlorpyrifos	II	NC	A3; B3; C3; D0; E3	PSNI	C	C	C	NC	NC	PSNI	NC	NC
Clothianidin		NC	A0; B0; C3; D0; E3	PSNI	PSNI	NC	C	NC	NC	DU	NC	DU
Thiamethoxam		NC	A3; B3; C3; D0; E0	NC	NC	NC	NC	NC	PSNI	DU	NC	DU
Abamectin		PSNI	DU	P	C	NC	DU	DU	DU	DU	DU	DU
Nicosulfuron		PSNI	A3; B3; C3; D0; E3	DU	DU	NC	NC	C	C	C	C	DU
Pymetrozine		C	A3; B3; C3; D0; E0	DU	C	NC	NC	C	NC	DU	NC	DU

Note: ED: Endocrine disruption. RD: reproductive disorders. CI: cholinesterase inhibition. ND: nervous system disorders. RP: respiratory problems. SI: skin irritations. SS: skin sensitization. EP: eye problems. Ib: Highly hazardous; II: Moderately hazardous; III: Slightly hazardous; U: Unlikely to pose acute hazard under normal use. C: Known to cause health consequences; NC: Known not to cause health consequences; P: Possibly; PSNI: Possibly, status has not been identified; DU: Data unavailable. # Human health consequences were retrieved from the PPDB databases which were maintained by the University of Hertfordshire, UK (Retrieved on: 23 November 2019). Genotoxicity: A: Chromosome aberration; B: DNA damage/repair; C: Gene mutation; D: Genome mutation; E: Unspecified genotoxicity type (Data sources: EFSA database and others). 0: Data not available; 1: Positive; 2: Mixed/ambiguous results; 3: Negative.

Table S4.6 (Continued).

Pesticides	WHO class	Cancer	Genotoxicity	ED	RD	CI	ND	RP	SI	SS	EP	Phototoxicity
Imidacloprid	II	NC	A3; B3; C3; D3; E2	DU	C	NC	PSNI	NC	PSNI	DU	PSNI	DU
Tebuconazole	III	PSNI	A3; B3; C3; D0; E0	DU	C	NC	NC	NC	NC	DU	C	DU
Atrazine		DU	A0; B0; C0; D0; E0	DU	DU	DU	DU	DU	DU	DU	DU	DU
Acetamiprid		NC	A0; B0; C0; D0; E3	DU	NC	NC	NC	NC	C	DU	PSNI	DU
Propamocarb	U	DU	A0; B0; C0; D0; E0	PSNI	DU	NC	PSNI	DU	C	PSNI	NC	DU
Tribenuron-methyl		PSNI	A3; B3; C3; D0; E3	PSNI	PSNI	NC	NC	C	NC	C	NC	NC
Fipronil	II	PSNI	A3; B3; C3; D0; E0	PSNI	PSNI	NC	C	DU	C	DU	C	DU

Table S4.7 Hazard quotients (HQs) and hazard indexes (HIs) based on the maximum pesticide concentrations in dust.

Pesticides	HQ_{ing}-child	HQ_{ing}-adult	HQ_{der}-child	HQ_{der}-adult	HI-child	HI-adult
Carbofuran	2.47E-03	1.36E-03	1.86E-03	8.07E-04	4.33E-03	2.17E-03
Chlorpyrifos	5.64E-02	3.12E-02	4.25E-02	1.84E-02	9.89E-02	4.96E-02
Dimethomorph	6.42E-03	3.55E-03	4.84E-03	2.10E-03	1.13E-02	5.65E-03
Chlorantraniliprole	9.11E-06	5.04E-06	6.87E-06	2.98E-06	1.60E-05	8.02E-06
Avermectin	2.35E-03	1.30E-03	1.78E-03	7.70E-04	4.13E-03	2.07E-03
Nicosulfuron	6.78E-05	3.75E-05	5.12E-05	2.22E-05	1.19E-04	5.97E-05
Lufenuron	4.66E-04	2.58E-04	3.51E-04	1.52E-04	8.17E-04	4.10E-04
Pymetrozine	1.70E-02	9.38E-03	1.28E-02	5.55E-03	2.97E-02	1.49E-02
Pendimethalin	5.84E-04	3.23E-04	4.40E-04	1.91E-04	1.02E-03	5.14E-04
Atrazine	1.72E-02	9.53E-03	1.30E-02	5.63E-03	3.02E-02	1.52E-02
Prochloraz	2.10E-02	1.16E-02	1.58E-02	6.87E-03	3.68E-02	1.85E-02
Pyridaben	3.37E-02	1.86E-02	2.54E-02	1.10E-02	5.91E-02	2.96E-02
Fipronil	1.11E-01	6.11E-02	8.34E-02	3.62E-02	1.94E-01	9.73E-02
Clothianidin	3.05E-04	1.69E-04	2.30E-04	9.99E-05	5.36E-04	2.69E-04
Thiamethoxam	3.62E-01	2.00E-01	2.73E-01	1.18E-01	6.35E-01	3.18E-01
Imidacloprid	1.30E-02	7.20E-03	9.82E-03	4.26E-03	2.28E-02	1.15E-02
Acetamiprid	1.28E-01	7.09E-02	9.68E-02	4.20E-02	2.25E-01	1.13E-01
Tebuconazole	7.48E-03	4.14E-03	5.64E-03	2.45E-03	1.31E-02	6.58E-03
Difenoconazole	2.90E-02	1.60E-02	2.19E-02	9.48E-03	5.09E-02	2.55E-02
Carbendazim	3.39E-02	1.87E-02	2.56E-02	1.11E-02	5.94E-02	2.98E-02
Thiophanate-Methyl	2.25E-02	1.24E-02	1.69E-02	7.35E-03	3.94E-02	1.98E-02
Carbofuran	2.47E-03	1.36E-03	1.86E-03	8.07E-04	4.33E-03	2.17E-03
Propamocarb	2.46E-04	1.36E-04	1.86E-04	8.05E-05	4.32E-04	2.17E-04
Carbofuran	2.47E-03	1.36E-03	1.86E-03	8.07E-04	4.33E-03	2.17E-03

Chapter 5
Exposure Risk to Rural Residents: Insights into Particulate and Gas Phase Pesticides in the Indoor-Outdoor Nexus

Based on:
Mu, H., Yang, X., Wang, K., Osman, R., Xu, W., Liu, X., Ritsema, C. J., & Geissen, V. (2024). Exposure risk to rural Residents: Insights into particulate and gas phase pesticides in the Indoor-Outdoor nexus. Environment international, 184, 108457. Advance online publication.
https://doi.org/10.1016/j.envint.2024.108457.

Abstract

Rural residents are exposed to both particulate and gaseous pesticides in the indoor-outdoor nexus in their daily routine. However, previous personal exposure assessment mostly focuses on single aspects of the exposure, such as indoor or gaseous exposure, leading to severe cognition bias to evaluate the exposure risks. In this study, residential dust and silicone wristbands (including stationary and personal wearing ones) were used to screen pesticides in different phases and unfold the hidden characteristics of personal exposure via indoor-outdoor nexus in intensive agricultural area. Monte-Carlo Simulation was performed to assess the probabilistic exposure risk by transforming adsorbed pesticides from wristbands into air concentration, which explores a new approach to integrate particulate (dust) and gaseous (silicone wristbands) pesticide exposures in indoor and outdoor environment. The results showed that particulate pesticides were more concentrated in indoor, whereas significantly higher concentrations were detected in stationary outdoor wristbands ($p < 0.05$). Carbendazim and chlorpyrifos were the most frequently detected pesticides in dust and stationary wristbands. Higher pesticide concentration was found in personal wristbands worn by farmers, with the maximum value of 2048 ng g^{-1} for difenoconazole. Based on the probabilistic risk assessment, around 7.1 % of farmers and 2.6 % of bystanders in local populations were potentially suffering from chronic health issues. One third of pesticide exposures originated mainly from occupational sources while the rest derived from remoting dissipation. Unexpectedly, 43 % of bystanders suffered the same levels of exposure as farmers under the co-existence of occupational and non-occupational exposures. Differed compositions of pesticides were found between environmental samples and personal pesticide exposure patterns, highlighting the need for holistic personal exposure measurements.

5.1 Introduction

In order to meet the global food demand of a growing population, farmers use pesticides to increase crop production, using nearly 2.7 million tons of active substances in 2020 (FAO, 2022). Despite its vital contribution to securing food availability (Tang et al., 2021), the massive input of pesticides has caused ubiquitous contamination in environmental matrices in fields and residential areas (Geissen et al., 2021; W. Jiang et al., 2016; Jiang, 2012; Jiang et al., 2016; Mu et al., 2023). Pesticide exposure may result in accumulation in body tissues and contribute to multiple health problems, including cancer, asthma, diabetes, Alzheimer's disease and reproductive issues (Huang et al., 2019; Hayden, 2010; Kumar, 2004; Balluz et al., 2000; Rusiecki et al., 2006; Velmurugan et al., 2017). Approximately 44% of global farmers are facing the consequences of pesticide exposure which is responsible for a human death rate between 0.4 and 1.9% (Boedeker et al., 2020; Hassaan et al., 2020). Thus, concerns have been raised regarding the potential pesticide exposure risk for rural residents.

Rural residents can be exposed to both particulate and gaseous pesticides present in their surroundings. Specifically, pesticide exposure may occur via inhalation of gaseous pesticides in the ambient air, ingestion of pesticide-contaminated dust or direct skin contact with pesticide drifts or particles (Koelmel et al., 2022; Mu et al., 2022). Individual exposure risks from indoor and outdoor environments can differ due to the different degradation rates of pesticides which can be caused by several factors including wind, humidity, temperature, and solar radiation (Jiang et al., 2016). Unfortunately, most studies related to pesticide risk exposure assessments focus mainly only on individual aspects of exposure, such as indoor or outdoor exposure (Degrendele et al., 2022; Msibi et al., 2021; Mu et al., 2022; Waheed et al., 2017), which may lead to substantial discrepancies when compared with actual combined exposures.

Given the highly individualized daily routines of bystanders and the differing agricultural tasks they carry out, measuring direct personal pesticide exposure is challenging. An active air sampling technique using a pump and collection device which actively absorbs ambient air is often used to measure personal exposure to airborne chemicals, especially in occupational settings (Estill et al., 2020; Nguyen et al., 2022; NIOSH, 2018). However, the sampler is burdensome to use and thus may interfere with accurate participant measurements. Biomonitoring examines internal exposure to certain chemicals by analyzing biological samples, such as hair, urine, milk, and blood plasma, but this sampling procedure can be invasive (Henríquez-Hernández et al., 2022; Huber et al., 2022; LaKind et al., 2009; Legrand, 2005; Thompson et al., 2023). Silicone wristbands, with the ability to absorb volatile and semi-volatile chemicals, have been used as low-cost samplers for a wide range of airborne contaminants, reflecting personal exposure profiles primarily from inhalation and partial dermal contact (deposition of contaminated dust and drifts on skin) (Hendryx et al., 2020; Kile et al., 2016; Nguyen et al., 2022; O'Connell et al., 2014; Samon et al., 2022). Due to their ease of use, silicone wristbands have been given to residents (Aerts et al., 2017), children (Kile et al., 2016; Harley, 2019; Koelmel et al., 2022), industrial workers (Hendryx et al., 2020; Nguyen et al., 2022), and even pets (Wise, 2020; Wise et al., 2021) to monitor their exposure to hundreds of chemicals including pesticides, polycyclic aromatic hydrocarbons, flame retardants and polychlorinated biphenyl. O'Connell built predictive models for silicone wristbands to translate the measured concentrations in wristbands to the equivalent air concentrations under equilibrium conditions, which provides a new approach to assess gas phase contaminants (O'Connell et al., 2021). By transforming pesticide measurements into air concentrations, wristbands can serve as wearable sensors to address the spatial variances of pesticide levels across the indoor-outdoor nexus and to obtain real individual exposure to gaseous pesticides during daily routines. Currently, exposure assessment studies rely mostly on active/passive sampling programs that neglect exposure resulting from highly individualized daily routines (Liu et al., 2022; Mamontov et al., 2022). Consequently, there is an urgent need to integrate the personal exposure profiles collected from silicone wristbands with the results of risk assessments.

The North China Plain is a major grain producing area in China, accounting for only 3% of the total national land area but contributing to one third of the total national pesticide input (NBS, 2020). The intense pesticide use in this region has led to soil contamination and potential risks to ecological endpoints (Mu et al., 2022b; Mu et al., 2023). Pesticides were frequently misused in the study region with excessive amounts of fungicides application observed (Mu et al., 2022a). Meanwhile, multiple residues were detected in surface soils, moreover, nearly half of monitored sites showed high ecological risks to soil biota (Mu et al., 2023). To date, little is known about the exposure risk of pesticides to rural residents in this region. To address this, we performed a probabilistic exposure risk assessment of pesticides for the local populations in this region, integrating major exposure routes using a Mento-Carlo simulation. The objectives of this study were: 1) to investigate the occurrence of particulate and gas phase pesticides in the indoor-outdoor nexus via dust and wristbands measurements; 2) to obtain the individualized pesticide exposure profiles using wristbands; and 3) to assess the probabilistic health risks of pesticides for the local population by integrating the major exposure routes to particulate and gaseous pesticides in the indoor-outdoor nexus. This study expanded on former exposure assessments by using direct measurements collected from personal wristbands and comparing these measurements to the equivalent air concentrations and inhalation risks, thereby determining comprehensive pesticide exposure risk for local residents.

5.2 Materials and methods

5.2.1 Study design

Prior to sampling, farmer interviews were carried out in Quzhou, a typical agricultural county in the North China Plain (NCP), to investigate the usage patterns of pesticides in different farming systems. During the interviews, farmers who plant apples and grapes are prone to using more pesticides, as well as reporting more frequently misuse behaviours (Hongyu Mu, Kai Wang, et al., 2022). To explore more details of exposure risks of pesticide, those groups of farmers were selected for the wristband experiment. To make sure the selected farmers could be representative, some extra criteria were concerned: 1) participants should be willing to attend the wristband experiment and follow the sampling protocols, 2) participants must be scattered in villages nearby the main streets, and 3) participants should be registered in the villages and they are continuously living in the village, thereby having a regular daily routine within or around the villages. In total, 35 participants were recruited, including 21 farmers and 14 bystanders. Forty-six (46%) of participants were female, aged from 29 to 66. Among them, thirty-eight (38%) of recruited farmers were reported to have applied pesticides more than twice during the monitoring period. When preparing and using pesticides, farmers were told to use self-protective measures, such as gloves and water-proof cloths, to avoid direct contact with pesticide drifts. Based on the interview results, 24 commonly used pesticides were selected and analyzed in this study. Usage patterns of selected pesticides were listed in the supplementary materials **(Table S5.1)**. The names, chemical groups, molecular mass, and Chemical Abstracts Service (CAS) numbers are summarized in **Table S5.2**.

Along with the wristbands participants were given to wear around their wrists, additional wristbands were placed in their homes (hanging in the living room) and in outdoor environments close to fields (only for farmers) to monitor the background pesticide exposure levels in domestic and field environments, respectively. Given that pesticides can keep low diffusion rates in silicone wristbands in summer for a month with promising recovery rates (Anderson et al., 2017), the monitoring period for wristbands was set at 4 weeks to monitor personal exposure during the peak summer season for agricultural activities. Participants were informed that they could take off their wristbands during showers and when sleeping, and they were assured that they could quit the experiment at any time. During the first and last days of the experiment, dust samples were collected from the floors with a vacuum cleaner (T10 mix, Puppy Electronic Appliances Internet Technology Beijing Co., Ltd.) in indoor (living room) and outdoor (main street or pavement surface near houses) locations for each participant. After sampling, dust and any other garbage collected by the vacuum were transferred to a prepared self-sealing bag and transported to the lab. In the lab, each collected sample was first passed through a 0.15 mm sieve to separate surface dust from larger particles. All wristbands and sieved dust samples were placed in self-sealing bags and stored at -20℃ until analysis could be completed.

5.2.2 Pesticide determination

5.2.2.1 Pre-treatment, chemicals, and solvents

Collected dust samples were passed through a 0.15 mm sieve to remove other materials such as hair, stones and tiny pieces of domestic garbage and then placed into self-sealing bags stored at -20℃. Standard adult size wristbands (20 cm L × 1.2 cm W × 0.2 cm T) were purchased online (https://www.1688.com/). Before use, a precleaning procedure was conducted to eliminate possible interference from unexpected chemicals (O'Connell et al., 2014). The wristbands were cleaned in a shaker followed by a two-step procedure: 1) 30 min extraction using ethyl acetate and a hexane solvent (1:1, v: v) and 2) 30 min extraction using ethyl acetate and a methanol solvent (1:1, v: v). After the extraction, wristbands were dried under a nitrogen stream and placed in the freezer (4℃).

The analytical reference standards of analyzed pesticides were purchased from Alta Scientific Co., Ltd. For the determination of dust samples, the standard stock solution and mixed standard solution were prepared in acetonitrile at concentrations of 1000 and 100 mg L^{-1}. The calibration curve for instrumental analysis was prepared by diluting the mixed standard solution to reach the concentrations of 0.01, 0.05, 0.1, 0.5, 1 and 2 mg L^{-1} in acetonitrile. For the determination of wristband samples, the mixed standard solution was prepared at a concentration of 0.1 mg L^{-1}. A standard ^{13}C-caffeine solution was used as an internal standard. The calibration curve for instrumental analysis was prepared by diluting the mixed standard solution to reach the concentrations of 1, 5, 20, 50 and 100 μg mL^{-1} in acetonitrile. All solutions were stored in the refrigerator at -20℃ until use.

5.2.2.2 Pesticide extraction and instrumental analysis

The analytical method for dust samples was modified and based on the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method (Anastassiades, 2003). Briefly, dust samples, along with water, acetonitrile and NaCl, were vortexed and centrifuged for pesticide extraction. $MgSO_4$ and C_{18} were then added into centrifuge tubes with extracts to remove interfering substances. The upper layer supernatants were filtered and transferred into glass vials.

Wristband samples were spiked with ethyl acetate and ^{13}C caffeine. The samples were then mixed and transferred to evaporation flasks and evaporated until dryness using dimethyl sulfoxide (DMSO) as a keeper. The remaining solvents were reconstituted and filtered into LC vials by adding acetonitrile and ultrapure water. All samples were stored at –20℃ while awaiting instrumental analysis. Full details of the pretreatment of dust and wristband samples are provided in **Text S5.1** in the supplementary materials.

Instrumental measurements were carried out using liquid chromatography coupled with LC-MS/MS with a triple quadrupole mass spectrometer (Shimadzu LCMS-8045, Shimadzu Corporation, Tokyo, Japan) and a Shimadzu LC system coupled to a triple quadrupole mass spectrometer QTRAP (6500+, Sciex, Canada) for dust samples and wristbands, respectively. Full details of instrumental analysis procedures for dust and wristband samples are provided in **Text S5.2**, **Table S5.3** and **Table S5.4** in the supplementary materials.

5.2.2.3 Quality assurance and quality control

To avoid possible cross contamination during the dust sampling process, the electric motor of the vacuum cleaner was removed, and the remaining parts of the vacuum cleaner were thoroughly washed by hand with soap and water between each sampling interval. Prior to the lab analysis, untreated bare soil samples were collected in Quzhou and passed through a 0.15 mm sieve to serve as 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.

For wristband samples, additional worn wristbands were precleaned and used as blank samples. The blanks were then fortified with the mixed standard solution at concentrations of 0, 0.2, 0.5, 1, 5 and 10 μg L^{-1} for recovery assessment and method validation. The calibration curve solutions were injected after 10 successive sample injections to recalibrate the machine. Recovery efficiencies of analyzed pesticides were acquired within a range of 70% to 110%, except for thiophanate-methyl which was excluded from the measurement list. The calibration curves obtained good linearity with the correlation coefficients over 0.99.

The calibration curve solutions were injected at the beginning of the measurements and again after each 10 successive sample injections. Deviations of the analytical results of each calibration curve solution sample were within 30%. Recovery efficiencies of analyzed pesticides for fortified blank samples and calibration curve solutions were both acquired within a range of 70 % to 110 %. The calibration curves obtained good linearity with the correlation coefficients over 0.99.

5.2.3 Pesticide risk assessment

In this study, the chronic lifetime exposure risk of pesticides for individuals was assessed based on the health risk assessment method. In the assessment, Hazard Quotients (HQs) were calculated for individual exposure routes and further summed up as a Hazard Index (Feng et al.). For a HI > 1, the daily exposure could result in chronic health risks, otherwise the risk can be considered negligible. The assessment was conducted mainly based on the measurements taken from dust samples and personal wristbands. Specifically, measurements of indoor and outdoor dust samples were run through the model to assess the exposure risk from dust / particle ingestion and dermal contact routes in the indoor and outdoor environments. Wristband results mainly represented pesticide inhalation risks of participants as they carried out their daily routines. It should be noted that pesticide concentrations in the wristbands represent only the pesticides taken up by the silicone within a fixed period. In this case, concentrations collected from personal wristbands were converted into air concentrations for the sake of the exposure assessment.

5.2.3.1 Equivalent air concentrations

The amount of pesticides absorbed by the wristbands increased over time before reaching a constant exposure level, following a dose-response relationship (Bartkow et al., 2005). The uptake process of chemicals by passive samplers, such as wristbands, can normally be divided into three phases, including kinetic (linear), intermediate (curvilinear) and equilibrium (Feng et al., 2022). To calculate equivalent concentrations for certain passive samplers under equilibrium conditions, well-established quantitative models are available which are based on Fick's first law of diffusion (O'Connell et al., 2021). This model adapts to the uptake of chemicals from any phase and follows rate constant-based equations **(Equation 5.1** and **5.2)**.

$$C_a = \frac{N_{compound}}{V_s \times K_{sa} \times (1 - e^{(-k_e \times t)})} \tag{5.1}$$

or

$$C_a = \frac{N_{compound}}{V_s \times K_{sa} \times \left(1 - e^{-\frac{R_S \times t}{V_S \times K_{sa}}}\right)} \quad (5.2)$$

where C_a represents the equivalent air concentration of pesticides converted from wristband concentrations. $N_{compound}$ and Vs represent the amount (mass) of pesticides in the sampler and the volume of the sampler, respectively. The wristbands used in this study were the regular adult sized version, which was approximately 5.30 g and 0.00445 L of silicone (O'Connell et al., 2021). R_s and k_e are rate-based parameters that stand for the sampling and dissipation rate, respectively. K_{sa} is a partitioning coefficient demonstrating the ratios between concentrations in the passive sampler and ambient environment matrix at equilibrium during the deployment stage.

Boiling point (BP)-based models, including the BP-TEST (toxicity estimation software tool, **Equation 5.3 and 5.4**) and the BP-OPERA (open structure-activity/property relationship app, **Equation 5.4 and 5.5**) models were considered as the best performance model and secondary model, respectively. The predicted BPs and other calculated model parameters are listed in **Table S5.5**.

$$logk_e = -0.012 \times BP(°\mathrm{C} - TEST) + 2.04 \quad (5.3)$$
$$logK_{sa} = 0.02BP(°\mathrm{C} - TEST) + 0.517 \quad (5.4)$$
$$logk_e = -0.009 \times BP(°\mathrm{C} - OPERA) + 1.55 \quad (5.5)$$
$$logK_{sa} = 0.019 \times (BP°\mathrm{C} - OPERA) + 0.9 \quad (5.6)$$

5.2.3.2 Probabilistic health risk assessment

The chronic exposure risks of pesticides are assessed based on the health risk assessment model developed by the US Environmental Protection Agency (USESA). This model requires inputs of the environmental concentrations of chemicals and exposure parameters, which are normally set as the mean or maximum values of corresponding parameters to give deterministic assessment results. The deterministic assessments from former studies present general-case or worst-case scenarios for the exposure risk, potentially causing elevated uncertainties and leading to under- or overestimates of the health risk. Thus, this study takes the uncertainties of each input variable into account and provides probabilistic risk assessments of the local populations by using a Mente-Carlo simulation.

The processing procedure of the Mento-Carlo simulation mainly includes: 1) setting random variables and inputting the corresponding distribution; 2) setting simulation variables; and 3) running the model for 10000 iterations at a 95% confidence level (Yuan et al., 2023). The probabilistic health risks were calculated for farmers and bystanders separately. To present the best estimates of the underlying risks, pesticide exposure was separated into 5 different sections for each group of the population: daily inhalation (personal wristband data), indoor ingestion, indoor dermal exposure, outdoor ingestion, and outdoor dermal exposure. Since individuals spend over 80% of their daily lives in an indoor environment, a time-weighted exposure frequency was set to determine the best estimates of the exposure risks under simulations of realistic exposure scenarios. Lists of random variables and their distributions, including pesticide concentrations and exposure parameters, are summarized in the supplementary information from **Table S5.6** to **Table S5.8**.

5.2.4 Statistical analysis

Descriptive statistics for all samples were conducted using SPSS (version 26; IBM, USA). The Kolmogorov-Smirnov test was used for the normality test. The one-way ANOVA and Mann-Whitney U tests were used to compare means between the pesticide concentrations of samples from different subgroups. Origin 2021 was used to draw the box plots and the lollipop chart. The heatmap of personal pesticide exposure profiles was created using R programming language (lattice package). For the multivariant analysis, partial least squares-discriminant analysis (PLS-DA) was conducted using MetaboAnalyst (NSERC, 2022) to visualize and compare pesticide exposure between farmers and bystanders. Raw data was transformed to mean centered and lognormal prior to the analysis. The ellipses in the biplot represent the 95% confidence level of the two groups of participants. Variable importance in projection (VIP) scores, quantifying the impacts of each of the predictor variables to the response variable, were calculated to determine the contributions of the components to the distinctive exposure characteristics of farmers and bystanders. The Mento-Carlo simulation was performed to assess the probabilistic health risks of pesticides for the local populations using the Oracle Crystal Ball version 11.

5.3 Results and discussion

In this study, we monitored pesticide concentrations in dust samples and stationary wristbands to determine the personal pesticide exposure of rural residents in the indoor-outdoor nexus. Over the course of 4-weeks, we collected 136 dust samples and retrieved 77% of the distributed wristbands (n=70) from farmers and bystanders as well as some that were hanging in indoor and outdoor locations.

5.3.1 Occurrence of pesticides in particulate and gas phases in the indoor-outdoor nexus

5.3.1.1 Levels of pesticides in dust

Multiple pesticide residues were found in all dust samples **(Fig. S5.1A)** with 3 to 24 residues detected in each sample. Notably, over 40% of samples contained more than 15 pesticide residues. Measured concentrations were widely distributed in 4 orders of magnitude in dust with the highest concentrations reaching 50345 ng g^{-1} (for atrazine from an indoor location). Carbendazim, thiamethoxam and acetamiprid were the most frequently detected pesticides and measured in more than 90% of the samples. The presence of pesticides in dust differed largely among the different locations. More residues and higher concentrations of residues were found in indoor dust samples **(Fig. 5.1A, B)**. There were on average 17 and 13 pesticide residues detected in indoor and outdoor dust samples, respectively. The accumulation levels of pesticides in indoor dust were 1.3 to 25 times higher than those of outdoor dust, except for atrazine, chlorantraniliprole and lufenuron **(Table 5.1)**. Pesticides were more frequently detected and found in higher concentrations in the dust samples from locations surrounding farmers' residences **(Fig. 5.1C, D)**. The geomeans of pesticide concentrations were between 1.02 to 20 times higher in the samples from farmers than those from bystanders, except for the concentrations of atrazine, carbendazim, tebuconazole and prochloraz.

This study revealed the distribution pattern of pesticides in indoor and outdoor dust collected from farmers and bystanders. Pesticides in residential dust mainly originated from the wind facilitated transport of pesticide contaminated soil particles from adjacent fields, and the take-home pathway (Dereumeaux et al., 2020). In particular, the take-home pathway by farmers has been found to be a nonnegligible contributor to their non-occupational exposure via transferring pesticides from contaminated clothes, shoes, and skin to the residential environments (López et al., 2019). Despite not handling pesticides on their own, bystanders have more complex daily routine and higher possibilities for non-occupational pesticide exposures compared to farmers. Thus, pesticides in residential dust collected from bystanders may also originate from the take-home pathway, especially for those who incidentally had contact with pesticides in their daily routine. In this study, higher concentrations of carbendazim, atrazine, and prochloraz were found in dust samples collected at locations around bystanders **(Fig. 5.1C)**. These pesticides were commonly used in the greenbelt along the road near the village, which might be exposed to bystanders and further transferred into residential area through the take-home pathway. The unexpected distribution pattern of certain pesticides between farmers and bystanders revealed that all residents living in the intensive farming regions are potentially suffering from pesticide exposure.

Despite the variances in the sampling locations and seasons, these results were consistent with those of previous studies performed in other regions but had much higher outliers (S. Mukerjee, 1997; Simaremare et al., 2021; Velázquez-Gómez et al., 2019) **(Table S5.9)**. As one of the most detected pesticides, chlorpyrifos was measured at much higher concentrations in the indoor dust with a maximum value at 15463 ng g^{-1}, which is 1.6 and 141 times higher than studies carried out in Taiwan province and California, USA (Mahler, 2009; Hung et al., 2018), respectively.

5.3.1.2 Levels of pesticides in stationary wristbands

Pesticides were detected in all stationary wristbands with the number of residues ranging from 2 to 19. Up to 65% and 33% of samples were determined to contain more than 5 and 10 pesticide residues, respectively **(Fig. S5.1B)**. Atrazine and chlorpyrifos were the most frequently detected pesticides showing up in more than 90% of samples. The largest concentration of a pesticide found in a stationary wristband sample was that of tebuconazole which was detected at 6475 ng g^{-1} from an outdoor location. As compared to dust samples, wristbands from outdoor locations exhibited significantly higher pesticide levels **(Fig. 5.1A, B)**. Higher concentrations of all pesticides were detected in the stationary wristbands from outdoor locations and the geomeans for individual pesticides were 1.04 to 14.5 times higher than those from indoor wristbands **(Table 5.1** and **Fig. 5.1D)**.

This study found much higher pesticide levels in stationary wristbands located in outdoor environments, which could be attributed to the successive outdoor pesticide applications occurring during the monitoring period. Similar trends were observed by Aerts where more pesticides were detected in the wristbands from outdoor locations rather than indoor locations (Aerts et al., 2017). There were no significant differences in the pesticide concentrations between stationary wristbands collected from farmers and bystanders through Mann-Whitney U test **(Figure. 5.1D)**, indicating that bystanders may have suffered the same level of inhalation risk from pesticides inside their homes, despite the fact they had not had any direct exposure to pesticide use for a long period.

Table 5.1 Measured concentrations (ng g^{-1}) of pesticides in dust and wristbands in the indoor and outdoor environments.

Pesticides	Indoor dust		Outdoor dust		Indoor wristbands		Outdoor wristbands	
	Geomean (Detection rate, %)	Range	Geomean (Detection rate, %)	Range	Geomean (Detection rate, %)	Range	Geomean (Detection rate, %)	Range
Abamectin	227.700 (71.0)	ND-2152.30	42.7000 (26.9)	ND-215.000	5.00000 (96.3)	ND-58.4000	5.20000 (30.8)	ND-17.2000
Acetamiprid	1570.80 (97.1)	ND-293122	113.500 (88.1)	ND-9854.20	3.20000 (3.7)	ND-3.20000	16.1000 (92.3)	ND-1601.00
Atrazine	126.000 (75.4)	ND-50345.6	171.400 (53.7)	ND-26122.5	3.20000 (33.3)	ND-27.9000	15.2000 (100)	ND-92.5000
Carbendazim	1579.90 (98.6)	ND-61928.0	469.300 (100)	17,0 - 22305.3	10.0000 (18.5)	ND-27.3000	29.4000 (76.9)	ND-231.100
Carbofuran	80.4000 (63.8)	ND-1127.30	52.3000 (74.6)	ND-182.900	2.80000 (48.1)	ND-20.5000	8.00000 (100)	ND-217.800
Carbofuran 3Hydroxy	40.1000 (17.4)	ND-426.400	14.3000 (3.0)	ND-17.0000	NA	NA	2.00000 (15.4)	ND-3.40000
Chlorantraniliprole	76.7000 (56.5)	ND-566,800	180.100 (10.4)	ND-1299.00	NA	NA	3.90000 (15.4)	ND-4.30000
Chlorobenzuron	856.900 (94.2)	ND-44850,6	260.900 (83.6)	ND-12268.9	8.60000 (40.7)	ND-202,300	31.0000 (100)	ND-1701.40
Chlorpyrifos	400.100 (97.1)	ND-15463,9	96.8000 (89.6)	ND-807.700	7.10000 (96.3)	ND-246,2	41.2000 (100)	ND-989.800
Clothianidin	94.7000 (91.3)	ND-2707,40	30.0000 (16.4)	ND-273.200	1.70000 (3.7)	ND-1,7	1.30000 (7.7)	ND-1,30000
Difenoconazole	2099.50 (24.6)	ND-25204,2	102.300 (91.0)	ND-26500.0	3.10000 (22.2)	ND-21,6	10.7000 (92.3)	ND-404.400

Note: ND, not detected; NA, not applicable.

Table 5.1 (Continued).

Pesticides	Indoor dust Geomean (Detection rate, %)	Range	Outdoor dust Geomean (Detection rate, %)	Range	Indoor wristbands Geomean (Detection rate, %)	Range	Outdoor wristbands Geomean (Detection rate, %)	Range
Dimethomorph	453.400 (85.5)	ND-29336,0	71.2000 (88.1)	ND-2900.00	6.70000 (29.6)	ND-29,3	97.3000 (76.9)	ND-1156.00
Fipronil	97.8000 (33.3)	ND-2020,30	39.1000 (4.5)	ND-200.000	2.90000 (14.8)	ND-12,2	10.6000 (69.2)	ND-175.200
Fipronil sulfone	72.3000 (44.9)	ND-824,400	34.6000 (10.4)	ND-63.0000	2.30000 (3.7)	ND-2,30000	4.50000 (69.2)	ND-69.2000
Imidacloprid	2044.00 (98.6)	ND-71390,3	101.100 (91.0)	ND-8255.40	2.60000 (33.3)	ND-11,9000	9.50000 (84.6)	ND-345.700
Lufenuron	43.2000 (75.4)	ND-638.600	157.100 (1.5)	ND-157.100	6.20000 (3.7)	ND-6.20000	5.20000 (7.7)	ND-5.20000
Nicosulfuron	75.2000 (92.8)	ND-12401.3	23.2000 (61.3)	ND-274.300	NA	NA	NA	NA
Pendimethalin	80.9000 (73.9)	ND-2134.70	50.5000 (89.6)	ND-159.200	2.00000 (48.1)	ND-5.90000	9.60000 (100)	ND-533.200
Prochloraz	182.200 (60.9)	ND-17268.2	74.2000 (35.8)	ND-6800.00	5.00000 (3.7)	ND-5.00000	3.50000 (7.7)	ND-3.50000
Propamocarb	185.000 (10.1)	ND-4372.80	159.900 (22.4)	ND-6527.00	1.20000 (3.7)	ND-1.20000	2.20000 (7.7)	ND-2.20000
Pymetrozine	153.500 (53.6)	ND-46502.7	119.300 (10.4)	ND-4474.80	NA	NA	NA	NA
Pyridaben	152.700 (42.0)	ND-30794.0	118.500 (22.4)	ND-598.600	NA	NA	3.70000 (15.4)	ND-7.70000
Tebuconazole	1689.90 (47.8)	ND-20513.5	142.400 (67.2)	ND-9124.80	7.70000 (44.4)	ND-123.300	63.8000 (100)	ND-6475.00
Thiamethoxam	859.500 (91.3)	ND-859943	87.8000 (94.0)	ND-6268.10	5.80000 (18.5)	ND-18.7000	3.40000 (38.5)	ND-6.10000

5.3.1.3 Comparisons between pesticides detected in dust and wristbands

More residues and higher concentrations of residues were measured in dust samples as compared to stationary wristbands from both indoor and outdoor environments **(Fig. 5.1A, B)**. The mean concentrations and number of residues from dust samples (2325 μg kg^{-1} and 15 residues) were 12.5 and 1.5 times higher than those from wristbands, respectively. Pesticides were found in all samples. Over 90% of dust samples contained more than 10 residues, while only 37.5% of wristband samples had such levels. For individual pesticides, measured concentrations were found to differ across locations and mediums **(Fig. S5.2)**. Specifically, 7 out of the 24 pesticides found in dust, such as abamectin, imidacloprid and chlorpyrifos, varied significantly across the indoor-outdoor nexus and were found in significantly higher concentrations in indoor locations with at least 2-fold differences. For pesticides found in wristbands, higher concentrations of atrazine, acetamiprid, tebuconazole, chlorpyrifos and pendimethalin were found in outdoor stationary wristbands. The varied pesticide distribution patterns among collected samples indicates that particulate pesticides tended to accumulate in indoor environments, whereas gaseous pesticides accumulated more in outdoor spaces. It should be noted that pesticides commonly used or reported being used at excessive dosage in this area, were all found to be heavily accumulated in both dust and stationary wristband samples. Imidacloprid and acetamiprid, the most frequently used pesticides with usage frequencies exceeding 40%, were shown up in more than 90% and 50% of dust and stationary wristband samples, respectively. Farmers grow vegetables and apple orchards applied substantial amounts of dimethomorph and difenoconazole to prevent plant diseases, leading to much higher concentrations at monitored sites.

The cumulative patterns of pesticides found in the different locations varied depending on what phase the pesticide was detected in **(Fig. S5.3)**. Despite low usage frequency **(Fig. 5.2A)**, chlorpyrifos was the most abundant pesticide found in both dust and wristband samples, with detection frequencies exceeding 90% in the two mediums. This was followed by atrazine. Chlorpyrifos, targeting primarily the central and peripheral nervous systems, is recognized as a class II moderately hazardous pesticide by the World Health Organization (WHO, 2020). Along with having negative effects on the nervous system, exposure to chlorpyrifos has been associated with acute poisoning effects such as eye irritation, dermatological defects, endocrine disruption and cardiovascular disease (David L Eaton, 2008; Ubaid ur Rahman et al., 2021). Similarly, atrazine was found to cause toxic effects on the nervous system by inducing cerebellar toxicity (Chevrier et al., 2011). In addition, particular attention should be given to prenatal exposure to atrazine, which was found to cause adverse birth outcomes (Xia et al., 2017). The widespread existence of these compounds raises concerns for the environmental exposure risks from pesticides in our surroundings and highlights the need for a shift in pesticide use patterns in the major farming systems in the NCP.

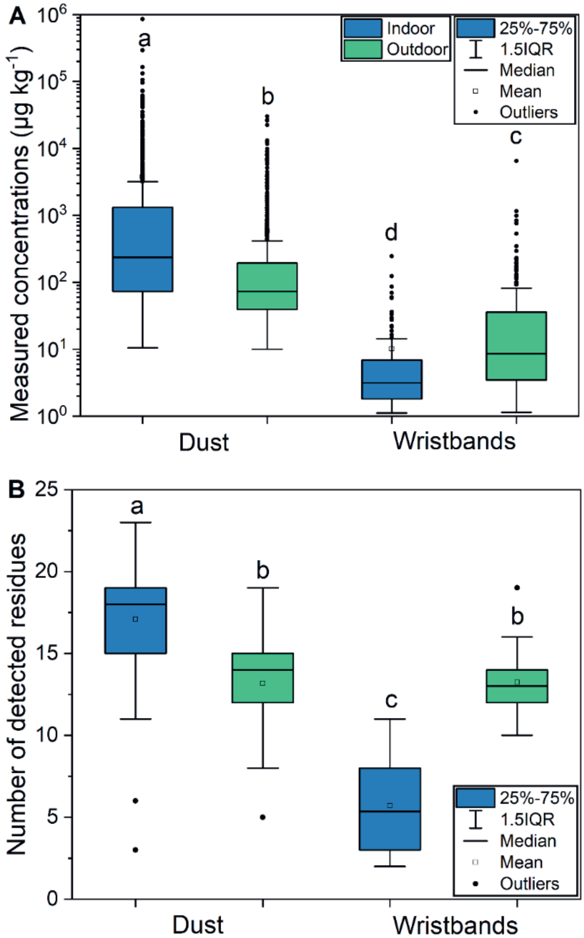

Fig. 5.1 Pesticide levels found in dust and wristbands in the indoor and outdoor nexus: A: pesticide concentrations in dust and wristbands collected from indoor and outdoor locations; B: number of detected residues in dust and wristbands from different locations; C: lollipop chart of the geomeans of pesticide concentrations in indoor and outdoor dust; D: lollipop chart of the geomeans of pesticide concentrations from indoor and outdoor stationary wristbands. Figures in red font in A and B represent the overall means and medians of dust and wristband samples. IQR, interquartile range.

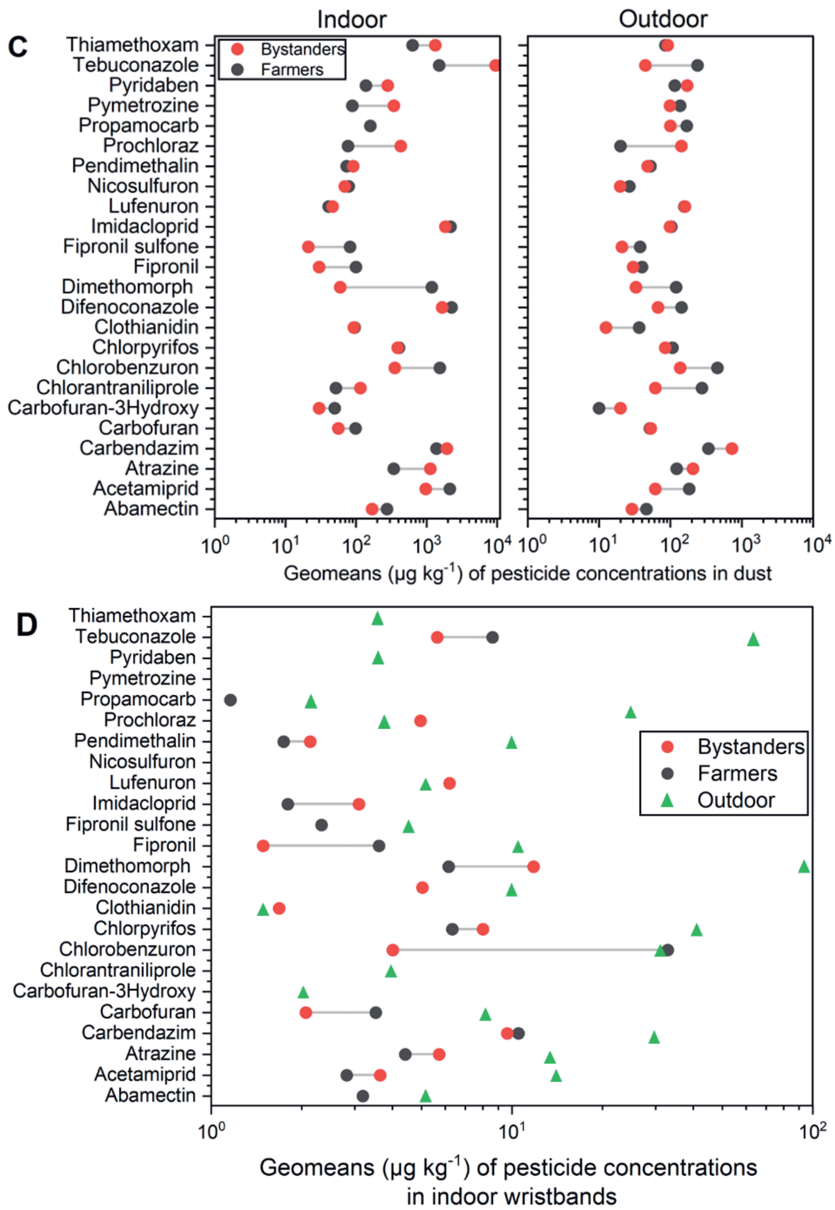

Fig. 5.1 (Continued).

5.3.2 Personal pesticide exposure profiles

The personal pesticide exposure from daily routines was monitored using silicone wristbands for 4 weeks during the peak summer season of pesticide applications.

The number of detected residues in wristbands worn by farmers (mean value of 13) was higher than that of bystanders (mean value of 10), yet the difference was not significant **(Fig. 5.2A)**. More than 10 residues were detected in 88% and 37% of wristbands worn by farmers and bystanders, respectively. Significantly higher concentrations of pesticides were measured in wristbands worn by farmers as compared to those from bystanders **(Fig. 5.2B, C)**. The maximum concentration of a pesticide found in personal wristbands was determined for difenoconazole at over 2000 ng g^{-1}, followed by dimethomorph and tebuconazole. The mean values of measured concentrations in wristbands worn by farmers were 1 to 17 times higher than those of bystanders, except for thiamethoxam and prochloraz **(Table 5.2)**. It should be noted that both farmers and bystanders tended to be exposed to pesticides that were frequently used in the region at higher concentrations **(Fig. 5.2C)**.

Table 5.2 Measured pesticide concentrations (ng g^{-1}) in wristbands worn by farmers and bystanders.

Pesticides	Overall			Farmers			Bystanders		
	Detection rate (%)	Geomeans	Range	Detection rate (%)	Geomeans	Range	Detection rate (%)	Geomeans	Range
Abamectine	53.30	7.400	ND-152.1	75.00	10.80	ND-152.1	28.60	2.400	ND-4.200
Acetamiprid	83.30	15.00	ND-1592	93.80	27.00	ND-1592	71.40	6.200	ND-49.70
Atrazine	90.00	10.00	ND-168.7	93.80	8.800	ND-168.7	85.70	11.70	ND-81.00
Carbendazim	40.00	25.50	ND-132.1	56.30	28.90	ND-132.1	21.40	17.60	ND-115.7
Carbofuran	43.30	7.600	ND-298.5	43.80	13.80	ND-298.5	42.90	3.800	ND-14.30
Carbofuran 3hydroxy	13.30	3.600	ND-11.60	12.50	8.200	ND-11.60	14.30	1.600	ND-2.300
Chlorantraniliprole	26.70	4.300	ND-409.8	25.00	7.600	ND-409.8	28.60	2.500	ND-3.900
Chlorobenzuron	90.00	12.80	ND-1590	93.80	24.60	ND-1590	85.70	5.600	ND-52.00
Chlorpyrifos	93.30	7.500	ND-888.6	87.50	9.400	ND-888.6	100	6.000	1,1-107.3
Clothianidin	13.30	2.400	ND-7.700	6.300	7.700	ND-7.700	21.40	1.600	ND-2.100
Difenoconazole	73.30	22.00	ND-2048	100.0	24.80	1,1-2048	42.90	15.90	ND-184.3

Note: ND, not detected; NA, not applicable.

Table 5.2 (Continued).

Pesticides	Overall Detection rate (%)	Geomeans	Range	Farmers Detection rate (%)	Geomeans	Range	Bystanders Detection rate (%)	Geomeans	Range
Dimethomorph	66.70	30.70	ND-1936	81.30	132.4	ND-1936	50.00	2.000	ND-4.200
Fipronil	30.00	8.300	ND-176.4	56.30	8.300	ND-176.4	0.000	NA	ND-NA
Fipronil sulfone	36.70	5.700	ND-126.6	68.80	5.700	ND-126.6	0.000	NA	NA
Imidacloprid	83.30	9.700	ND-185.4	93.80	13.20	ND-185.4	71.40	6.100	ND-44.20
Lufenuron	30.00	8.700	ND-554.4	18.80	38.70	ND-554.4	42.90	4.200	ND-126.8
Nicosulfuron	3.300	6.500	ND-6.500	6.300	6.500	ND-6.5	0.000	NA	NA
Pendimethalin	70.00	3.600	ND-79.90	81.30	3.500	ND-79.9	57.10	3.800	ND-29.30
Prochloraz	16.70	3.200	ND-37.90	12.50	1.300	ND-1.5	21.40	5.700	ND-37.90
Propamocarb	0.000	NA	NA	0.000	NA	NA	0.000	NA	NA
Pymetrozine	0.000	NA	NA	0.000	NA	NA	0.000	NA	NA
Pyridaben	0.000	NA	NA	0.000	NA	NA	0.000	NA	NA
Tebuconazole	90.00	49.50	ND-1707	100.0	151.6	1.4-1707.0	78.60	9.700	ND-515.8
Thiamethoxam	70.00	6.400	ND-511.6	62.50	3.700	ND-72.6	78.60	10.30	ND-511.6

PLS-DA was used to study the differences between the personal pesticide exposure profiles of farmers and bystanders. The biplot allows us to see a clear distinction between the personal exposure profiles of farmers and bystanders **(Fig. 5.2D)**. The slightly overlapping ellipses show different exposure patterns for most participants in the two groups. It is worth noting that the overlapping area between the ellipses indicates that 43% of bystanders may have suffered the same level of pesticide exposure as farmers. VIP scores were further calculated to identify which pesticides contributed to the differences in the personal exposure patterns between farmers and bystanders **(Fig. 5.2E)**. Difenoconazole and dimethomorph were evaluated as the pesticides that contributed the most to these differences with VIP scores exceeding 1.9. One-third of the analyzed pesticides showed VIP scores exceeding 1, indicating their significant contributions to the different exposure patterns.

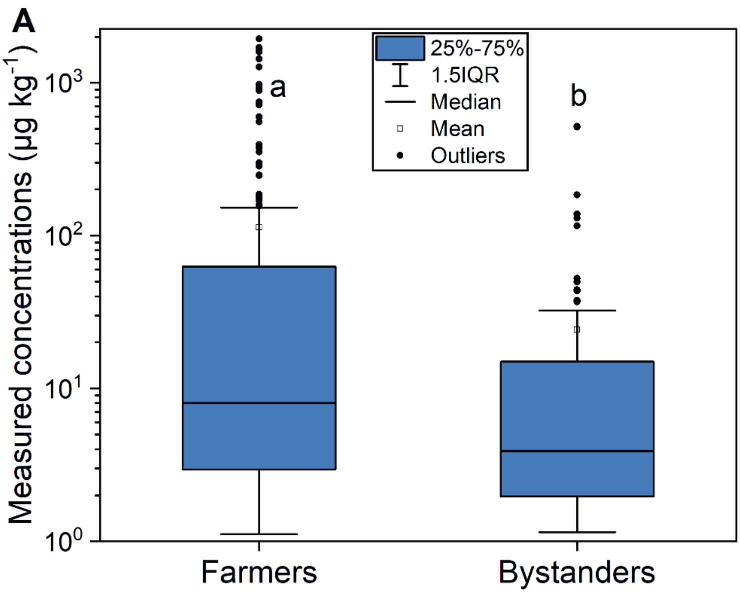

Fig. 5.2 Personal pesticide exposure profiles of farmers and bystanders: A, boxplot of measured pesticide concentrations in wristbands worn by farmers and bystanders; B, boxplot of number of detected residues in wristbands worn by farmers and bystanders; C, heatmap of measured pesticide concentrations in personal wristbands; D, biplot of the PLS-DA (partial least square discrimination analysis), ellipses represent the 95% confidence levels of two groups of participants; E, underlying exposure sources for individual pesticides based on VIP (variable importance in projection) scores. IQR, interquartile range.

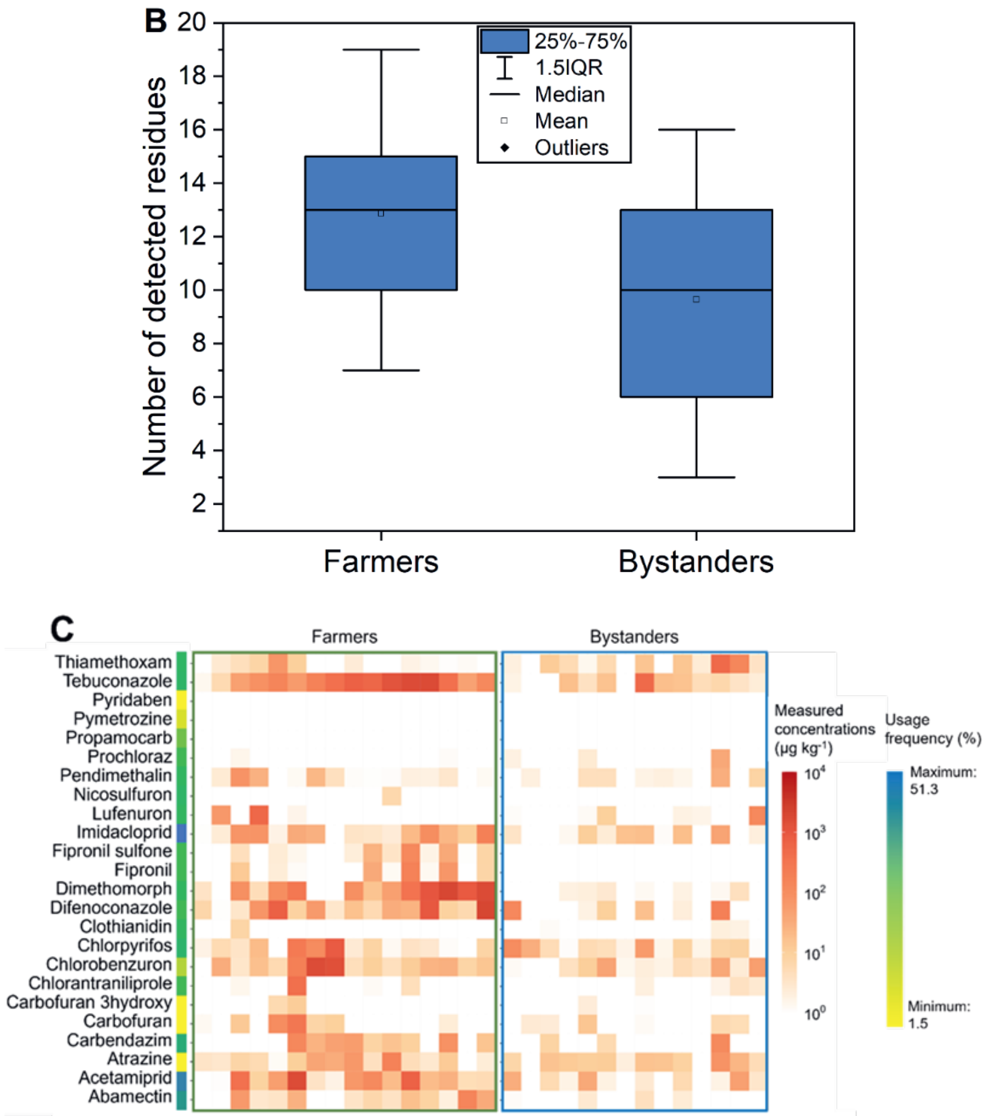

Fig. 5.2 (Continued).

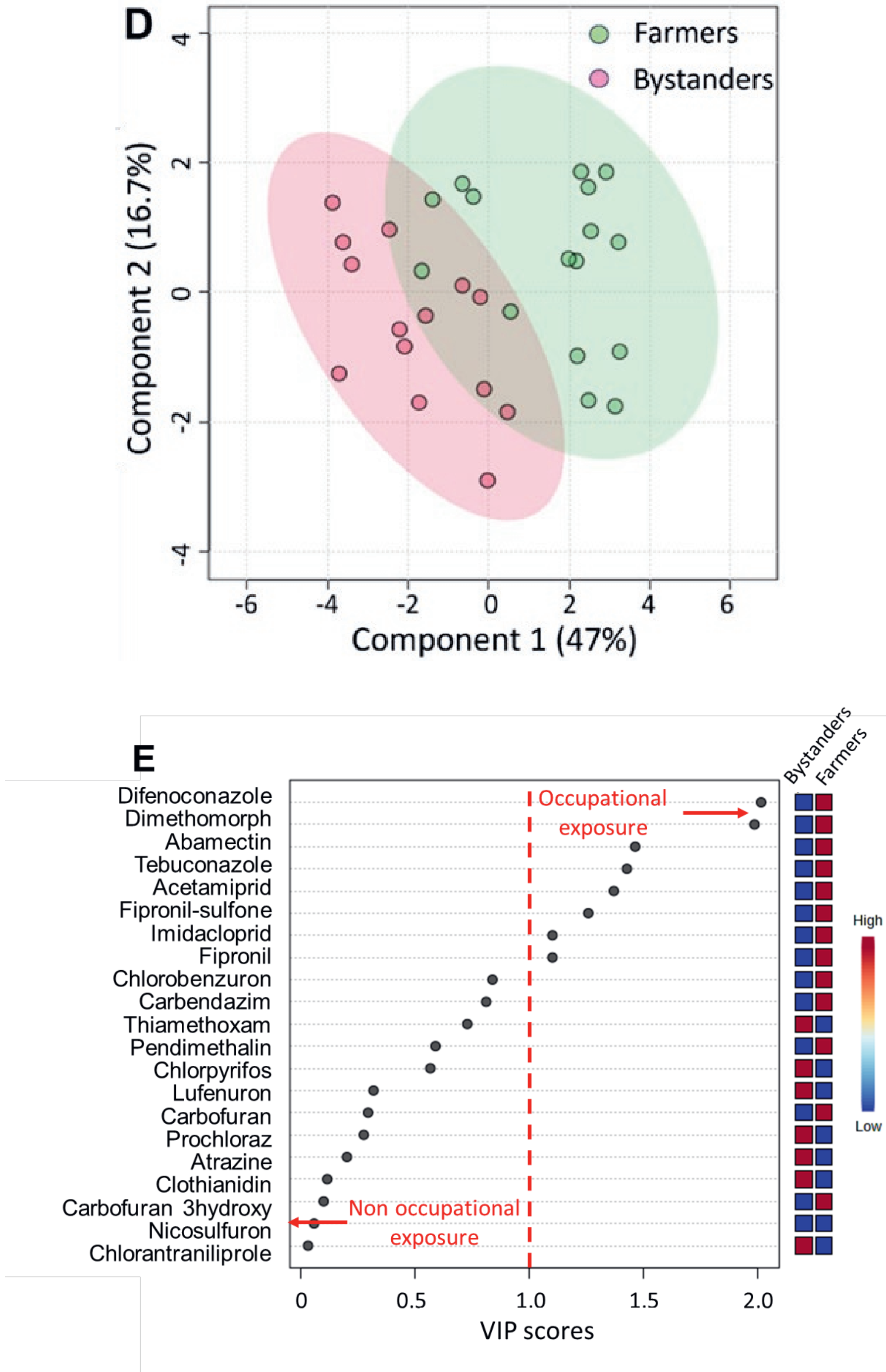

Fig. 5.2 (Continued).

The personal pesticide exposures of farmers and bystanders were characterized by a holistic silicone wristbands-dust approach. Particularly, pesticide concentrations in worn wristbands reflect the levels of airborne exposure in monitored periods. Despite protective measures taken by farmers during the pesticide preparation and application, the direct contact between pesticide drifts and wristbands cannot be totally avoided. But, practically speaking, to date, our approach could indicate the personal exposure risks of pesticide from airborne exposure. Farmers who applied pesticides more than 2 times suffered higher exposure risks than individuals came into fields less frequently with their average pesticide concentrations at 2373 and 722 ng g^{-1}, respectively. It is challenging to compare the pesticide concentrations due to lack of comparable studies with similar experiment settings, analytical list, and monitoring duration. Thus, the time-weighted concentrations were computed as ratios of the measured concentrations and the monitoring period **(Table S5.10)**. For most of the compared pesticides (Aerts et al., 2017; Arcury, Chen, Quandt, et al., 2021; Fuhrimann et al., 2022; Harley, 2019), the current study detected higher pesticide concentrations, which is probably due to the longer monitoring period. Compared with former studies, participants in this study had higher daily exposure rates of fungicides including tebuconazole and carbendazim (Aerts et al., 2017; Fuhrimann et al., 2022) and lower exposure rates of chlorpyrifos (Arcury et al., 2021).

Farmers and bystanders had diverse exposure patterns, as exhibited by the small overlapping area of the ellipses **(Fig. 5.2D)**. The VIP scores **(Fig. 5.2E)** further showed that difenoconazole and other 7 pesticides with VIP scores exceeding 1 were drivers for the differing exposure patterns seen between farmers and bystanders. For exposure sources, personal pesticide exposure of farmers consists of occupational and non-occupational exposure, while the pesticide exposure of bystanders subjected to non-occupational sources. Thus, pesticides can be categorized into two groups: 1) 8 driver pesticides of the different exposure patterns between farmers and bystanders with VIP scores exceeding 1 that mainly originated from occupational exposure, and 2) other 16 pesticides with VIP scores lower than 1 that mainly came from non-occupational exposure. Furthermore, fungicides, including tebuconazole and dimethomorph, were the predominant pesticides that farmers were exposed to, whereas thiamethoxam contributed the most to the exposure of bystanders **(Fig. S5.4)**. Given that these fungicides were used in significantly higher dosages in the study region (Mu et al., 2022a), they contributed substantially to the occupational exposure of farmers during pesticide applications. The overlap between the driver pesticides and the exposure contributors to farmers and bystanders indicates that the exposure to driver pesticides might have originated from occupational exposure, while the exposure to other pesticides could have originated from dissipated pesticide drifts from other regions. Despite the fact that bystanders did not participate in agricultural activities, the biplot of PLS-DA showed that approximately 43% of bystanders had exposure patterns that were similar to farmers which means that they suffered the same level of health risks as farmers **(Fig. 5.2D)**. In summary, for pesticide exposure, one-third can be attributed to occupational exposure and two-thirds can be attributed to diverse non-occupational sources. To some extent, the non-occupational exposure to a majority of the pesticides measured in this study poses the same health risks to farmers as to bystanders.

5.3.3 Probabilistic health risk assessment of pesticides for residents

This assessment addresses the following exposure concerns: 1) daily inhalation exposure; 2) indoor ingestion; 3) indoor dermal exposure; 4) outdoor ingestion and 5) outdoor dermal exposure. The ingestion and dermal exposures were assessed based on the occurrence of pesticides in indoor and outdoor dust. The assessment of daily inhalation exposures was carried out by translating measured concentrations from personal wristbands into the equivalent air concentrations under equilibrium conditions.

The equivalent air concentrations were calculated based on the BP-TEST and the BP-OPERA model **(Table S5.11)**. Tebuconazole was the most abundant pesticide detected in daily routines with the highest concentration exceeding 1478 ng m^{-3}, followed by acetamiprid and chlorpyrifos. Furthermore, probabilistic health risks of pesticides for local populations were assessed using the Mento-Carlo simulation. The forecasts of the hazard index (Feng et al.) were computed for farmers and bystanders separately. Despite the fact that the 95% CI of HIs for both farmers (from 2.8E-03 to 9.6E-01) and bystanders (from 3.7E-04 to 2.1E-01) were below the threshold levels, the probability of a possible chronic health risk to farmers and bystanders were approximately 7.1% and 2.6% **(Fig. S5.5)**, respectively. As a high-density region of population, the NCP accounted for 3% of the national land area with over 24% of populations living in this region. Thus, the assessment results indicate that a large number of residents in this region are potentially suffering chronic exposure risk to pesticides even though relatively low proportions of farmers and bystanders were assessed at risk.

Sensitivity analysis was performed to identify critical factors affecting the forecasts for the HI **(Fig. S6)**. For farmers, fipronil contributed the most to the sensitivity (over 60%), followed by abamectin and chlorpyrifos, which in total accounted for over 82% of the sensitivity. For bystanders, concentrations of carbofuran and tebuconazole contributed the most to the sensitivity (over 83%). The probabilistic assessment revealed concerning levels of pesticide exposure risk to both farmers and bystanders. Compared to previous monitoring studies, the current study obtained higher HI forecasts (Arani et al., 2023; Vasseghian et al., 2022) and uncovered a potential chronic health risk for a small proportion of the general population by simulating realistic exposure scenarios and integrating all possible daily exposure routes.

5.3.4 Implications and future study

So far, this is the first study to characterize personal exposure to environmental pesticides covering major exposure routes including dermal, oral and inhalation. Consequently, there is a potential of chronic risk to populations living close to agricultural fields. The combined silicone-environmental medium approach could be a promising model to obtain individualized exposure profiles and determine personal exposure rates. Based on this workflow, epidemiological studies should be carried out to examine the links between pesticide exposure and health outcomes. Additionally, this study discovered highly distinct connections between personal and environmental exposures to pesticides in both dust and wristbands **(Fig. S5.3** and **S5.4)**. This finding reveals that the composition and abundance of pesticides in environmental samples taken from fixed sampling locations and within a fixed sampling radius probably cannot correctly mirror realistic personal exposure patterns, which highlights the need for more flexible and integrated personal exposure monitoring.

5.4 Conclusion

The present study revealed the distribution of pesticides in particulate and gaseous phases in the indoor-outdoor nexus sampling residential dust and silicone wristbands. The findings indicate that the daily pesticide exposure could pose chronic health risk to rural residents considering the ubiquitous of pesticides in surroundings, especially for farmers who are working with these compounds in farming practices. For the sources of pesticide exposure, only one third of the pesticides that participants exposed to originated from occupational path, the rest were from remote dissipation. Unexpectedly, around 43% of the bystanders suffered the same level of pesticide exposure as the farmers due to the non-occupational exposure. This study explores a new approach to link personal exposure with environment quality which may help further study to understand personal exposure risk to environmental pollutants comprehensively.

Acknowledgement

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Supplementary information

Text S5.1 pretreatment procedures for dust and wristband samples.

For dust, 1.0 ± 0.01 g of a sample was weighed and placed in a centrifuge tube along with 1.0 mL water, 2.5 mL of acetonitrile and 0.5 g NaCl and then placed on a vortex for 15 min at a rotation rate of 2500 rpm. Tubes were then centrifuged for 5 min at a rotation rate of 3800 rpm. 1 mL of the remaining supernatant was transferred into 2 mL centrifuge tubes for further treatment. Sequentially, 100 mg of $MgSO_4$ and 50 mg of C_{18} were added to each centrifuge tube with the extracts. The tubes were placed on a vortex for 30 s and then centrifuged in a high-speed centrifuge at a speed of 10000 rpm. The upper layer supernatants were passed through 0.45 µm filters and stored in glass vials at −20℃ for tandem mass spectrometry (LC-MS/MS) based instrumental analysis.

For wristbands, samples were first cut into pieces and placed in 50 mL centrifuge tubes. Each tube was spiked with 20 mL ethyl acetate and 25 µL 10 µg mL^{-1} 13C caffeine (as internal standard) and further rotated in an overhead shaker. Sequentially, solvent from each tube was transferred into evaporation tubes using a plastic pipet, with 100 µL dimethyl sulfoxide (DMSO) added as keeper, for evaporation in a water bath under nitrogen flow at 40℃ until dryness (only 100 µL solvent left). The remaining solvents were reconstituted into LC vials with a 0.45 µm filter by adding 0.5 mL acetonitrile and 0.5 mL ultrapure water. During the reconstitution process, the LC vials were all vortexed after adding each solvent to the LC vials. After extraction, the LC vials were stored in the freezer at -20 ℃ until analysis.

Text S5.2 Instrumental analysis.

For dust samples, the measurements were performed by using liquid chromatography coupled with LC-MS/MS with a triple quadrupole mass spectrometer (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. The analysed compounds were separated in the mobile phase, consisting of eluent A (100% acetonitrile) and B (ultrapure water with 0.1% formic acid). The dry gas (N_2) had a temperature of 300 °C at a flow rate of 11.0 L min^{-1}. The nebulizer pressure was 15.0 psi and the electrospray voltage was + 4000 V. The precursor and corresponding product ions for the multi-reaction monitoring detection of each target compound are presented in Table S2. Gradient elution was optimized at a flow rate of 0.25 mL min^{-1} 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, and 6.5–7.5 min 20%. The injection volume was 2 μL at the first-time of analysis and 0.2 μL for samples with concentrations exceeding the maximum addition concentration (2 mg L^{-1}) of the calibration curve. The limit of qualification (LOQ) for analysed chemicals in dust samples is 10 ng g^{-1}.

For wristband samples, the instrumental analysis was carried out by using a Shimadzu LC system which is consisted of 2 LC pumps (Nexera X2 LC- 30AD), autosampler (Nexera SIL-30 AC) and column thermostat (CTO-20AC prominence column oven) coupled to a triple quadrupole mass spectrometer QTRAP (6500+, Sciex, Canada) with an electrospray ionization (ESI) in the multiple reaction monitoring (MRM) based on the two most abundant transitions operated in both positive and negative ion modes. A Acquit UPLC HSST3 RP C18 column (100 mm X 2.1 mm, 1.8 μm particle size, Water, USA) was used for separation. The flow rate and column temperature were 0.4 mL min^{-1} and 45 °C for positive (ESI+) mode and 0.3 mL min^{-1} and 35 °C negative (ESI–) mode. The cycle time for a single transition is 14 minutes. The collision gas, curtain gas, gas 1, and gas 2 were 6, 35, 55 and 55 psi, respectively. The IonSpray Voltage was 4500 V and the source temperature was 450°C. The injection volume was 5 μL. The LOQs were 5 ng g^{-1} for carbendazim, nicosulfuron and pymtrozine and 1 ng g^{-1} for rest of chemicals. Detailed MS/MS parameters for each pesticide are listed in **Table S5.3**.

Table S5.1 Pesticide usage frequencies of analyzed pesticides in the study region based on the farmer interview results.

Pesticides	Usage frequency (%)
Acetamiprid	41.1
Atrazine	1.5
Carbendazim	15.7
Chlorantraniliprole	4.6
Clothianidin	5.6
Difenoconazole	4.6
Dimethomorph	5.6
Imidacloprid	51.3
Nicosulfuron	8.1
Pendimethalin	5.6
Propamocarb	3.6
Pymetrozine	2.0
Fipronil-sulfone	4.6
Chlorobenzuron	2.5
Tebuconazole	8.1
Thiamethoxam	7.1
Pyridaben	1.5
Fipronil	4.6
Lufenuron	5.6
Carbofuran	1.5
Chlorpyrifos	10.2
Carbofuran, hydroxy	1.5
Abamectine	27.4
Prochloraz	4.6

Table S5.2 Names, group, molecular mass, and CAS numbers of analyzed pesticides.

Pesticides	Substance group	Molecular mass	CAS number
Abamectin	Avermectin nematicide	866.6	71751-41-2
Acetamiprid	Neonicotinoid insecticide	222.67	135410-20-7
Atrazine	Triazine herbicide	215.68	1912-24-9
Carbendazim	Benzimidazole fungicide	191.21	10605-21-7
Carbofuran	Carbamate insecticide	221.26	1563-66-2
Carbofuran 3hydroxy	Metabolite	237.25	16655-82-6
Chlorantraniliprole	Diamide insecticide	483.15	500008-45-7
Chlorobenzuron		309.15	57160-47-1
Chlorpyrifos	Organophosphate insecticide	350.58	2921-88-2
Clothianidin	Neonicotinoid insecticide	249.7	210880-92-5
Difenoconazole	Conazole fungicide	406.26	119446-68-3
Dimethomorph	Morpholine fungicide	387.86	110488-70-5
Fipronil	Phenylpyrazole insecticide	437.15	120068-37-3
Fipronil sulfone	Metabolite	453.14	120068-36-2
Imidacloprid	Neonicotinoid insecticide	255.66	138261-41-3
Lufenuron	benzoylurea insecticide	511.16	103055-07-8
Nicosulfuron	Sulfonylurea herbicide	410.41	111991-09-4
Pendimethalin	Dinitroaniline herbicide	281.31	40487-42-1
Prochloraz	Conazole fungicide	376.7	67747-09-5
Propamocarb	Carbamate fungicide	188.3	24579-73-5
Pymetrozine	Pyridine insecticide	217.23	123312-89-0
Pyridaben	Pyridazinone insecticide	364.93	96489-71-3
Tebuconazole	Triazole fungicide	307.82	107534-96-3
Thiamethoxam	Neonicotinoid insecticide	291.71	153719-23-4

Table S5.3 Instrumental conditions and LODs for pesticide determination of dust samples.

Compound name	Precursor ion	Product ion	Retention time (min)	Q1 Pre Bias (V)	Q3 Pre Bias (V)	CE	Mode
Carbendazim	192.05	160.05	0.593	-30	-30	-17	ESI+
Carbofuran 3Hydroxy	238.1	163.1	2.679	-27	-17	-14	ESI+
Chlorpyrifos	351.9	199.9	6.369	-27	-21	-18	ESI+
Clothianidin	250	169.1	2.009	-29	-17	-12	ESI+
Dimethomorph	388.1	301	3.725	-19	-21	-20	ESI+
Thiamethoxam	292	211.1	1.69	-30	-22	-11	ESI+
Chlorantraniliprole	484	452.9	3.743	-24	-30	-19	ESI+
Abamectin	895.5	449.3	7.336	-32	-32	-46	ESI+
Nicosulfuron	411.1	182.1	3.008	-21	-19	-20	ESI+
Lufenuron	509	326	6.088	24	15	19	ESI+
Pymetrozine	218.1	105.05	0.541	-26	-20	-20	ESI+
Carbofuran	222.1	165.1	3.364	-25	-17	-11	ESI+
Imidacloprid	256.05	175.1	2.596	-29	-17	-18	ESI+
Tebuconazole	308.1	70.1	4.457	-22	-27	-22	ESI+
Difenoconazole	406.1	251.1	5.003	-30	-27	-25	ESI+
Pendimethalin	282.2	212.05	6.543	-30	-23	-10	ESI+
Atrazine	216.1	174.05	3.722	-30	-17	-18	ESI+
Prochloraz	376	308	4.14	-19	-21	-11	ESI+
Pyridaben	365.1	309.05	7.348	-18	-22	-12	ESI+
Acetamiprid	223.1	126.05	2.668	-30	-30	-22	ESI+
Propamocarb	189.2	102.05	0.68	-30	-23	-20	ESI+
Fipronil	435	330	4.887	10	21	16	ESI–
Chlorobenzuron	307	154.15	4.695	21	29	11	ESI–

Table S5.4 Instrumental conditions for pesticide determination of wristbands.

Pesticides	Q1 mass	Q3 mass	Retention time (min)	Declustering potential (V)	Entrance potential (V)	Collision energy (V)	Cell exit potential (V)	Mode
Abamectine	890,5	305,3	9,86	86	10	31	22	ESI+
	890,5	567,3	9,86	86	10	35	12	ESI+
Acetamiprid	223,2	126,1	4,25	76	10	29	8	ESI+
	225,2	128,1	4,25	81	10	29	8	ESI+
Atrazine	216,2	174	6,13	86	10	25	12	ESI+
	218,1	176,1	6,13	71	10	25	10	ESI+
Carbendazim	192	160	3,92	106	10	27	16	ESI+
	192	132	3,92	106	10	41	18	ESI+
Carbofuran	222	123	5,41	81	10	31	20	ESI+
	222	165	5,41	81	10	19	20	ESI+
Carbofuran,	255	163	4,25	46	10	27	16	ESI+
hydroxy	255	220	4,25	46	10	17	12	ESI+
Chlorantraniliprole	484	286	6,49	71	10	15	12	ESI+
	482	284	6,49	71	10	15	12	ESI+
Chlorpyrifos	349,9	96,9	9,03	41	10	41	20	ESI+
	349,9	198	9,03	41	10	25	20	ESI+
Clothianidin	250	169,1	4,06	96	10	19	25	ESI+
	250	132,1	4,06	96	10	19	25	ESI+
Difenoconazole	406	251	8,22	136	10	39	26	ESI+
	406	337	8,22	136	10	25	26	ESI+
Dimethomorph	388	301	6,8	66	10	27	12	ESI+
	388	165	6,8	66	10	43	12	ESI+

Table S5.4 (Continued).

Pesticides	Q1 mass	Q3 mass	Retention time (min)	Declustering potential (V)	Entrance potential (V)	Collision energy (V)	Cell exit potential (V)	Mode
Fipronil	437	367,7	7,56	35	10	22	12	ESI+
	439	369,7	7,56	35	10	22	12	ESI+
Imidacloprid	256,1	175,1	4,01	41	10	25	12	ESI+
	256,1	209,1	4,01	41	10	23	14	ESI+
Lufenuron	510,9	158,2	8,87	81	10	27	25	ESI+
	510,9	141,2	8,87	81	10	67	25	ESI+
Nicosulfuron	411	182	5,22	81	10	25	12	ESI+
	411	213	5,22	81	10	23	12	ESI+
Pendimethalin	282,2	212,1	9,08	61	10	17	12	ESI+
	282,2	194,1	9,08	61	10	27	12	ESI+
Prochloraz	376	308	8,02	36	10	17	25	ESI+
	376	265,9	8,02	36	10	23	25	ESI+
Propamocarb	189,3	102	3,4	76	10	25	18	ESI+
	189,3	144	3,4	76	10	19	14	ESI+
Pymetrozine	218	105	3,37	76	10	27	12	ESI+
	218	79	3,37	76	10	47	12	ESI+
Pyridaben	365,1	309,1	9,62	46	10	19	25	ESI+
	365,1	147,2	9,62	46	10	31	25	ESI+
Tebuconazole	308,1	70	7,8	41	10	39	14	ESI+
	308,1	124,9	7,8	41	10	47	25	ESI+

Table S5.4 (Continued).

Pesticides	Q1 mass	Q3 mass	Retention time (min)	Declustering potential (V)	Entrance potential (V)	Collision energy (V)	Cell exit potential (V)	Mode
Thiamethoxam	292	211	3,74	76	10	19	18	ESI+
	292	181	3,74	76	10	33	18	ESI+
Fipronil	450.9	281.9	7.81	-11	-10	-34	-15	ESI–
sulfone	450.9	414.7	7.81	-11	-10	-20	-15	ESI–
Chlorbenzuron	307	154	7.70	-60	-10	-30	-12	ESI–
	309	154	7.70	-60	-10	-30	-12	ESI–

Table S5.5 BPs and other model input parameters for the calculation of equivalent air concentrations.

Pesticides	BP (°C)	$LogK_{sa}$	K_{sa}	$LogK_e$	K_e
Abamectine	807.05	16.67	5.E+16	-7.64	2.27E-08
Acetamiprid	339.97	7.33	2.E+07	-2.04	9.13E-03
Atrazine	312.19	6.77	6.E+06	-1.71	1.97E-02
Carbendazim	374.38	8.01	1.E+08	-2.45	3.53E-03
Carbofuran	319	6.91	8.E+06	-1.79	1.63E-02
Chlorantraniliprole	549.54	11.52	3.E+11	-4.55	2.79E-05
Chlorobenzuron	434.43	9.22	2.E+09	-3.17	6.71E-04
Chlorpyrifos	364	7.81	6.E+07	-2.33	4.70E-03
Clothianidin	432.5	9.18	2.E+09	-3.15	7.08E-04
Difenoconazole	413.93	8.81	6.E+08	-2.93	1.18E-03
Dimethomorph	464.84	9.82	7.E+09	-3.54	2.90E-04
Fipronil	481.42	10.16	1.E+10	-3.74	1.83E-04
Imidacloprid	378.84	8.10	1.E+08	-2.51	3.12E-03
Lufenuron	444.95	9.43	3.E+09	-3.30	5.02E-04
Nicosulfuron	614.84	12.82	7.E+12	-5.34	4.59E-06
Pendimethalin	363.28	7.79	6.E+07	-2.32	4.79E-03
Prochloraz	407.61	8.68	5.E+08	-2.85	1.41E-03
Propamocarb	237.24	5.27	2.E+05	-0.81	1.56E-01
Pymetrozine	429.95	9.13	1.E+09	-3.12	7.60E-04
Pyridaben	421.72	8.96	9.E+08	-3.02	9.54E-04
Tebuconazole	344.86	7.42	3.E+07	-2.10	7.97E-03
Thiamethoxam	379.61	8.12	1.E+08	-2.52	3.05E-03
Abamectine	807.05	16.67	5.E+16	-7.64	2.27E-08
Acetamiprid	339.97	7.33	2.E+07	-2.04	9.13E-03

Note: BP (°C) were derived from the TEST toxicity estimation software tool (Martin et al., 2016), OPERA open structure-activity/property relationship app (Mansouri et al., 2018) and EPA Comptox database QSARs (quantitative structure-activity relationships): https://comptox.epa.gov/dashboard/dsstoxdb/batch_search.

Table S5.6 Distributions of pesticide concentrations in indoor and dust collected from farmers' surroundings and the equivalent air concentrations from personal wristbands.

Pesticides	Indoor dust		Outdoor dust		Equivalent air concentrations	
	Distribution	Parameters	Distribution	Parameters	Distribution	Parameters
Abamectin	Min Extreme	Min (109, 191)	Triangular	T (4.08, 67.65, 5)		
Acetamiprid	Lognormal	LN (4286, 116404)	Lognormal	LN (211, 249)	Lognormal	LN (211, 249)
Atrazine	Lognormal	LN (1530, 212089043)	Lognormal	LN (1.3, 25402)	Weibull	W (0.52, 0.43, 0)
Carbendazim	Lognormal	LN (14885.75, 29175)	Lognormal	LN (3393, 17932)	Lognormal	LN (1.3, 25402)
Carbofuran	Lognormal	LN (18.35, 208)	BetaPERT	BP (-5.94, 60.93, 59.97)	Normal	N (0.11, 1.04)
Chlorantraniliprole	Weibull	W (112, 0.78, 5)	Uniform	U (2.34, 84.84)	Lognormal	LN (3393, 17932)
Chlorpyrifos	Gamma	Γ (3801, 0.3)	Student's t	t (3)		
Clothianidin	Lognormal	LN (50.24, 177)	Uniform	U (4.72, 13.4)	BetaPERT	BP (-5.9, 60.9, 60.0)
Difenoconazole	Beta	B (100, 100)	Lognormal	LN (190, 618)	Lognormal	LN (0.25, 290984)
Dimethomorph	Max Extreme	Max (33, 30.71)	Gamma	Γ (0.37, 999, -342)	Lognormal	LN (1.45, 353.29)

Table S5.6 (Continued).

Pesticides	Indoor dust		Outdoor dust		Equivalent air concentrations	
	Distribution	Parameters	Distribution	Parameters	Distribution	Parameters
Fipronil	Normal	N (11, 4)	No Fit		Lognormal	LN (0, 5998)
Imidacloprid	Lognormal	LN (319, 2820)	Lognormal	LN (346, 1747)		
Lufenuron	Max Extreme	Max (30, 30)	No Fit		Weibull	W (0.19, 0.42, 0)
Nicosulfuron	Lognormal	LN (165, 208)	Max Extreme	Max (11.06, 11.69)	Max Extreme	Max (0.66, 0.22)
Pendimethalin	Beta	B (0.34, 1.22)	Gamma	Γ (0.59, 999, -544)		
Prochloraz	Lognormal	LN (7410, 50757)	Lognormal	LN (235, 2991)	Max Extreme	Max (0.55, 0.22)
Propamocarb	No Fit		Uniform	U (1.77, 102)	Weibull	W (0.03, 0.41, 0)
Pymetrozine	Weibull	W (399, 0.34, 5)	Weibull	W (15.7, 0.3, 5)	Normal	N (-0.41, 0.46)
Pyridaben	Weibull	W (140, 0.31, 5)	Uniform	U (-0.77, 178)	Lognormal	LN (0,43451)
Tebuconazole	Min Extreme	Min (7231, 3518)	Exponential	Exp (0.03)	Exponential	Exp (2.17)
Thiamethoxam	Lognormal	LN (1606, 278860)	Lognormal	LN (122, 372)		

Table S5.7 Distributions of pesticide concentrations in indoor and dust collected from bystanders' surroundings and the equivalent air concentrations from personal wristbands.

Pesticides	Indoor dust		Outdoor dust		Equivalent air concentrations	
	Distribution	Parameters	Distribution	Parameters	Distribution	Parameters
Abamectin	Min Extreme	Min (109, 191)	Triangular	T (4.08, 67.65)		
Acetamiprid	Lognormal	LN (4286, 115404)	Lognormal	LN (45.01, 249)	Weibull	W (0.52, 0.43, 0)
Atrazine	Lognormal	LN (1530, 212089043)	Lognormal	LN (62.33, 25403)	Normal	N (0.11, 1.04)
Carbendazim	Lognormal	LN (14886, 29175)	Lognormal	LN (3393, 17932)		
Carbofuran	Lognormal	LN (18.35, 208)	BetaPERT	BP (-5.9, 60.0, 60.9)	Lognormal	LN (0.25, 290985)
Chlorantraniliprole	Weibull	W (112, 199, 5)	Uniform	U (2.34, 84.84)	Lognormal	LN (1.45, 353)
Chlorpyrifos	Gamma	Γ (3801, 0.3, 5)	Student's t	t (3)	Lognormal	LN (0, 5999)
Clothianidin	Lognormal	LN (50.24, 177)	Uniform	U (4.72, 13.4)		
Difenoconazole	Beta	B (100, 100)	Lognormal	LN (190, 618)	Weibull	W (0.19, 0.42, 0)
Dimethomorph	Max Extreme	Max (33, 31)	Gamma	Γ (0.37, 999, 0)	Max Extreme	Max (0.66, 0.22)
Fipronil	Normal	N (11.28, 4)	No Fit			
Imidacloprid	Lognormal	LN (319, 2820)	Lognormal	LN (36.11, 1749)	Max Extreme	Max (0.55, 0.22)
Lufenuron	Max Extreme	Max (30, 30.11)	No Fit		Weibull	W (0.03, 0.41, 0)
Nicosulfuron	Lognormal	LN (165, 208)	Max Extreme	Max (11.06, 11.69)	Normal	N (-0.41, 0.46)
Pendimethalin	Beta	B (0.34, 1.22)	Gamma	Γ (0.59, 999, 0)	Lognormal	LN (0, 43451)
Prochloraz	Lognormal	LN (7410, 50757)	Lognormal	LN (63.07, 2991)	Exponential	Exp (2.17)

Table S5.7 (Continued).

Pesticides	Indoor dust		Outdoor dust		Equivalent air concentrations	
	Distribution	Parameters	Distribution	Parameters	Distribution	Parameters
Propamocarb	No Fit		Uniform	U (1.77, 101.82)		
Pymetrozine	Weibull	W (399, 0.34, 5)	Weibull	W (15.7, 0.3)		
Pyridaben	Weibull	W (140,0.31, 5)	Uniform	U (-0.77, 178.16)		
Tebuconazole	Min Extreme	Min (7231, 3518)	Exponential	Exp (0.03)	Weibull	W (0.2, 0.41, 0)
Thiamethoxam	Lognormal	LN (1606, 278860)	Lognormal	LN (23.66, 372)	Lognormal	LN (0, 2258)

Table S5.8 Distribution of constant parameters for the health risk assessment.

Parameters	Unit	Potential distribution	Parameters	Reference
Exposure Duration (ED)	year	Uniform	UN (0, 24)	(Lei et al., 2022)
Exposure frequency (EF)	day $year^{-1}$	Triangle	TR (180, 350, 365)	(Sun et al., 2022)
Body Weight (BW)	kg	Fixed value	40	(Duan et al., 2014; Duan et al., 2016)
Ingestion Rate of Soils (IngR)	mg day^{-1}	Log-normal	LN (50, 75)	(Duan et al., 2014; Duan et al., 2016)
Skin Surface area (SA)	m^2	Fixed value	0.53	Average value for male and female (Huang et al., 2021; Shi et al., 2022)
adherence factor (AF)	mg cm^{-2} day^{-1}	Log-normal	LN (0.49, 0.54)	(Shi et al., 2022)
Dermal adsorption factor (ABF)	-	Point	0.001	(MEPRC, 2018)

Table S5.9 Comparisons of pesticide concentrations (mean or median, mg kg^{-1}) in the indoor and outdoor dust.

Locations	Measured concentrations						Sources
	Fipronil	Fipronil sulfone	Chlorpyrifos	Carbofuran	Atrazine	Pendimethalin	
Indoor dust							
Texas, USA	9.8, maximum						(Mukerjee et al., 1997)
Taiwan, China			0.11, maximum				(Hung et al., 2018)
California, USA			9.81, maximum				(Jiang et al., 2016)
Barcelona, Spain			0.07				(Velazquez-Gomez et al., 2019)
Taiwan, China				0.004			(Simaremare et al., 2021)
Texas, USA			Spring: 0.299 Summer: 0.557		0.02	Spring: 0.04 Summer: 0.02	(Mukerjee et al., 1997)
Australia			0.61				(Wang et al., 2019)
Quzhou, China	0.10	0.07	0.40	0.08	0.13	0.08	The present study
Outdoor dust							
Texas, USA	0.3, maximum						(Mukerjee et al., 1997)
California, USA	0.06, maximum	0.18, maximum	0.06, maximum				(Jiang et al., 2016)
Taiwan, China			0.14, maximum	0.24, maximum			(Hung et al., 2018)
Quzhou, China	0.04	0.04	0.10	0.08	0.17	0.05	The present study

Table S5.10 Comparisons of time-weighted pesticide concentrations (mean or median, ng $g^{-1}day^{-1}$) in personal wristbands.

Study site	Duration (days)	Measured concentrations (detection rate, %)						Source
		Fipronil	Fipronil sulfone	Tebuconazole	Imidacloprid	Carbendazim	Chlorpyrifos	
Leuven, Belgium	5	4.54 (33.3)	0.79 (23.3)	0.33 (20.0)	0.15 (10.0)	0.14 (6.7)		18
North Carolina	7						Farmworkers: 2.34 (67.1) Non-farmworker: 2.31 (40.0)	19
California, US	7	NG (10.4)	0.1 (45.4)				0.07 (36.1)	20
South Africa	6			0.8 (5.3)			10.2 (80.3)	21
Quzhou, China	28	0.04 (31.4)	0.12 (30.0)	**1.55 (74.3)**	0.13 (**64.3**)	**0.72 (38.6)**	0.28 (**95.7**)	The present study

Note: NG, data not given.

Table S5.11 Calculated equivalent air concentrations of pesticides in personal wristbands.

Pesticides	Calculated equivalent air concentrations (ng m^{-3})				
	Mean	25% percentile	Median	75% percentile	Maximum value
Abamectin	0.0002	0	50	75	0.01
Acetamiprid	18.79	0	0	0	406.28
Atrazine	7.69	1.44	0.55	5.21	81.95
Carbendazim	1.92	0	3.45	7.02	28.83
Carbofuran	5.41	0	0	1.88	122.5
Chlorantraniliprole	0.03	0	0.54	1.71	1.93
Chlorpyrifos	8.29	0.36	0	0	151.94
Clothianidin	0.01	0	1.18	3.19	0.32
Difenoconazole	4.14	0	0	0	119.38
Dimethomorph	3.11	0	0.10	0.81	43.63
Fipronil	0.15	0	0.03	0.87	2.93
Imidacloprid	1.99	0	0	0.023	39.51
Lufenuron	0.36	0	0.22	1.49	18.08
Nicosulfuron	0.0001	0	0	0	0.01
Pendimethalin	2.52	0	0	0	83.05
Prochloraz	0.05	0	0.25	0.68	2.49
Propamocarb	0.32	0	0	0	14.51
Pymetrozine	0	0	0	0	0
Pyridaben	0.0068	0	0	0	0.39
Tebuconazole	52.59	0	0	0	1478.49
Thiamethoxam	1.41	0	1.66	22.91	57.59

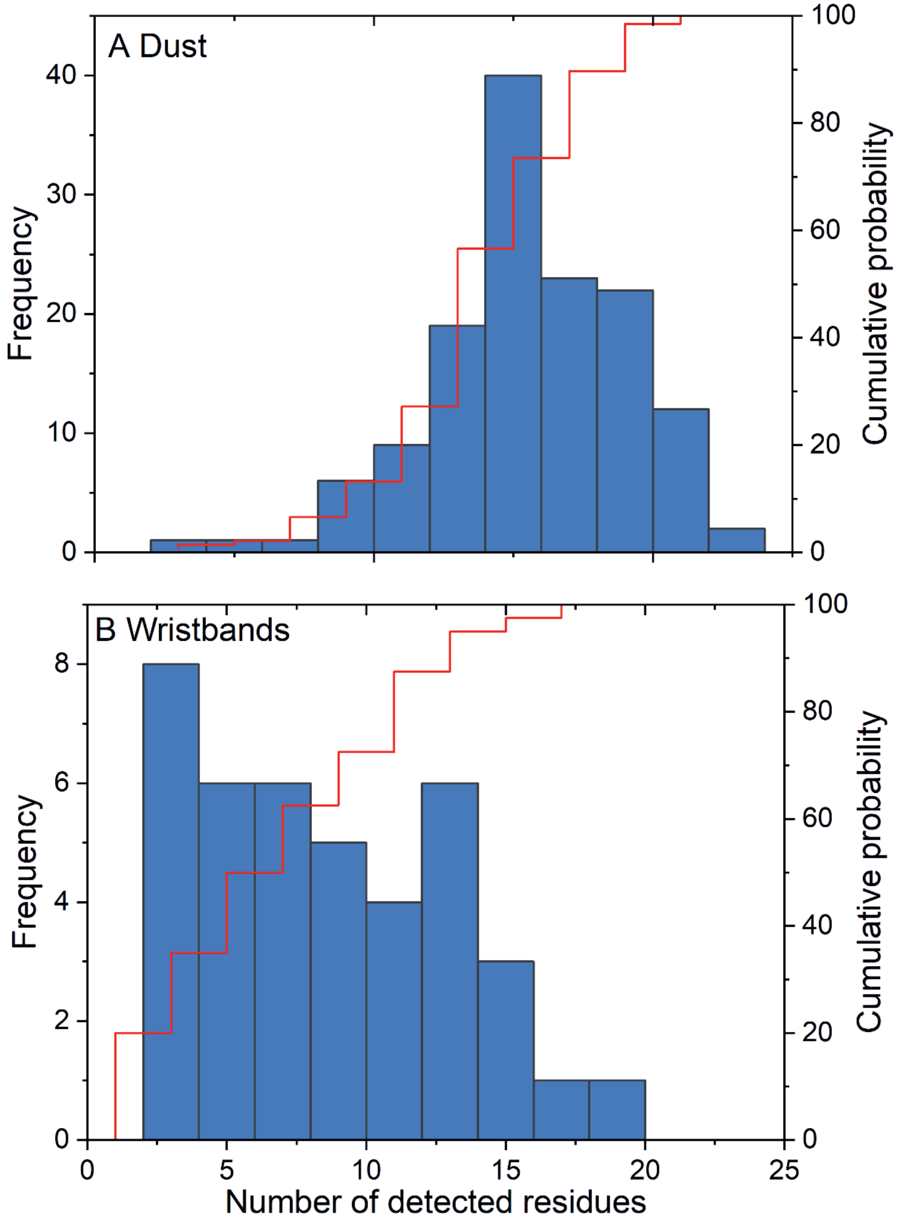

Fig. S5.1 Number of detected residues and the cumulative probabilities in A: dust and B: stationary wristbands.

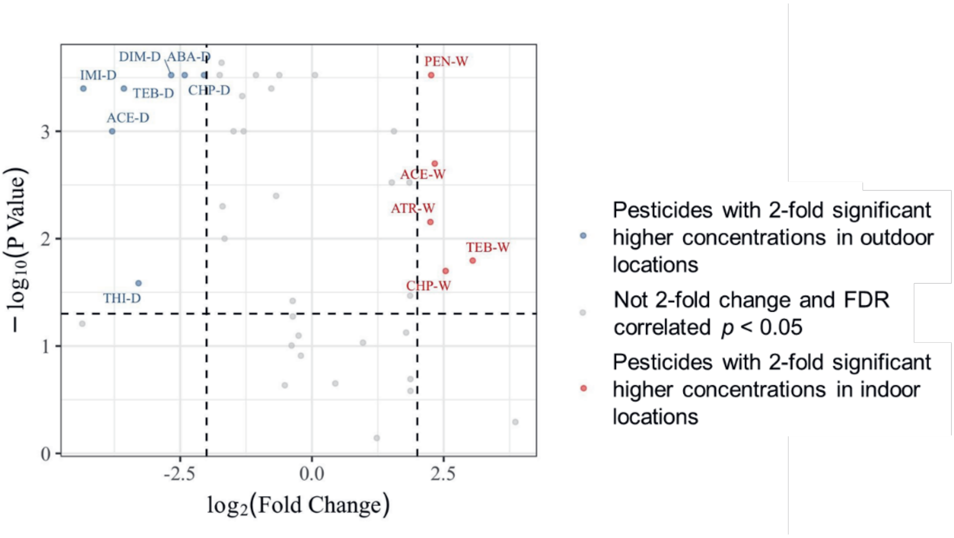

Fig. S5.2 Volcano plot for pesticide concentrations in dust and wristbands in the indoor and outdoor nexus. Fold Change, the ratio between the mean value of pesticide concentrations in samples between outdoor and indoor locations. FDR: false discovery rate, D: dust samples, W: wristbands, ABA: abamectin, ACE: acetamiprid, ATR: atrazine, CHP: chlorpyrifos, DIM: dimethomorph, IMI: imidacloprid, TEB: tebuconazole, THI: thiamethoxam.

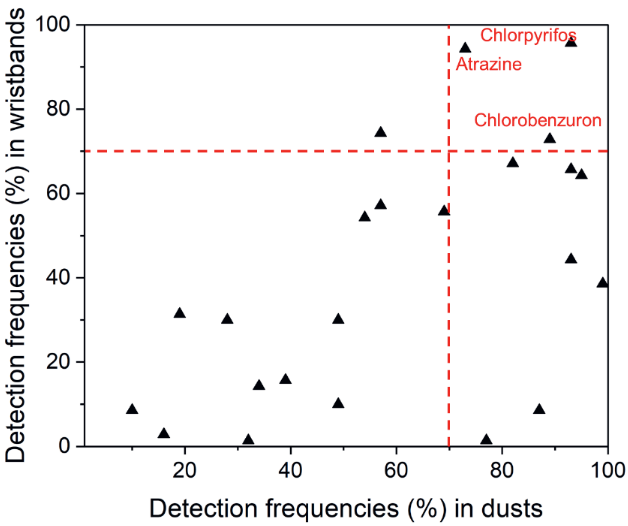

Fig. S5.3 Detection frequencies (%) of pesticides in wristband and dusts.

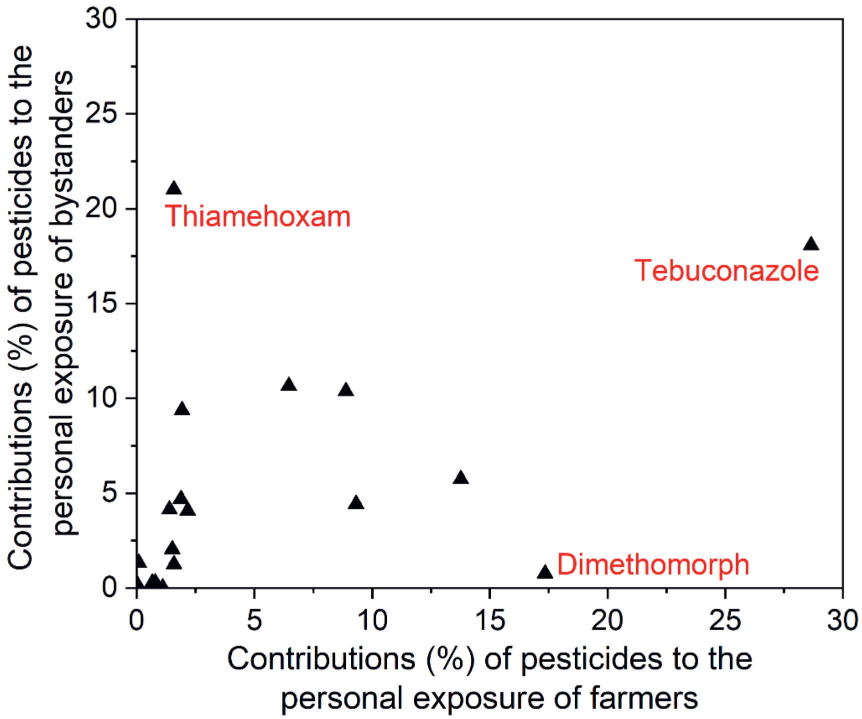

Fig. S5.4 Contributions (%) of pesticides to the personal exposure of farmers and bystanders.

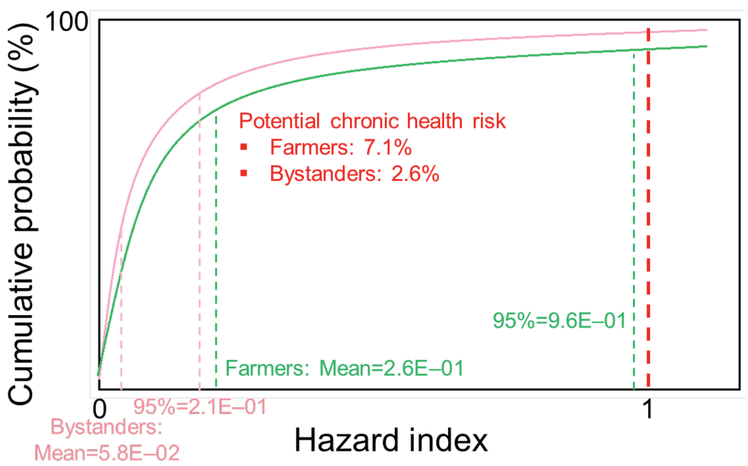

Fig. S5.5 Cumulative probability of the health risks of pesticides to farmers and bystanders

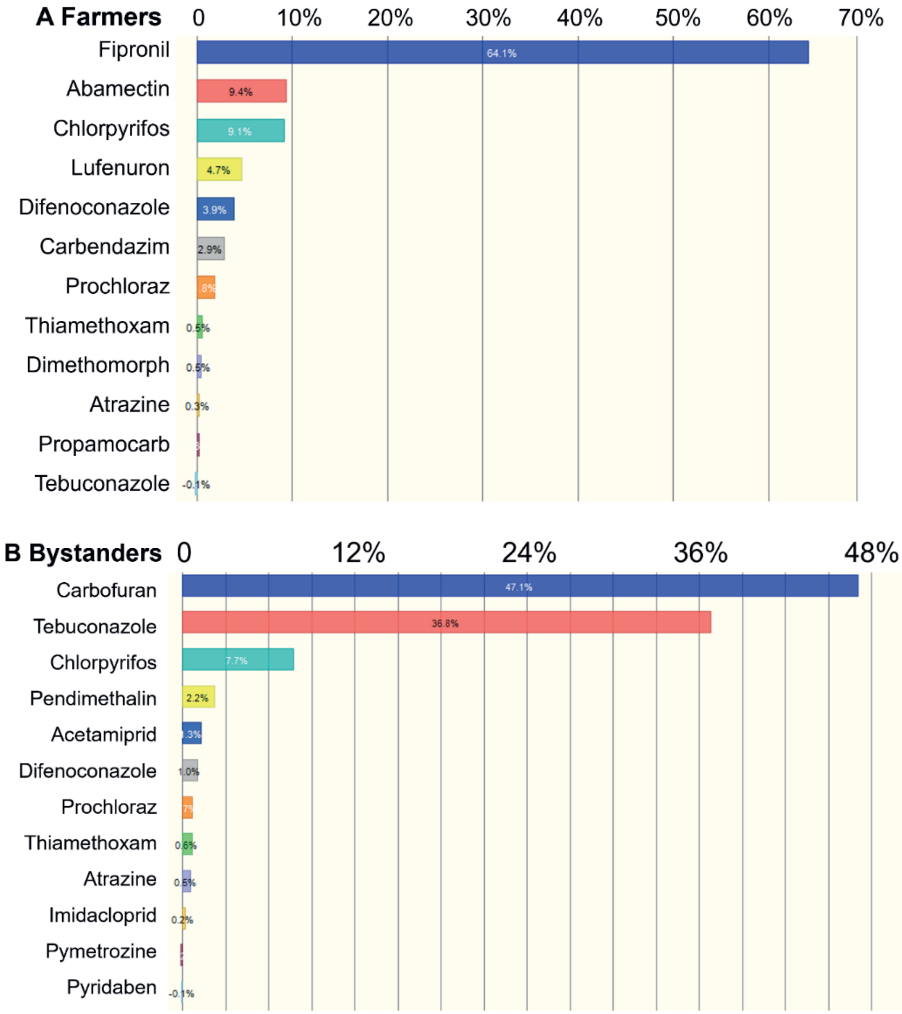

Fig. S5.6 Sensitivity analysis.

Chapter 6
Synthesis

6.1 General conclusions and main findings

This thesis provides new insights into the exposure risks of pesticides to non-target species and rural residents in the North China plain, a region with intensive agricultural production and pesticide use. Based on an integrated field-modelling approach, this study evaluated pesticide application patterns and analyzed pesticide residue concentrations in soils of agricultural fields before application and after harvesting. Furthermore, the associated exposure risks of pesticides to soil biota and pollinators in the ecosystem was assessed.

To assess exposure and health risks to human populations in Quzhou, North China Plain (NCP), we monitored pesticide residue levels in in both the particulate (residential dust) and gaseous (stationary silicone wristbands) phases in indoor and outdoor environments. The health risks of pesticide residues to local farmers and bystanders were assessed by integrating personal exposure profiles and the environmental exposures to particulate and gaseous pesticides, in the indoor-outdoor nexus.

The health risks due to pesticides are mainly determined by the exposure amount and the toxicity of the pesticides. Thereby the major contributors to the exposure risks were further identified following risk assessments. In the end, this study identifies the sources of personal pesticide exposures and highlights the non-occupational exposure from the remote dissipation of pesticides, which is often overlooked. The main findings are summarized and illustrated in **Fig. 6.1** based on an adapted Process-Risk module.

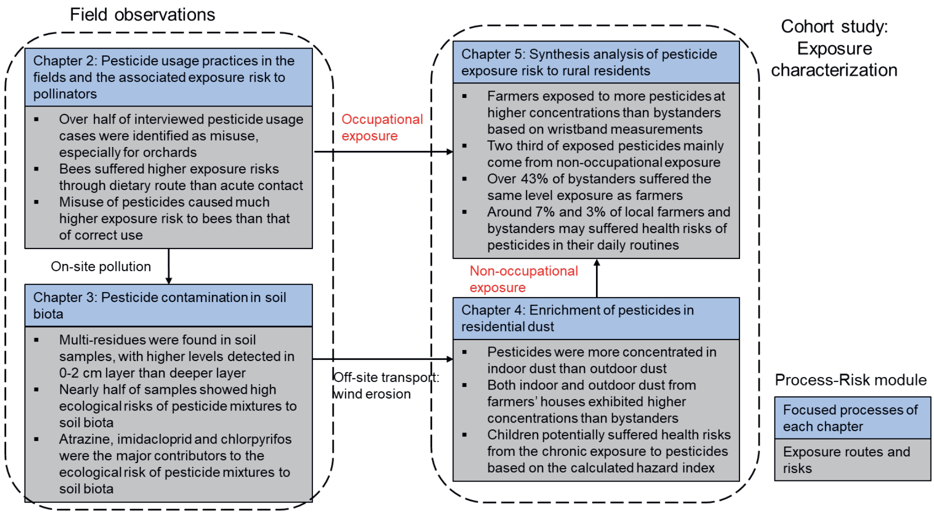

Fig. 6.1 Outline of the main findings of this thesis

Chapter 2 reports the outcomes of interviews of farmers (in total 197 respondents) in Quzhou county, NCP, to investigate pesticide usage patterns in the major farming systems, including wheat/maize, vegetables, cottons, grapes, and apples, and assess the exposure risk to bees and how it relates to the pesticide application patterns. Overuse, underuse, and the use of forbidden/restricted pesticides were classified as pesticide misuse. Based on the interviews, misuse was apparent in more than half of all cases, with misuse more frequently occurring in orchards. Farmers' pesticides usage performance was positively correlated with their specialized training experience related to pesticides. The Bee-REX model was used to assess the exposure risk of bees to currently applied pesticides via acute contact and dietary ingestion and showed that bees suffered higher risks via the dietary route. Pesticide misuse significantly increased the exposure risks to bees compared to cases with correct usage. Abamectin, fipronil and neonicotinoids were the major contributors to exposure risks.

In **Chapter 3** we monitored pesticide residue concentrations in 40 fields at 0-2 cm and 2-10 cm depths. Pesticides were mostly concentrated in the 0-2 cm layer of soils rather than in the 2-10 cm layer, and chlorantraniliprole was the most frequently detected pesticide. Higher concentrations of most pesticide residues were found in samples taken after crops were harvested. TERs and the RQ approach were applied to assess the risks to non-target species posed by single pesticides and mixtures, respectively. Chlorpyrifos, carbendazim and imidacloprid posed chronic risks to *E. fetida*, *F. candida* and *E. crypticus*. Regarding the risks posed by mixtures, nearly half of the samples were identified as having high ecological risks, while more than 70% of investigated samples were assessed to pose potential risks to soil biota. Abamectin, tebuconazole, chlorantraniliprole and chlorpyrifos were identified as the most hazardous pesticides to soil biota regarding the ecological risks caused by their presence in soil.

In **Chapter 4** we recruited 35 rural residents (21 farmers and 14 bystanders) to screen pesticide residues in indoor and outdoor dust from their residences, and further assess the health risks to residents caused by daily exposure to pesticide-contaminated dust. Higher concentrations and more residues were found in indoor dust than in outdoor dust, with carbendazim and imidacloprid detected in almost all samples. Significantly higher concentrations of pesticide residues were detected in indoor dust samples from farmer's houses than from bystander's houses. The health risks were assessed with a Hazard Quotient (HQ)-based approach. Children were subject to higher health risks than adults, with the highest HQ values approaching the threshold for potential chronic health risk (HQ = 1). Pesticide preparation inside homes was found to be positively linked to the health risks of residents, highlighting the need for farmers to change their pesticide handling and management methods.

Chapter 5 investigated levels of both particulate bound pesticide residues in dust samples and pesticide residues in the gaseous phase (collected by stationary silicone wristbands for 4 weeks) in the indoor-outdoor nexus. Furthermore, silicone wristbands were worn by each participant for 4 weeks, to monitor their personal pesticide exposures (as displayed in **Fig. 6.2**). Based on the personal exposure profiles and concentrations of pesticide residues in both particulate and gaseous phases in indoor and outdoor environments, health risks of pesticides to farmers and bystanders were assessed by Mente-Carlo Simulations. Particulate bound pesticide residues were concentrated in indoor dust, whereas for residues in the gaseous phase, significantly higher residue concentrations were found in stationary wristbands placed in fixed locations outdoors than at the worn wristbands. Carbendazim and chlorpyrifos were the most frequently detected pesticide residues in the particulate and gaseous phases. For personal pesticide exposure, significantly higher concentrations were found in personal wristbands worn by farmers than by bystanders. Based on Mento-Carlo simulations, around 7% and 3% of farmers and bystanders in the study region may suffer potential chronic health risks of pesticides in their daily routine through inhalation, ingestion, and dermal contact routes. Two-thirds of pesticide exposure was found to originate from non-occupational sources such as remote dissipation, while the rest of the exposure is mainly due to occupational exposure in the surrounding fields. Differing abundance patterns of pesticides were found between environmental samples and personal exposure profiles, indicating that the environmental abundance of pesticides cannot correctly mirror personal exposure patterns.

To conclude, this thesis assessed the exposure and health risks of pesticides for the soil ecosystems and rural residents in the study region. Intensive pesticide usage has caused unneglectable exposure risks to non-target species, including pollinators and soil biota. For rural residents, both farmers and bystanders potentially suffer chronic health risks from pesticides, as most pesticide exposures occur in non-occupational settings. Findings from the thesis have revealed the negative impacts of pesticides to non-target species, and bystanders who do not experience direct occupational exposures. This has highlighted the need to change existing pesticide application practices and move towards using more biopesticides or low toxicity pesticides.

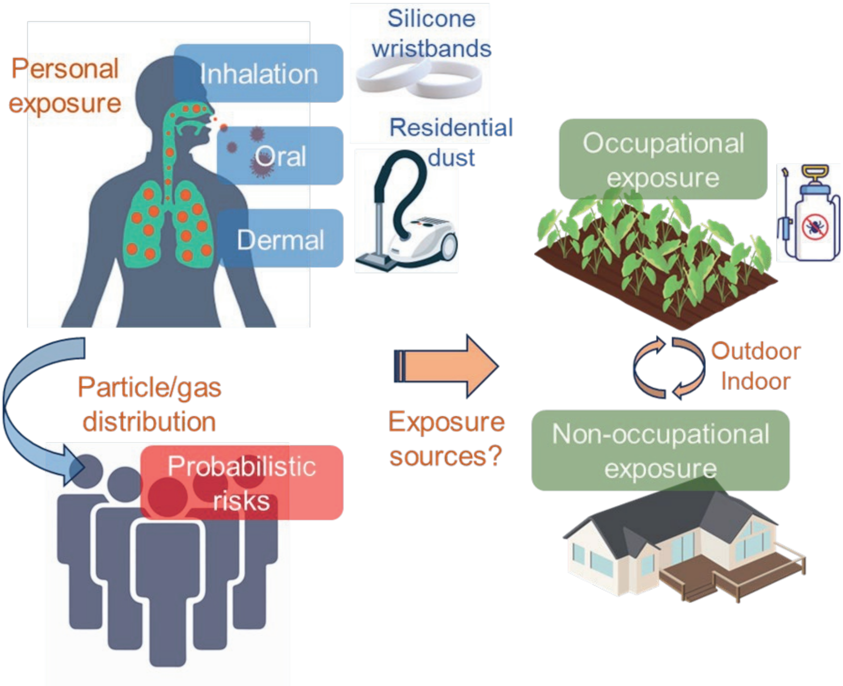

Fig. 6.2 Exposure matrix to pesticides for rural residents.

6.2 General discussion

6.2.1 Pesticide usage in intensive farming systems

As exhibited in chapter 2, pesticides have been frequently misused in the study region, as pesticides have been applied in excessive dosages, and banned pesticides have been used. Similar trends in pesticide usage were also found in other regions of China (Sun, 2019; Zhang et al., 2015) and in developing countries, especially in southeast Asia (Grovermann et al., 2013; Jauhari et al., 2022; Schreinemachers et al., 2020). In Quzhou county, over half of the survey respondents showed pesticide misuse, with the highest misuse rates in orchards. Misuse of pesticides mainly occurred when combating stem borers and aphids. The overuse of pesticides described in our study is in line with the findings of Sun et al. (2019) and Zhang et al. (2015), who found excessive applications in tomato and cumcumber fields in China. Pesticide misuse has also been reported in India, Cambodia, Laos, Thailand, and Vietnam (Grovermann et al., 2013; Jauhari et al., 2022; Schreinemachers et al., 2020), with a misuse rate exceeding 77%. In particular, all interviewed vegetable growers in Vietnam were found to overuse pesticides, posing a highly concerning level of potential exposure risks to farmers and to the environment. The excessive pesticide usage observed in this study also indicates that there is a potential to significantly reduce applied pesticide dosages by up to 42%, while preserving current levels of crop productivity and profitability (Lechenet et al., 2017).

The willingness and ability to correctly use pesticides is mainly determined by the accessibility of accurate information. Due to the coexistence of multiple pesticides that are both affordable and accessible, choosing the appropriate pesticide to be applied is an information-intensive activity that requires large information inputs regarding the appropriate application frequency, dosages, and suitability of pesticide products (Pan et al., 2017; Jin et al., 2015). This study has found that farmers with specialized training experience have access to sufficient pesticide related information, and they therefore tend to use pesticides properly and avoid overusing pesticides. Studies performed in other regions of China also confirmed the high relevance of information accessibility to farmers' pesticide application behaviours, and highlights the need for increased public education (Liu et al., 2013). It should be noted that other than traditional information sources, content creators in mobile social networks, such as Kwai, TikTok, and WeChat, were found to be influential amongst young and middle-aged farmers in the study region. These content creators may produce video streams that convey up-to-date information about pesticide use and crop protection. Label information is also vital for guiding farmers to follow the correct usage patterns. Labels on pesticide bottles also provide information related to the safe use of pesticide products, and the recommended procedures for the mixing and spraying processes (Damalas et al., 2017; Dugger-Webster et al., 2018; Madaki et al., 2023). However, doubts have been raised regarding the effectiveness of labels in informing farmers, due to the use of non-native languages, pictorial contents, and complex textual messages (Oludoye et al., 2021; Wilkinson et al., 1997). In summary, collective efforts from the government, retailers, manufacturers, and other content creators should be devoted towards providing adequate and accurate information to farmers, to prevent the misuse of pesticides.

6.2.2 Exposure risk of pesticides to pollinators

This study has revealed concerning levels of pesticide exposure risks to bees, by applying the Bee-REX model. Based on the concentration-addition approach, Risk Quotients (RQs) were calculated as the sum of concentrations of all pesticide-related active substances. The results showed that most pesticide usage cases were prone to cause large exposure risks to bees, with the highest RQ 1880 times higher than the threshold (RQ = 1). However, the toxicity of pesticide mixtures to bees may be underestimated, as synergistic effects may not be understood well. For instance, sterol biosynthesis inhabiting fungicides (SBI) have showed low toxicity, but combined exposure to SBI fungicides and insecticides, such as difenoconazole with bifenthrin, or triazole myclobutanil with bifenthrin/thiamethoxam, can interact synergistically to pose severe toxic effects to bees (Sgolastra et al., 2016). Synergistic effects were also found amongst various combinations of commonly used fungicides and insecticides, including mixtures of acephate with pyrethroids and chlorpyrifos with pyrethroids (Wang et al., 2020). Aside from combinations of fungicides and insecticides, the use of multiple types of insecticides, such as binary mixtures of thiamethoxam with λ-cyhalothrin and abamectin, may also cause greater toxicity to bees (Wang et al., 2019). In this study, farmers used 88 combinations containing multiple active substances of pesticides to protect their crops, which may cause synergistic toxicity effects that lead to greater harm to bees. Interactions between mixtures of commonly used pesticides should be further examined, so as to inform more precise guidelines for pesticide usage that minimize the risks of synergistic toxicities to bees.

In this thesis, the exposure risk to bees resulted from the wide usage of highly toxic insecticides, including abamectin, fipronil, and neonicotinoids, which accounted for over 95% of the total RQs from both acute contact and the dietary route. As a biological pesticide extracted from *Streptomyces avermitilis,* abamectin was classified as extremely toxic to insects and bees, especially *M. scutellaris* (Brigante, 2021; Salman, 2022). Specifically, abamectin could increase the mortality of bees through multiple pathways, such as amino acid metabolism, the immune system, locomotion, carbohydrate metabolism, and developmental processes, through the alterations of several identical gene families (Li, 2022). Another commonly used insecticide in the study region, fipronil, is also highly toxic pesticide to bees, and can cause reduced vitality (Zaluski, 2015). By causing neuron death and brain function impairments, fipronil may cause agitation, seizures, tremors, and paralysis, potentially threatening individuals and even populations of bees (Morais, 2018; Zaluski, 2015). Neonicotinoid insecticides have been widely used by farmers both, in the study region and worldwide to eliminate pests effectively (Gibbons, 2015). However, neonicotinoids were reported to cause immunotoxicity, neurological and endocrine disruptive toxicities to bees and further cause population density decline (Baines, 2017; Faro et al., 2021; Lundin et al., 2015; Blacquière et al., 2012). It should be noted that various bee species have diverse lifestyles (solitary or socialized styles), behavioural patterns, sensitivities to pesticides, and post-exposure recovery abilities, leading to species-differentiated risks (Schmolke et al., 2021). In summary, to reduce risks to bees, alternative pesticides and better integrated pest management methods are necessary.

6.2.3 Pesticide residues in the soil and the associated ecological risks

Pesticide residues are widely present in agricultural soils subject to repeated field applications (Laitinen et al., 2006; Yang et al., 2015). In chapter 3, multiple pesticides were detected in all monitored sites at both depths and in different sampling times, with insecticides, especially neonicotinoids, being the most detected group of pesticides. Different compositions of pesticide residues were found in studies conducted at other locations. Herbicides, mostly triazines and chloroacetanilides, were the most present pesticides in agricultural soils in Czechia, with the highest concentrations detected for pendimethalin (Kosubová et al., 2020). In vegetable fields in Nepal, fungicides were the most exhibited pesticides, showing up in around half of collected samples (Bhandari et al., 2019). Another regional study revealed that in European soil, glyphosate and aminomethylphosphonic acid (AMPA) is the prevalent pesticide combination (Silva et al., 2019). These differences in pesticide compositions might be attributed to the diverse pesticide usage patterns, farming systems, and historical applications.

The vertical distribution of pesticides in soils indicates the potential for transport to other environmental domains, and the associated risks. Specifically, pesticides enriched in surface soil and in the 0-2 cm layer are highly susceptible to wind erosion (Silva et al., 2018), indicating the potential for off-site pesticide transport through the atmosphere. For pesticides deeper in the soil, there is a potential for leaching and groundwater contamination (Zhang et al., 2009). In chapter 3, pesticide residues were found to be concentrated in 0-2 cm soil depth, especially residues of dimethomorph, chlorantraniliprole, lufenuron, and atrazine. The concentration of pesticide residues in shallow soil being 2-3 times higher than in deeper soil layers is consistent with the studies of (Laitinen, 2006; Yang et al., 2015). The residual level of tebuconazole was significantly higher at deeper layers (2-10 cm), indicating a potential leaching risk.

The soil biota contributes to biodiversity and the maintenance of soil functions by facilitating nutrient cycling and improving soil quality. However, the soil biota is highly susceptible to pesticide exposures (Bhandari et al., 2021; Romero et al., 2023). Therefore, the ecological risks to pesticides of soil biota were assessed in monitoring studies, and major contributing factors to these risks were identified in chapter 3. Despite not being frequently detected in soils, carbendazim, chlorpyrifos, and lufenuron made substantial contributions to the ecological risks, leading to high risks in nearly half of the studied sites. The ecological risks to pesticides of soil biota varied across regions in China, ranging from 11% to 98% in Horqin Left Middle Banner in the Three Gorges Reservoir Area, and in Zhejiang province (Yang et al., 2022; Zhou et al., 2023; Zuo et al., 2024). As also explained in chapter 4, some pesticides can pose substantial risks to soil species even at extremely low concentrations in soil.

6.2.4 Pesticides in residential dust

As shown in chapter 3, pesticides were widely accumulated in surface soils under repeated applications, and potentially transported by drift, evaporation, and wind erosion into the surroundings. This transport of pesticides can take place in the gaseous phase, or in the particulate phase for pesticides bound to dust particles. In Chapter 4 we investigated the number and concentration of pesticide residues in the residential dust (indoor and outdoor dust) to examine the associated health risks posed by the chronic exposure of particulate pesticides. In our study, we detected extremely high concentrations (max concentration at 859 mg kg^{-1} for thiamethoxam) of commonly used pesticides in indoor dust samples collected from farmers' residences, with the most frequently detected residues being those of imidacloprid, acetamiprid, chlorpyrifos, dimethomorph, difenoconazole and thiophanate-methyl. The detected concentrations were much higher than in residential dust collected in other rural regions in China and in the US under agricultural settings (Hung et al., 2018; Hazard et al., 2023; Harnly et al., 2009; Jiang et al., 2016). Meanwhile, the detected maximum pesticide concentrations were higher in this study than in residential dust collected close to nearby fields by 1-3 orders of magnitude (Figueiredo et al., 2022). This unexpected difference in observed concentrations suggests that the practice of pesticide preparation inside homes contributes greatly to pesticide concentrations in residential dust. Most pesticide residues were present in higher concentrations in samples from farmers' residences than those of bystanders, likely due to the practice of pesticide preparation indoors at home.

There are multiple factors associated with pesticide levels in residential dust, including distance from homes to surrounding fields (Mahler et al., 2009; Hazard et al., 2023; Kuiper et al., 2022; Figueiredo et al., 2022), indoor application of insecticides (Al-Alam et al., 2022; Hazard et al., 2023), pesticide use in outdoor lawns (Barbara J Mahler, 2009), pesticide concentrations in the air (Figueiredo et al., 2022), house cooling strategies (Kuiper et al., 2022), and the possible access to secondary occupational exposures in the fields (Kuiper et al., 2022). In this study, although pesticides were reported to be used only in field conditions rather than homes, pesticide preparation activities including the mixing of pesticide ingredients are frequently conducted inside homes and may be a major factor that affects pesticide levels and exposure risks in the indoor environments of farmers.

In chapter 3 and 4 we systemically screened pesticides in residential dust and in the surrounding soils. The distance between sampling locations of residences and fields were mostly within 2 miles. Pesticide residue concentrations were much higher in residential dust than in soils, except for tebuconazole. In particular, the largest differences were found for carbendazim and atrazine, with median concentrations

39 and 16 times higher in indoor dust than in soil samples. This concentration of pesticide residues in dust indicates much higher exposure risks of pesticides through ingestion and direct dermal contact routes. Considering that the people spend most of their time in domestic environments, more attention should be paid to residential exposures, especially in indoor environments. It should be noted that the sampling times for dust and soil samples were quite different: dust samples were collected during summer peak season, while soil samples were collected before seeding and after harvest. These differences in sampling time may cause uncertainties regarding the concentration comparisons between soil and dust concentrations of pesticides. Current studies mostly focus on the monitoring of individual exposure pathways, such as agricultural soil (Chen et al., 2023; Mahdavi et al., 2023), or indoor/outdoor dust (Degrendele et al., 2022; Kuiper et al., 2022; Ward et al., 2023; Yang et al., 2022). A comprehensive analysis of all exposure pathways for all commonly used pesticides is highly needed, especially in intensive farming areas.

6.2.5 Exposure to pesticides of rural residents

In chapter 5, indoor and outdoor dust and silicone wristbands (including stationary and personal wearing ones) were used to screen pesticides in different phases in the indoor-outdoor nexus, and to quantify the personal exposure risks of the studied subjects (21 farmers and 15 bystanders) in intensive agricultural area. Monte-Carlo simulations were performed to probabilistically assess the health risks, by transforming adsorbed pesticide residues from wristbands into atmospheric concentrations. This is a new approach to integrate exposures to particulate (indoor dust) and gaseous (silicone wristbands) phase pesticides in the indoor and outdoor environments. For the particulate phase, the median concentrations of pesticide residues in indoor dust were 1.2 (propamocarb) to 20.2 (imidacloprid) times higher than those in outdoor dust. This was probably caused by pesticide preparation practices inside homes. Similar trends were observed in a monitoring study in rural settings, which revealed that the use of pesticides at home causes residue accumulation in indoor dust (Mahler et al., 2009; Hung et al., 2018). As one of the most detected pesticides, chlorpyrifos was measured at much higher concentrations in indoor dust, with a maximum value at 15463 ng g^{-1}, which is 1.6 and 141 times higher than reported by studies carried out in Taiwan province and California, USA (Mahler et al., 2009; Hung et al., 2018), respectively. For gaseous pesticides, almost all analysed compounds had higher concentrations at outdoor locations, except clothianidin and thiamethoxam. The differences in pesticide levels between indoor and outdoor air indicate the much higher background exposure levels of pesticides in the fields due to intensive application. It is therefore critical to study the gas-particle partitioning characteristics of pesticides, to better understand their environmental fate and the associated risks. Monitoring studies that have been conducted by stationary sampling of atmospheric particles and air at outdoor locations, indicate that these partitioning coefficients are mainly dependent on the physiochemical properties of pesticides, agricultural activities, and meteorological factors such as temperature and humidity (Wang et al., 2024; Wang et al., 2021; Wang et al., 2023). This study expands upon former monitoring studies, by studying the distribution patterns of pesticides in both indoor and outdoor spaces. As a following step, seasonal and temporal variations in pesticide distributions should be determined.

Analysis of environmental samples, biomonitoring, and silicone wristbands are important approaches for characterizing personal exposures to chemicals (Hammel et al., 2020). Environmental samples, such as soil, dust, and air, have been extensively sampled to estimate daily exposures to chemicals through the ambient environment (Bergh et al., 2011; Luongo et al., 2016; Stapleton et al., 2009; Shoeib et al., 2002; Marklund et al., 2003). This approach estimates daily exposure dosages by integrating measured concentrations in the various environmental domains with their exposure factors, such as exposure frequencies and times, which introduces large uncertainties to the exposure estimates. As discovered in chapter 5, certain pesticides could contribute greatly to health risks despite extremely low detection frequencies or concentrations in environmental samples, highlighting the need for accurate risk assessment methods and direct measurements of exposures. Biomonitoring aims to measure the internal exposure of individuals to chemicals through biological samples, such as hair, sweat, and urine (Brunmair et al., 2021; Tagne-Fotso et al., 2023; Zhang et al., 2023), whereas silicone wristbands capture mainly personal exposures from gaseous pollutants and partially integrate internal and dermal exposures (Samon et al., 2022). Given the complexity of the exposure sources and routes, the characterization of personal exposures to pesticides relies on the combination of multiple monitoring approaches. Similar attempts have been made by applying dust-handwipe-silicone wristbands (Hammel et al., 2020), silicone wristbands-handwipes (Hammel et al., 2016), silicone wristbands-urine (Wise et al., 2021), and silicone wristbands-air (Nguyen et al., 2022) monitoring. These studies aim at examining correlations between exposure measurements across the different matrices, thus a holistic characterization of exposure risks is still missing. Systematic research is needed to build linkages between different matrices for exposure measurements.

The health risk assessment in Chapter 5 found that a small portion of local farmers and bystanders may suffer health risk through the chronic exposure to both particulate and gaseous pesticides. Previous studies only focus on the health risk posed by pesticide residues from single phase, such as dust (Fuentes-Ferragud et al., 2023) and air (Zhao et al., 2023), which may underestimate the exposure dosage to local residents and neglect the potential health risks.

The health risk assessment was conducted based on the concentration addition (CA) approach, that assumes the toxicity of all existing pesticide mixtures are addictive. However, synergistic and antagonistic effects are known to widely occur among pesticide mixtures, especially for combinations that contain both insecticides and fungicides (An et al., 2024; Li et al., 2023; Wang et al., 2023). The CA-based risk assessments may thus cause uncertainties to the risk assessment results, as they ignore synergistic and antagonistic effects.

6.3 Implications

6.3.1 Pest control strategies and associated risks to pollinators

This study investigated pesticide usage patterns in farming systems in Quzhou and assessed the exposure risks to pesticides of pollinators. The findings in chapter 2 imply a substantial potential in reducing pesticide use when coping with crop issues and the associated risks to bees. Specialized training sessions organized by the government or agricultural extension agencies are highly recommended to help enhance farmers' knowledge about pesticides, and their negative impacts. Pesticides with major contributions to the exposure risk of bees should be used at lower dosages or replaced with low-risk pesticides. There is also a need for ecotoxicological tests to examine the effects of interactions in pesticide mixtures. Risk assessments should consider the vulnerability to pesticides across various bee species, and the synergistic/antagonistic effects of pesticide mixtures. Additionally, the risk assessment methods currently used may not be optimal for all bee species. More comprehensive risk assessment models, that consider the vulnerability of each species to pesticides, should be developed.

6.3.2 Pesticide residues in soils: Comprehensive monitoring and risk assessment

The findings in **Chapter 3** exhibited varying pesticide levels across different soil depths and sampling times, indicating complex dynamics of pesticide transport between soil and other environmental matrices within a crop growing season. Specifically, wind and water erosion events introduced exogenous pesticide inputs, while simultaneously facilitating the off-site transport of certain pesticides. The composition of pesticides in soils was found to greatly differ from their contributions to ecological risks, revealing the possibly large negative impacts of pesticides that are present in low concentrations and hence easily overlooked in regular monitoring programs.

Given the complex sources of pesticide inputs in soil, a combined non-target and target analysis of pesticides would be needed in future research, rather than only suspected screening. Specifically, a two-step workflow is recommended: 1) investigate the compositions of pesticides in soil samples through non-target screening (with semi-quantitative analysis), and 2) perform target analysis for the cases requiring special attention, such as pesticide residues at high concentrations or detection frequencies or existed highly toxic pesticides. The environmental fate and sources of pesticides in fields under different field management and pesticide application practices are still plausible. Field studies are needed to trace the utilization rates and transport of pesticides during and after pesticide application events with different application methods.

The Soil Environment Carrying Capacity (SECC)-based early warning system, a decision support tool, is recommended for estimating the maximum environmental loading of certain pollutants without impairments on soil ecological functions(Yang et al., 2022; Zhou et al., 2023). Based on the early warning system, pesticides could be prioritized based on their ecological impacts and the environmental capacities in study sites. Specially, residual levels of pesticides should be continuously monitored to predict the time dynamics of the SECC, which would contribute towards a more precise pollution control and land management efforts.

6.3.3 Particulate transport of pesticides from fields to households: The neglected exposure risk to rural residents

Chapters 3 and **4** reports on monitored pesticide levels in soil and residential dust, indicating a concentrated trend of pesticide levels between soil and residential particles. The findings also indicate the need to establish field facilities for water supply, to avoid the necessity for pesticide preparation inside homes and thereby reduce occupational exposures to pesticides in residential areas.

Future studies should focus on monitoring the particulate transport of pesticides from fields to residential areas during the growing season. Soil, paired indoor-outdoor dust, and window wipes should be simultaneously monitored to better understand the transport and accumulation trends of pesticides from fields to households. Furthermore, sources of particulate pesticides, including transport from close-by fields or remote regions, and domestic use in residential areas, could be more accurately traced if improved measurement methods and predictive models are developed.

6.3.4 Personal pesticide exposure and risk assessments

The findings of **Chapter 5** reveal differing compositions of pesticides between environmental matrices and personal exposure profiles, highlighting the importance of flexible and reliable personal exposure measurements. Silicone wristbands serve as a useful and promising tool for measuring highly individualized exposures to various organic compounds by taking individual activities and habits into account. However, silicone wristbands were used in only around 10% of exposure assessment studies, whereas most studies rely on the stationary sampling of environmental samples (Okeme et al., 2023; Wang, 2021). The use of silicone wristbands should be expanded in the future research through more flexible deployment to various wearing and sampling locations and sampling periods. The Concentration Addictive (CA)-based risk assessments used in this study may cause results to be overestimated or underestimated. To reduce uncertainty and obtain more indicative risk assessments, future studies should focus on the combined toxicity of common pesticide mixtures, and the establishment large datasets of pesticide interactions.

6.3.5 Policy implementations

Pesticides should be classified based on their toxicities to humans and non-target species such as bees and soil biota. The use of pesticides with high toxicity to bees and soil biota should be severely restricted or forbidden. Farmer education sessions should be organized by the government or research institutes to enhance their knowledge on the possible negative effects of pesticides, and on safe pesticide usage methods. Facilities for irrigation should be established in the fields to avoid the need for mixing/loading pesticides inside homes, to reduce residential exposures to pesticides.

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English summary

Pesticides have been widely used worldwide to protect crops and prevent yield losses. Pesticides can accumulate in various environmental domains under repeated applications. Despite their vital contributions in securing food availability, many pesticides are toxic to non-target species and humans, and depending on the level of exposure, can causee negative impacts on both eco-environment and human health.

China is one of the largest consumers of pesticides in the world, with an annual input of pesticides that has strongly increased over the past decades. After the government issued the "Zero Increase of pesticides" action plan in 2015, a steady decrease was observed in terms of both total input and application rates. Although the peak total input has already been passed, pesticide misuse has been frequently observed in field surveys, especially when eliminating pests. The massive use of pesticides has caused residue accumulation in the environment and puts non-target species at risk. To date, site specific studies have been conducted to screen pesticide levels and assess the associated risks. However, holistic studies are lacking, especially in the North China Plain (NCP), a major crop producing area. Thereby the objectives of this thesis are to 1) investigated pesticide application patterns in Quzhou, NCP and assess the associated health risk to pollinators, 2) screen pesticide residues in soil and assess the ecological risk of single and pesticide mixtures to soil biota, 3) monitor levels of pesticide residues in particulate (residential dust) and gaseous (silicone wristbands) phases in the indoor-outdoor nexus under rural setting, and 4) assess the probabilistic health risks of particulate and gaseous pesticide residues to local farmers and bystanders by integrating personal pesticide exposure profiles.

In **Chapter 2**, pesticide application patterns in wheat-maize rotation, vegetables and apple producing fields, were studied by interviewing farmers (197 respondents) in Quzhou County, the North China Plain. The potential misuse of pesticides was assessed by comparing the actual applied amounts to the recommended doses. Further, the risk quotient (RQ) based Bee-REX model was used to assess the exposure risks of pesticide residues to bees based on pesticide application data. The results showed that over half of interviewed farmers have misused pesticides, and in particular orchard owners showed the highest frequencies of misusing pesticides. Positive correlations were found between pesticide usage performance and farmers' specialized training experience related to pesticides. Forty-two pesticides, making up in total 88 types of mixtures, were

used by farmers in the study region. Pesticides applied in orchards have caused higher exposure risks to bees than in the other crops via acute contact and dietary ingestion. Pesticide misuse significantly elevates the exposure risk to bees with the mean RQ in misuse scenarios 5 times higher than that in correct use scenarios. Insecticides, including abamectin, fipronil and neonicotinoids, contributed most to the pesticide exposure risk to bees. The main findings of this study imply that more sustainable pest and pollinator management strategies, including the suspension of high-risk insecticide usage, and efforts towards integrated pest management that provides diverse flower resources and habitats, are highly needed. Additionally, measures such as farmer education through training programs should also be put on the agenda.

In **Chapter 3,** we studied the concentration of 15 commonly used pesticide residues in the topsoil of 41 fields in Quzhou county in the NCP. The ecological risks of pesticides to the soil biota, including earthworms, enchytraeids, springtails, mites and nitrogen mineralising microorganisms, were assessed using toxicity exposure ratios (TERs) and risk quotient (RQ) methods. Based on pesticide residue concentrations in the soils and RQs, pesticides were ranked in terms of ecological hazard using a Hasse diagram based on their ecotoxicities and detection frequencies in soil. The results show that pesticides were concentrated in the soil at 0–2 cm 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 chronic exposure risks to E. fetida, F. candida and E. crypticus, with TERs exceeding the corresponding trigger values by 2-3 orders of magnitude. 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 490 times higher than the high-risk threshold. 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 mitigation solutions are recommended, in which the use of hazardous pesticides would be replaced with low-risk pesticides with similar functions (as characterized by the Hasse diagram), or with biopesticides.

In **Chapter 4**, we screened pesticide residues in dust (indoor and outdoor) collected from the homes and yards of farmers (21 participants) and bystanders (14 participants) living in Quzhou County in the North China Plain, to assess the health risks related to the chronic exposure to pesticide-contaminated dust. The results showed that multiple pesticide residues were presented in the dust samples and that more than 90% of the samples contained over 10 pesticide residues. More residues, and higher concentrations of pesticide residues, were detected in indoor dust in farmer's homes than in bystanders' homes. The maximum detected number of residues was 23, out of the 25 pesticides currently used in the farming area. More residues and higher concentrations of pesticides were detected in indoor dust compared to outdoor dust. The concentrations of carbendazim, dimethomorph, dimethomorph and pendimethalin in paired indoor-outdoor dust samples were significantly correlated. The highest hazard index (HI) was found for children under indoor exposure. In addition, pesticide preparation practices in the home were found to be significantly correlated with farmers' indoor pesticide exposure level. Therefore, farmers should take precautionary measures, such as preparing pesticides outside of the house or in the open fields while using protective equipment, in order to decrease the exposure risk of pesticides associated with dust.

In **Chapter 5**, residential dust and silicone wristbands (placed at outdoor locations and worn by the participants) were used to screen pesticides in different phases via indoor-outdoor nexus to identify personal exposure risks in intensive agricultural areas. Both farmers (21 participants), and bystanders (14 participants) who do not participate in agricultural activities, were recruited for the sampling campaign and exposure measurements. Monte-Carlo Simulation was performed to assess the probabilistic exposure risk by transforming adsorbed pesticide residues from wristbands into atmospheric concentrations, which is a new approach for integrating residential (both indoor and outdoor) exposures to particulate (indoor dust) and gaseous (silicone wristbands) pesticides. The results showed that particulate bound pesticides were more concentrated indoors, whereas significantly higher concentration of pesticide residues in the gaseous phase were detected in stationary outdoor wristbands ($p < 0.05$). Carbendazim and chlorpyrifos were the most frequently detected pesticides in dust and stationary wristbands. Higher pesticide concentrations were found in personal wristbands worn by farmers than those worn by bystanders, with difenoconazole exhibiting the highest concentration at 2048 ng kg^{-1}. Based on the probabilistic health risk assessment, around 7% of farmers and 3% of bystanders in the local population were potentially suffering from related chronic health issues. One third of the pesticide exposures originated mainly from occupational sources, while the rest was derived from remote dissipation. Unexpectedly, 43 % of bystanders suffered the same levels of exposure as farmers under the co-existence of occupational and nonoccupational exposures. Differring compositions of pesticides were found in environmental samples and those observed in personal pesticide exposure patterns, highlighting the need for personal exposure measurements in determining health risks.

This thesis focuses on the pesticide usage patterns in the NCP and the environmental fate of pesticides from fields to the residential area. Furthermore, the personal exposure of pesticides to rural residents were characterized based on the combined sampling approaches. Findings of this thesis assesses exposure risks of pesticides in terms of human health and ecological functioning, and identifies the associated risk contributors, providing insights into the sustainable regional management of pesticides.

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About the author

Hongyu Mu was born on 11 May (12 April in Chinese Lunar calendar), 1995 in Rizhao, China. He obtained the BSc degree in Environmental Engineering in Shandong Agricultural University in June 2017. In the same year, he started the MSc program in Environmental Science and Engineering in China Agricultural University (CAU) and got the degree in June 2019. In September 2019, he joined the Soil Physics and Land Management (SLM) group in Wageningen University (WU) and started the PhD journey through the Sino-Dutch Agricultural Green Development (AGD) program. During the PhD study, he organized workshops with stakeholders and presented his research in both international and national conferences.

Publications

1. **Mu H**, Wang K, Yang X, et al. Pesticide usage practices and the exposure risk to pollinators: A case study in the North China Plain. **Ecotoxicol Environ Saf**. 2022;241:113713.
2. **Mu H**, Zhang J, Yang X, et al. Pesticide screening and health risk assessment of residential dust in a rural region of the North China Plain. **Chemosphere**. 2022;303 (Pt 2):135115.
3. **Mu H**, Yang X, Wang K, et al. Ecological risk assessment of pesticides on soil biota: An integrated field-modelling approach. **Chemosphere**. 2023;326:138428.
4. **Mu, H.**, Yang, X., Wang, K., Osman, R., Xu, W., Liu, X., Ritsema, C. J., & Geissen, V. (2024). Exposure risk to rural Residents: Insights into particulate and gas phase pesticides in the Indoor-Outdoor nexus. **Environment international**, 184, 108457.

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D I P L O M A

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educational PhD programme of SENSE.

Wageningen, 5th of June 2024

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The SENSE Research School declares that **Hongyu Mu** has successfully fulfilled all requirements of the educational PhD programme of SENSE with a work load of 37.0 EC, including the following activities:

SENSE PhD Courses

- Environmental research in context (2022)
- Research in context activity: "Organising a workshop for farmers titled 'Pesticide exposure risks from surrounding fields to the residential area: Implications for safe use and crop protection' (2023)

Other PhD and Advanced MSc Courses

- Personal leadership the basis of effective and efficient academic development, China Agricultural University and WUR (2019)
- Basic Statistics, PE&RC (2022)
- Linear Models, PE&RC (2022)
- Mixed Linear Models, PE&RC (2022)
- Scientific writing, Wageningen Graduate Schools (2022)
- Project and Time Management, Wageningen Graduate School (2023)

External training at a research institute

- Pesticide extraction of samples in complex matrices, Wageningen Food Safety Research (2022)
- Instrumental analysis based on LC-MS/MS, Wageningen Food Safety Research (2022)

Oral Presentations

- *Human exposure to pesticide residues in the soil-atmosphere nexus.* Agricultural Green Development Symposium, 1-3 December 2020, Haikou.
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