Environment International 182 (2023) 108342

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Full length article

Spatial-temporal distribution and potential risk of pesticides in ambient air in the North China Plain

Mingyu Zhao [a], Junxue Wu [b,*], Daniel M. Figueiredo [c], Yun Zhang [d], Ziyu Zou [b], Yuxuan Cao [a], Jingjing Li [a], Xue Chen [a], Shuping Shi [a], Zhiyun Wei [f], Jindong Li [e,f], Hongyan Zhang [d], Ercheng Zhao [b], Violette Geissen [g], Coen J. Ritsema [g], Xuejun Liu [a], Jiajun Han [d,*], Kai Wang [a,*]

[a] State Key Laboratory of Nutrient Use and Management, College of Resources and Environmental Sciences, National Academy of Agriculture Green Development, National Observation and Research Station of Agriculture Green Development (Quzhou, Hebei), China Agricultural University, Beijing 100193, China
[b] Institute of Plant Protection, Beijing Academy of Agriculture and Forestry Science, Beijing 100097, China
[c] Institute for Risk Assessment Sciences, Utrecht University, 3584 CM Utrecht, Netherlands
[d] Innovation Center of Pesticide Research, Department of Applied Chemistry, College of Science, China Agricultural University, Beijing 100193, China
[e] Shanxi Center for Testing of Functional Agro-Products, Shanxi Agricultural University, Taigu 030801, China
[f] Xinzhou Center for Disease Control and Prevention, Xinzhou 034099, China
[g] Soil Physics and Land Management Group, Wageningen University & Research, 6700 AA Wageningen, Netherlands

ARTICLE INFO

Handling Editor: Xavier Querol

Keywords:
Atmospheric pesticides
Spatial-temporal distribution
Crop systems
Health risk assessment
North China Plain

ABSTRACT

The intensive use of pesticides in the North China Plain (NCP) has resulted in widespread contamination of pesticides in the local atmosphere, posing risks to air quality and human health. However, the occurrence and distribution of atmospheric pesticides in the NCP as well as their risk assessment have not been well investigated. In this study, 300 monthly samples were collected using passive air samplers with polyurethane foam at ten rural sites with different crop systems in Quzhou county, the NCP, from June 2021 to May 2022. The pesticides were quantified using mass-spectrometric techniques. Our results revealed that chlorpyrifos, carbendazim, and atrazine were the most frequently found pesticides in the air samples, with detection frequencies of ≥ 87 % across the samples. The average concentrations of atmospheric pesticides during spring (7.47 pg m^{-3}) and summer (16.05 pg m^{-3}) were significantly higher than those during autumn (2.04 pg m^{-3}) and winter (1.71 pg m^{-3}), attributable to the intensified application of pesticides during the warmer seasons. Additionally, cash crop sites exhibited higher concentrations (10.26 pg m^{-3}) of atmospheric pesticides compared to grain crop (5.59 pg m^{-3}) and greenhouse sites (3.81 pg m^{-3}), primarily due to more frequent pesticides spraying events in cash crop fields. These findings indicate a distinct spatial–temporal distribution pattern of atmospheric pesticides influenced by both seasons and crop systems. Furthermore, the model-based inhalation risk assessment indicates that inhalation exposure to atmospheric pesticides is unlikely to pose a significant public concern.

1. Introduction

Pesticides play a crucial role in modern agricultural practices, mitigating the detrimental effects of diseases, pests, and weeds on crop growth to meet the increasing food demand of human society (Oerke, 2006). However, in the context of intensive agricultural production, farmers often apply multiple pesticides to address the complex composition of agro-ecosystems and manage resistance, leading to the occurrence of pesticides residue cocktails (Geissen et al., 2021; Silva et al., 2019). China is the largest consumer of pesticides in the world, with the application of approximately 1.8 million tons of pesticides in 2021 (FAO, 2021). The intensity of pesticides application in Chinese farmland in 2021 was 13.07 kg per hectare, significantly exceeds the recommended threshold of 7.65 kg per hectare set by the National Agricultural Green Development Index (FAO, 2021). Consequently, the excessive use of pesticides has resulted in a high level of concern due to the risk of pesticides contamination in China (Tang et al., 2021).

The efficiency of pesticides application in China (around 40 %) is relatively lower compared to 50–70 % in the United States and European countries (Dekeyser et al., 2014; Wang et al., 2021a; Wolters et al.,

* Corresponding authors.
E-mail addresses: wuxue0728@126.com (J. Wu), hanjiajun1990216@126.com (J. Han), kaiwang_ly@cau.edu.cn (K. Wang).

https://doi.org/10.1016/j.envint.2023.108342
Received 1 September 2023; Received in revised form 27 October 2023; Accepted 20 November 2023
Available online 23 November 2023

2008). This indicates that only a limited portion of applied pesticides reaches the target site and effectively acts on the crops (Metcalf, 1980). Substantial quantities of pesticides enter the environment through spray drift, volatilization, leaching, and runoff, subsequently undergoing migration, accumulation, and even transformation into highly toxic and persistent by-products (Boxall et al., 2004; Yang et al., 2016; Zhang et al., 2010). Pesticides contamination has the potential to disrupt ecosystems, posing hazards to mammals, birds, fish, insects, microorganisms, and humans (Beketov et al., 2013; Rani et al., 2021; Sanchez-Bayo, 2014).

The atmosphere plays a vital role as a carrier for the dissemination of pesticides within the environment (Degrendele et al., 2016; Qu et al., 2019). In general, the levels of pesticides residues in the environment tend to decrease with increasing distance from the spray site towards non-target areas (Figueiredo et al., 2021). However, direct volatilization and wind erosion facilitate the long-range atmospheric transport of pesticides in the form of gas-phase and particle-phase substances carried by air currents (Qu et al., 2019; von Waldow et al., 2010). As a result, pesticides can be transported from agricultural fields to nearby communities or even remote regions. In recent years, pesticides have been frequently detected in the ambient air around the world. Chlorpyrifos and eight pyrethroids were detected in the air samples collected in different seasons from an urban community in South China with the total concentrations in the range of 150 to 3816 pg m^{-3} (Li et al., 2014). The atmospheric concentrations of 36 current-use pesticides were measured in the Great Lakes basin ranged from 6 to 339 pg m^{-3} (Wang et al., 2021b). In a previous study using passive air sampling technics, the occurrence and seasonal variations of ten pesticides in the ambient air were assessed in Italy with the individual concentrations ranged from 0.2 to 1500 pg m^{-3} (Estellano et al., 2015). Several atmospheric pesticides have been quantified in Costa Rica (143 pg m^{-3}) and Uganda (34.5 pg m^{-3}) in 2019, including 21 organochlorine pesticides and 14 current use pesticides (Wang et al., 2019). To gain a comprehensive understanding of atmospheric pesticides, several cross-regional sampling networks have been established, employing consistent analytical procedures. For instance, the Global Atmospheric Passive Sampling Network has been successful in assessing global trends in airborne organochlorine pesticides since 2005 (Pozo et al., 2006; Schuster et al., 2021), while the Integrated Atmospheric Deposition Network has quantified atmospheric pesticides in the Great Lakes basin (Wang et al., 2018b; Wang et al., 2021b). Considering the significant health risks associated with the inhalation of pesticides suspended in the air, attention should be given to the issue of airborne pesticides pollution in China.

Quzhou county is situated in the central North China Plain (NCP), encompasses a population of 480,000 and approximately 48,000 ha of farmland, accounting for 82.5 % of the total area. The local climate, crop composition, and farming practices of Quzhou are consistent with the prevailing conditions observed in the majority of grain-producing regions located in northern China. As a representative agricultural region, conducting studies on atmospheric pesticides in Quzhou can contribute to a better understanding of the distribution patterns, pollution characteristics as well as their impact on the ecological environment and the health risks posed to residents in the NCP. Therefore, we conducted a comprehensive assessment of atmospheric pesticides in Quzhou from June 2021 to May 2022 based on 66 widely used pesticides in the local farming systems. This study aimed to achieve the following objectives: 1) identify the common mixtures of co-contaminated pesticides present in the ambient air of Quzhou; 2) explore the seasonal and spatial variations of atmospheric pesticides across Quzhou; and 3) assess the potential risks of atmospheric pesticides to residents and wildlife in Quzhou, as well as evaluate the primary sources of these risks.

2. Materials and methods

2.1. Chemicals and reagents

Target pesticides include 40 insecticides, 22 fungicides, and 4 herbicides. Analytical standards for the 66 pesticides were purchased from Alta Scientific Co., Ltd (Tianjin, China). HPLC-grade acetonitrile, methanol, n-hexane, and formic acid (purity $\geq$ 98.0 %) were acquired from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water was prepared using a Milli-Q system (Bedford, MA, USA). Detailed information on the analytes can be found in Table S1 in the supplementary material.

2.2. Air sampling

Air samples were collected using a passive air sampler (PAS) with a polyurethane foam (PUF) as the sampling medium. The PUF disks (PUFs, 14 cm diameter and 1.35 cm thick) were used to collect atmospheric pesticides at ten rural environmental monitoring sites located in ten villages in Quzhou, the NCP (see Fig. S1). Prior to deployment, PUFs were pre-cleaned by ultrasonic extraction with acetonitrile and n-hexane for 1 h in each solvent. The pre-cleaned PUFs were then deployed for approximately one month between 5 June 2021 and 31 May 2022, resulting in a total of 10 sampling periods. The seasons were defined as follows: March to May (spring), June to August (summer), September to November (autumn), and December to February (winter). The PAS devices were positioned 2 m above the ground and enclosed by a fence to prevent direct spraying of pesticides. Three replicates were used at each sampling site to assess sampling reproducibility. Following monthly exposure, all PUFs were retrieved and stored at –20 °C in the dark until analysis. The detailed information on deployment periods is presented in Table S2.

2.3. Sample extraction and instrumental analysis

A generic extraction method using ultrasonic-assisted extraction with methanol was developed for the extraction of pesticides from PUF samples. PUFs were extracted at 25 °C for 1 h in 100 mL methanol. Subsequently, 80 mL of the extracts were concentrated using rotary evaporation (R-215, Buchi Corporation, Switzerland) at 40 °C and then re-dissolved with 2 mL of acetonitrile. The extracts were cleaned up using a C_{18} solid-phase extraction column, which was activated with 5 mL acetonitrile and 5 mL ultra-pure water, respectively. The column was loaded with 2 mL of the extracts and eluted with an additional 2 mL of acetonitrile. A total of approximately 4 mL of eluate was collected and reduced to 0.8 mL using a rotary evaporator, as described above. The resulting extracts were filtered through a 0.22 μm nylon filter into a vial for subsequent instrumental analysis. Extracts were analyzed using a Waters ACQUITY TQD ultra-high performance liquid chromatography system coupled with a triple-quadrupole mass spectrometer (UHPLC-MS/MS) for 38 pesticides and an Agilent 7890B gas chromatograph coupled with an Agilent 7000C tandem mass spectrometer (GC–MS/MS) for 28 pesticides. Details on the UHPLC-MS/MS and GC–MS/MS methods are provided in Text S1, Table S3 and Table S4.

2.4. Quality assurance and quality control

Quality control was performed using procedural blanks and spike recovery samples. The blanks were briefly exposed to the sampling environment and processed in the same way as the analytical samples. None of the target pesticides were detected in the blank samples. The limits of quantitation (LOQs) were determined based on the average concentrations of the blanks plus three times the standard deviation of the blanks. The recoveries of the 66 target pesticides ranged from 44.4 % ± 4.8 % to 107.9 % ± 9.4 %. For nitenpyram, thiophanate-methyl, mesotrione, and trifloxystrobin, recoveries of these pesticides were relatively low, ranging from 44.4 % ± 4.8 % to 47.9 % ± 5.9 %, which led to a potential underestimation of concentrations. Detailed parameters regarding the method performance can be found in Table S5.

2.5. Calculation of pesticide concentration in ambient air

The concentrations (C_{air}, pg m^{-3}) of detected pesticides in ambient air were calculated by dividing the quantity of pesticides trapped by the PUF disk (m_{PUF}, pg PUF^{-1}) by the equivalent air volume (V_{air}, m^3) during each sampling period (Eq. (1).

$$C_{air} = m_{PUF}/V_{air} \quad (1)$$

where C_{air} is the concentration of each individual pesticide in ambient air during the sampling period (pg m^{-3}), m_{PUF} is the mass of detected pesticide in each PUF disk (pg PUF^{-1}), and V_{air} is the equivalent air volume (m^3) calculated using Eq. (2).

$$V_{air} = R \times t \quad (2)$$

where R is the sampling rate of the passive air sampler (m^3 d^{-1}) and t is the number of days during the deployment period (d). In this study, a generic sampling rate of 4 m^3 d^{-1} was used, which is supported by previous studies (Ahrens et al., 2013; Francisco et al., 2017). A sensitivity analysis was performed using a lower limit of 2 m^3 d^{-1} and an upper limit of 8 m^3 d^{-1} for the sampling rate, considering the effect of environmental factors (e.g., air flow) and sampler configuration (e.g., chamber design) (refer to Table S6).

2.6. Inhalation health risk to residents from atmospheric pesticides

The health risk of pesticides involved comparing the exposure dose with an appropriate health criterion (Murphy and Haith, 2007). In this study, the average daily dose via inhalation (ADD) was calculated using the United States Environmental Protection Agency (USEPA) exposure assessment tool (Eq. (3) (USEPA, 2019).

$$ADD = (C_{air} \times R_b)/(bw \times 10^9) \quad (3)$$

where ADD is the average daily dose via inhalation (mg kg^{-1} d^{-1}), R_b is the breathing rate (m^3 d^{-1}), and bw is the body weight (kg). In this study, standard reference R_b and bw for infants ($R_b = 5.4$, bw = 9.2), children ($R_b = 12$, bw = 31.8), and adults ($R_b = 16$, bw = 80) were used based on the exposure factors handbook (EFH) (USEPA, 2011). The factor "10^9" is used to convert pg m^{-3} to mg m^{-3}.

The ADD was then compared to the reference dose, which is considered the threshold of daily exposure dose. Recommended acceptable daily intake (ADI) value obtained from toxicological assessments was used here. The health risk was expressed as the hazard quotient (HQ, Eq. (4) for individual pesticide and the hazard index (HI, Eq. (5) for cumulative pesticides.

$$HQ = ADD/ADI \quad (4)$$

$$HI = \sum HQ \quad (5)$$

where HQ is the hazard quotient, ADI is the acceptable daily intake, and HI is the hazard index. The HI is calculated as the sum of the HQs of all detected pesticides in a given sampling period using the concentration-addition (CA) method. A value of HQ or HI above the toxicological threshold of "1″ indicates an unacceptable health risk caused by inhalation exposure of individual pesticides or total pesticides, respectively. The recommended ADI values for the target pesticides are available from the Pesticides Properties Database (PPDB) (refer to Table S7) (PPDB, 2023).

2.7. Inhalation health risk to wildlife from atmospheric pesticides

The inhalation risk assessment for potential health risks of atmospheric pesticides to avian and mammalian species was performed using the Screening Tool for Inhalation Risk (STIR) model developed by USEPA. By comparing the inhalation exposure estimates of pesticides with animal toxicity data, the model will be used to determine whether further analysis is necessary to evaluate potential risks through inhalation (USEPA, 2010a). The maximum inhalation dose (ID) was calculated as follows (Eq. (6).

$$ID = (C_{air} \times IR \times D)/\left(Aw \times 10^6 \times 10^9\right) \quad (6)$$

where ID is the maximum inhalation dose (mg $kg^{-1}h^{-1}$), IR is the inhalation rate of the assessed animal (cm^3 h^{-1}), D is the duration of exposure (h), and Aw is the body weight of the assessed animal (kg). Here, bobwhite quail (IR = 2514, Aw = 0.178) and rat (IR = 2370, Aw = 0.35) were selected as representatives of avian and mammalian for further risk assessment (USEPA, 2010b), D is 1 h. The factor "10^6" is used to convert cm^3 h^{-1} to m^3 h^{-1}, and the factor "10^9" converts the pg m^{-3} to mg m^{-3}.

For the toxicity endpoints, adjusted inhalation LD_{50} values (LD_{50adj}, mg kg^{-1} bw) for avian and mammalian species were estimated by applying the relationship between mammalian oral and inhalation LD_{50} values to the most sensitive avian oral LD_{50} value. Detailed information was provided in the STIR user guide (USEPA, 2010b). The ratio of the ID to the LD_{50adj} was calculated (Eq. (7) and then compared to the threshold value of "0.1", which is intended to be protective of all avian and mammalian species conservatively.

$$R_a = ID/LD_{50adj} \quad (7)$$

where R_a is the ratio of the maximum inhalation dose to the toxicity endpoint, LD_{50adj} is the adjusted inhalation LD_{50} value (mg kg^{-1} bw). A value of R above the toxicological threshold of "0.1" indicates that the available screening methodology cannot dismiss the potential for inhalation risk to wildlife. Animal toxicity data are available from the ECOTOX knowledgebase and PPDB (refer to Table S7) (PPDB, 2023; USEPA, 2023).

2.8. Data analysis

Statistical analyses were performed using R 4.1.2 (RStudio version 2022.12.0 + 353) and Microsoft excel 2019. Spearman correlation analysis was employed to assess potential correlation between the target pesticides. Statistical tests were considered significant at a two-tailed p-value < 0.05. Concentrations below the LOQs were treated as not detected but counted as a value of LOQ/2 in the health risk assessment for residents and wildlife (Mu et al., 2022). Plots were generated using R.

3. Results and discussions

3.1. Detections of pesticides in ambient air

The summarized statistics of concentration and detection frequency for the quantified pesticides are given in Table S8a and Table S8b. From June 2021 to May 2022, all PUF samples contained at least one pesticide residue. Thirty-two pesticides were detected during the sampling period, including fifteen fungicides, thirteen insecticides, and four herbicides. It is noteworthy that each of the thirty-two quantified pesticides is registered for use on at least one crop existing in Quzhou (MOA, 2023). The detection frequencies of these pesticides varied from 1 % (azoxystrobin) to 100 % (chlorpyrifos). The concentration of total pesticides during the sampling period between June 2021 and May 2022 ranged from 0.59 to 25.95 pg m^{-3}. The geometric mean concentrations of individual pesticide in ambient air ranged from 0.001 to 3.84 pg m^{-3}. The concentrations measured in this study were lower than the concentrations of 140–6409 pg m^{-3} in central China at Wuhan (Zhan et al., 2021) and of 150–3816 pg m^{-3} in South China at Guangzhou (Li et al., 2014), but similar to that measured of ND–27.25 pg m^{-3} in Southeast China at Pingtan (Jiao et al., 2018) and of 33.6–271 pg m^{-3} in Western China at

Sichuan basin (Huang et al., 2019). Notably, chlorpyrifos exhibited the highest concentration of 3.84 ± 5.37 pg m^{-3}, followed by atrazine and carbendazim of 1.36 ± 4.16 pg m^{-3} and 0.26 ± 0.42 pg m^{-3}, respectively. Insecticides were found to be the most abundant class of pesticides in the atmospheric samples collected from Quzhou, with an average concentration of 4.19 ± 5.51 pg m^{-3}, which was significantly higher than herbicides (1.42 ± 4.12 pg m^{-3}) and fungicides (1.21 ± 4.50 pg m^{-3}). Fig. 1 shows the categorization of the detected pesticides and ranked according to the detection frequency, and provides insights into the contribution of different pesticides types. Chlorpyrifos was detected in 100 % of the PUF samples, followed by carbendazim (97 %), atrazine (87 %), and dimethomorph (67 %). The detection frequencies of tebuconazole, chlorobenzuron, imidacloprid, propamocarb, pyraclostrobin, dichlorvos, acetamiprid, thiamethoxam, and pymetrozin ranged from 32 % to 64 %. The detection frequencies of the remaining nineteen pesticides were below 22 %. Among all 1227 quantifications, 549 were fungicides, accounting for 45 % of the total, while insecticides and herbicides accounted for 44 % (537) and 11 % (141), respectively.

The most frequently detected pesticides in the ambient air were chlorpyrifos, carbendazim, and atrazine, with detection frequencies exceeding 89 %. Interestingly, these prevalent pesticides belong to the categories of insecticides, fungicides, and herbicides, respectively, suggesting a potential uniformity in the selection of specific types of pesticides by farmers in Quzhou.

Chlorpyrifos is a highly influential insecticide that has been extensively used in various agricultural systems (Racke, 1993). Consequently, chlorpyrifos holds considerable significance in environmental monitoring. In this study, the atmospheric concentrations of chlorpyrifos ranged from 0.18 to 29.41 pg m^{-3}. These findings are comparable to concentrations reported in central China (0.18–69.4 pg m^{-3}) and the United States (0.1–2.2 pg m^{-3}) (Wang et al., 2021b; Zhan et al., 2021), but lower than those reported in Uganda (1.9–42 pg m^{-3}), Italy (3–580 pg m^{-3}), South Africa (10–16202 pg m^{-3}), and Chile (229.4–3470.2 pg m^{-3}) (Climent et al., 2019; Estellano et al., 2015; Veludo et al., 2022; Wang et al., 2019). The observed regional variation can be attributed to policy impacts. USEPA initiated restrictions on the application of chlorpyrifos in 2000 and eventually banned it completely in 2019. Similarly, China has prohibited the use of chlorpyrifos in vegetable cultivation since 2017, and all permits are expected to be revoked by 2023. Considering the substantial environmental accumulation of chlorpyrifos and its significant hazards, continuous monitoring of chlorpyrifos levels remains crucial in the foreseeable future.

Carbendazim is a broad-spectrum systemic fungicide, which was the most frequently quantified fungicide in the region. The concentrations of carbendazim in ambient air ranged from 0.04 to 0.89 pg m^{-3} in Quzhou. Prior to this study, there was one report on the atmospheric concentration of carbendazim at rural sites in Spain in 2007, which showed the values ranging from 41 to 572 pg m^{-3} (Coscolla et al., 2008). The concentrations observed in our study were significantly lower than those reported in Spain, but similar than levels obtained in Czech Republic (ND–12.5 pg m^{-3}) (Degrendele et al., 2016). To the best of our knowledge, this is the first report on the presence of carbendazim in ambient air in China. However, due to its potential carcinogenicity and genotoxicity, carbendazim has been prohibited in certain countries, including the United States and Europe. Consequently, most environmental monitoring programs exclude carbendazim from their target lists.

Atrazine is one of the most widely used herbicides in maize fields, but was removed as an option for European farmers when it failed to obtain re-registration in Europe in 2003. This exclusion is also reflected in the variation of atmospheric concentrations observed in different regions. Atmospheric concentrations of atrazine were found to be at similar levels in China (ND–24.86 pg m^{-3} in this study) and the United States (0.6–15 pg m^{-3}) (Wang et al., 2021b), both of which are major corn-producing regions. Furthermore, atrazine was also detected in South Africa at comparable concentrations ranging from ND to 76 pg m^{-3} (Veludo et al., 2022).

3.2. Seasonal variations of pesticide concentrations across Quzhou

Seasonal variations in the concentrations of the 32 pesticides in ambient air are presented in Fig. 2. Generally, higher concentrations

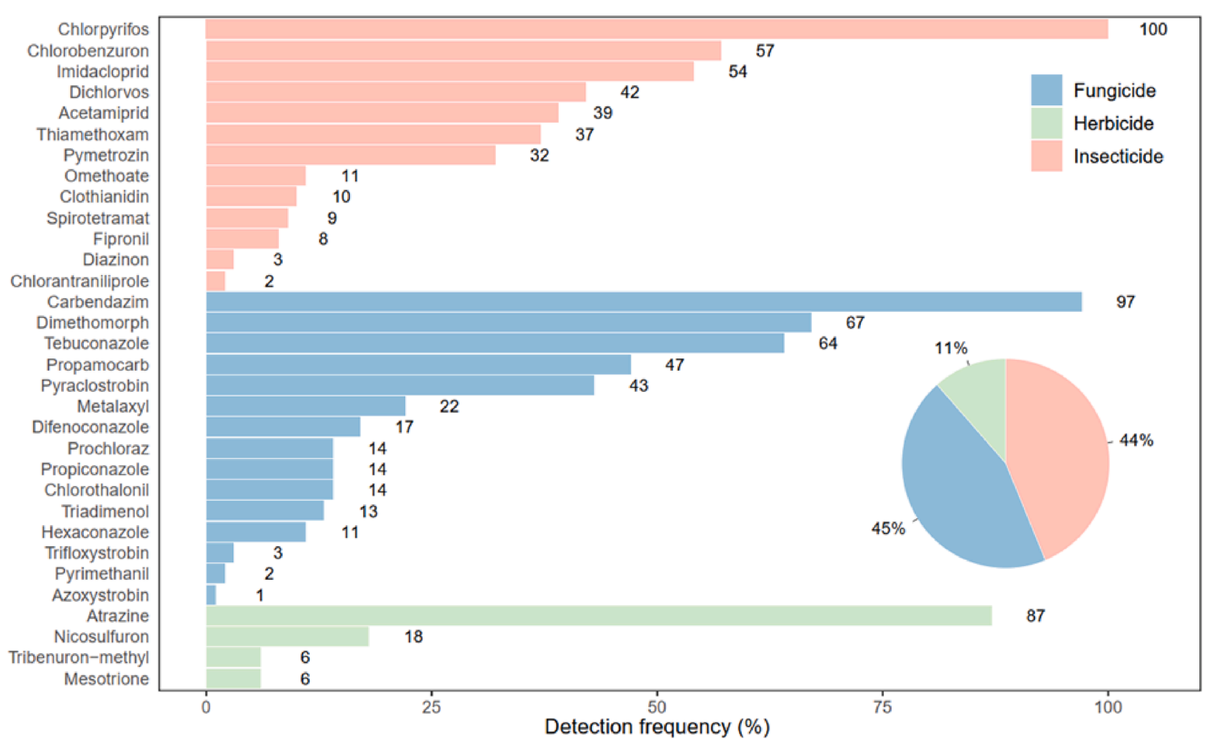

Fig. 1. Detection frequency (%) and proportion (%) of quantified pesticides in 2021/2022 using PUF-PAS. The contribution of different types of pesticides is shown in the pie chart. The detailed detection frequency is displayed at the top of the corresponding column. Different colors indicate different types of pesticides.

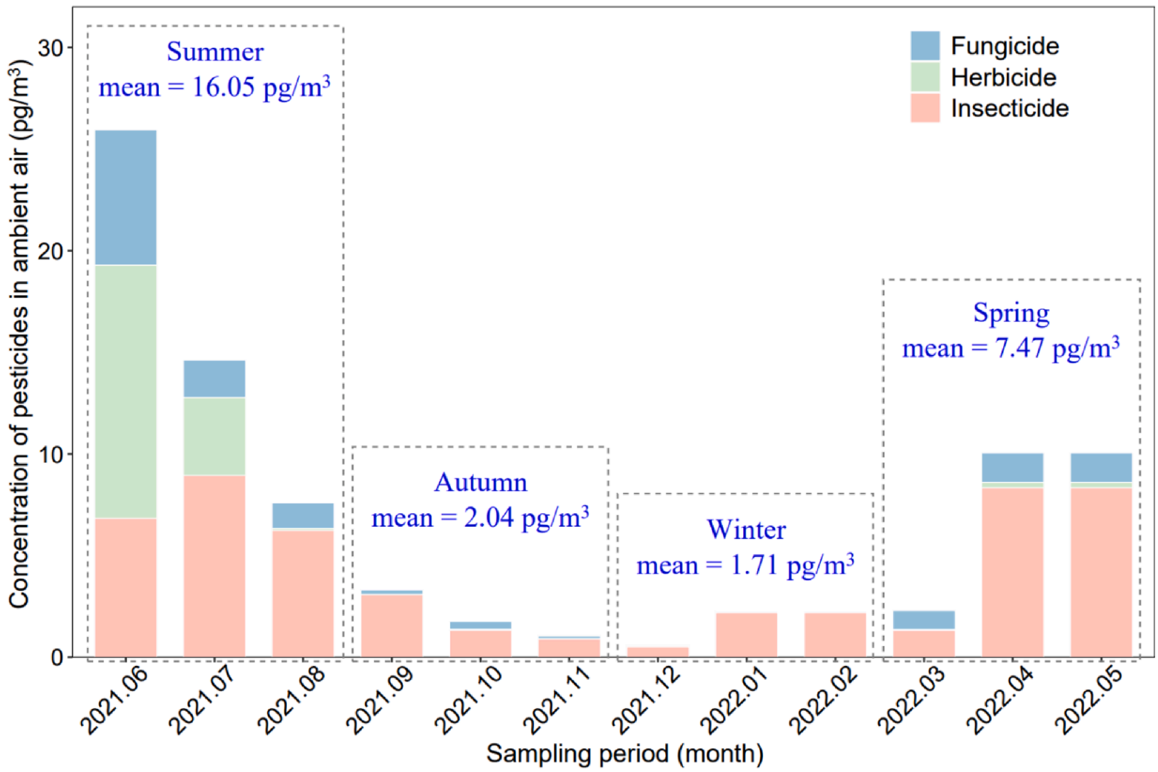

Fig. 2. Total concentration of pesticides in ambient air in different months in 2021/2022. The geometric mean concentrations during the season are shown in the plot. Different colors indicate different types of pesticides.

were observed during the warm seasons (i.e. March to August). The concentration of total atmospheric pesticides was significantly higher in summer (16.05 ± 12.58 pg m^{-3}) and spring (7.47 ± 7.23 pg m^{-3}) compared to autumn (2.04 ± 2.04 pg m^{-3}) and winter (1.71 ± 0.84 pg m^{-3}). The peak concentration of atmospheric pesticides occurred in June (25.95 ± 13.98 pg m^{-3}), followed by a gradual decrease until December (0.59 ± 0.22 pg m^{-3}), and a subsequent rise from January to May of the following year. In this study, the presence of herbicides was predominantly observed in June and July, while fungicides exhibited relatively high concentrations from March to August. Insecticides were consistently and predominantly detected in ambient air throughout most months of the year.

The variation in atmospheric concentrations of pesticides across seasons in Quzhou can be attributed to pesticides application strategies and temperature effects. Since spring and summer offer favorable light and temperature conditions for crop germination and growth, as well as serve as a prolific stage for pests and weeds, it is common practice to engage in active pesticide application during these seasons (Kumar et al., 2023). For instance, maize cultivation involves sowing in early June, with emergence occurring in the middle to late part of June. During this period, farmers often apply herbicides such as atrazine or nicosulfuron to control weeds which compete with seedlings for nutrients (Loddo et al., 2020). In our study, we observed the highest concentration of atrazine in June, reaching 24.86 pg m^{-3}. It has been reported that there is a positive correlation between the occurrence of pests and diseases and temperature (Tubiello et al., 2007). The combination of heat and humidity during the warm seasons promotes pest and pathogen infestation, creating favorable conditions for their multiplication. As a result, farmers tend to apply larger quantities of pesticides during this period. The atmospheric concentration of total pesticides in the summer season was found to be 16.05 ± 12.58 pg m^{-3}, which was over nine times higher than that observed in winter. This finding confirms the pattern observed in other studies, where atmospheric concentrations of pesticides remain relatively high during periods of elevated temperatures (Peck and Hornbuckle, 2005).

3.3. Spatial variations of pesticide concentrations across Quzhou

A variety of agricultural production systems are carried out in Quzhou, including wheat/maize rotation, greenhouses, vineyards, cotton, and orchards, different crop systems are associated with varying pesticides use strategies. Consequently, a diverse combination of pesticides cocktails is present in the environment. In this study, the ten sampling sites were categorized into three groups: grain crop (i.e. wheat and maize including sampling sites of ES, DHD, NLY, WZ, YZ, and BZ), cash crop (i.e. vineyard, cotton, and orchard including sampling sites of AZ, HC, and HQX), and greenhouse with sampling site of YMY (see Fig. 3). The atmospheric concentrations of pesticides ranged from 0.31 to 40.73 pg m^{-3} at grain crop sites, 0.37 to 57.55 pg m^{-3} at cash crop sites, and 0.58 to 9.41 pg m^{-3} at the greenhouse site. The concentration of pesticides was significantly higher at cash crop sites (10.26 ± 12.97 pg m^{-3}) compared to grain crop sites (5.59 ± 7.17 pg m^{-3}) and the greenhouse site (3.81 ± 2.89 pg m^{-3}). Cash crop sites such as HQX (11.47 ± 11.94 pg m^{-3}), HC (10.24 ± 10.57 pg m^{-3}), and AZ (9.08 ± 15.73 pg m^{-3}) exhibited higher atmospheric concentrations. Although the concentrations detected at grain crop sites showed slight variations, they were significantly lower than those at cash crop sites. The greenhouse site had the lowest concentration among all the sampling sites, with a concentration of 3.81 ± 2.89 pg m^{-3}.

In previous studies, the spatial variation of pesticides has been primarily attributed to factors such as land use, population density, and human activities (Kolpin et al., 1998; Zaller et al., 2022). However, in this study, the crop system was identified as the key variable. It is well-known that pesticides are always carefully selected to address specific crops issue. Cash crops require more pesticides applications than grain crops, because they are more attractive to pests (Rosenheim et al., 2020). Consistent with this understanding, the results demonstrated higher pesticides residue levels at cash crop sites compared to grain crop

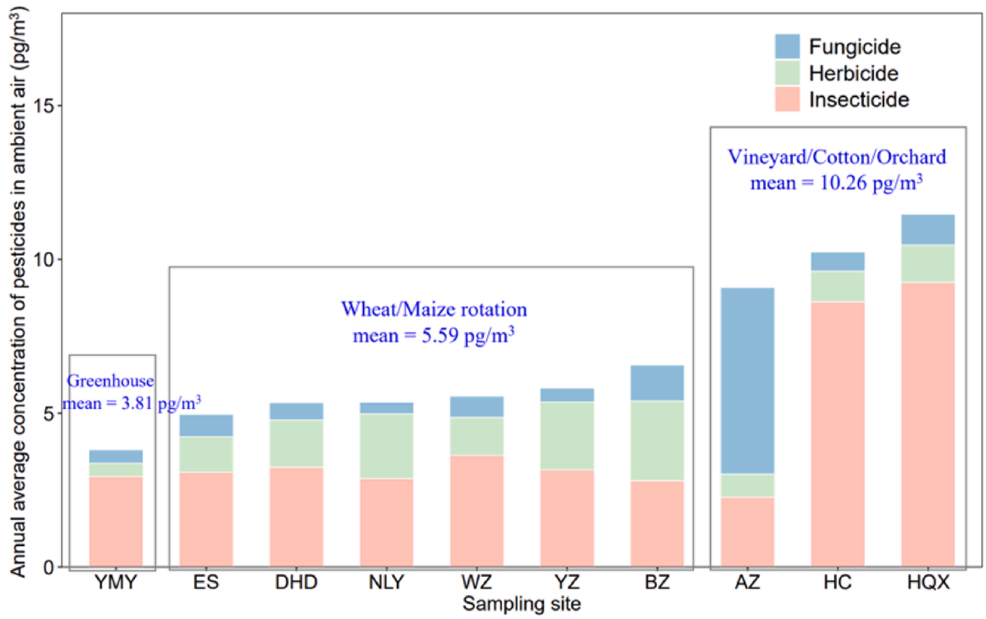

Fig. 3. The annual average concentration of pesticides in ambient air at different sampling sites in 2021/2022. The geometric mean concentrations of sampling sites attributed to the same category were shown in the plot. Different colors indicate different types of pesticides.

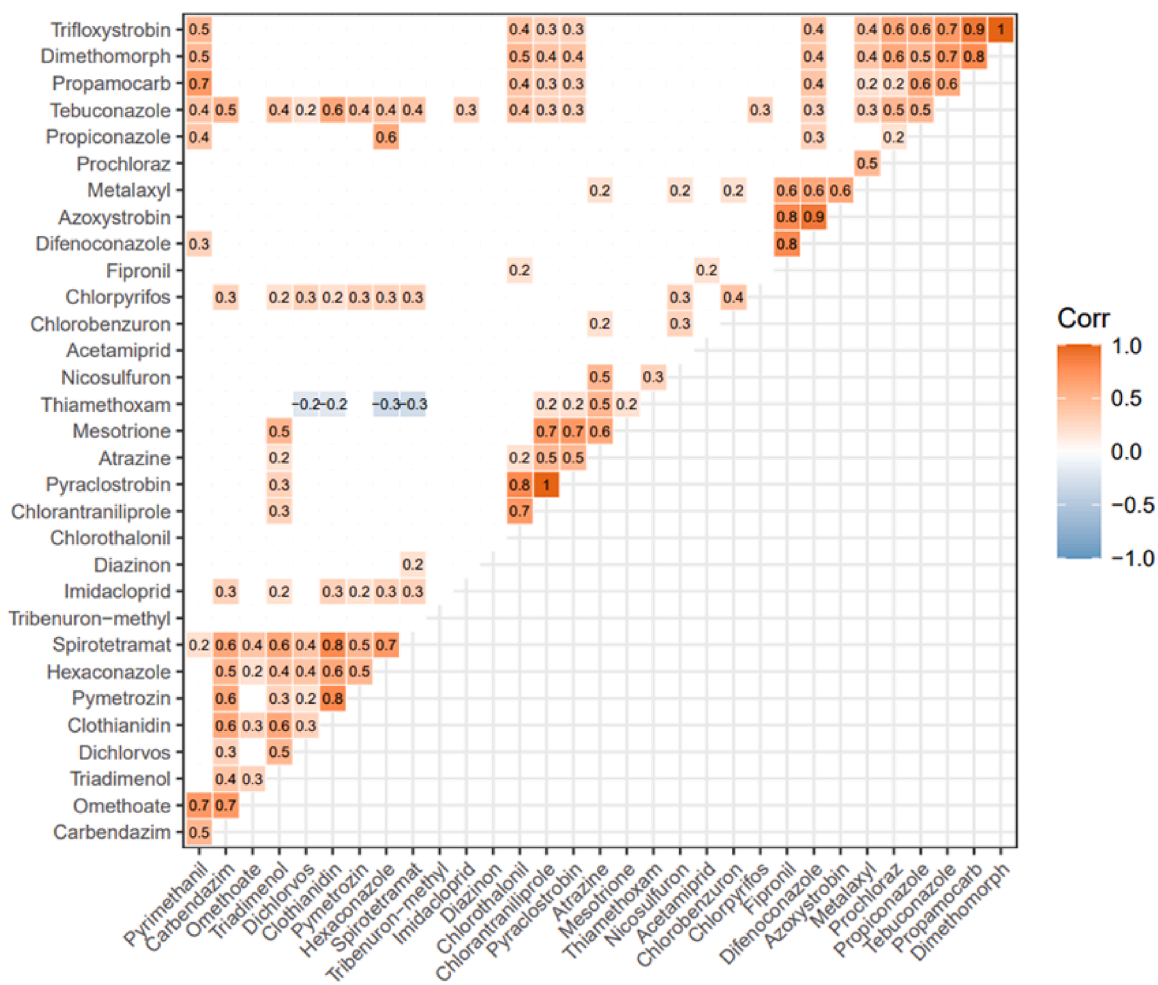

Fig. 4. Correlation plot using Spearman's correlation for targeted pesticides structured by hierarchical clustering. Orange and blue color represent significant positive correlations and negative correlations, respectively. Blank squares indicate that the correlations were not statistically significant. (p < 0.05). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sites. The lower pesticide concentrations at greenhouse sites can be explained by the fact that pesticides application events occur inside greenhouses with limited ventilation. Even if pesticides are transported into the air through drift, volatilization, or wind, most of them are trapped inside the greenhouse and cannot be captured by the passive air samplers deployed in the field. Interestingly, characteristic pesticides patterns were observed at specific locations. The AZ site, predominantly characterized by vineyards, showed a dominance of fungicides in the atmospheric pesticides composition, accounting for more than 66.7 % of the total pesticides. For the HC site (where cotton is cultivated) and the HQX site (which is closed to the orchard), insecticides were the most abundant pesticides, reflecting the key yield influencers and management practices of farmers in these crop systems. In contrast, grain crop sites exhibited similar concentrations (4.96–6.56 pg m^{-3}), indicating a consistent pesticides use strategy among farmers engaged in grain crop cultivation. Overall, the results highlight that atmospheric pesticides levels were higher at cash crop sites compared to grain crop sites, and the lowest concentrations observed at greenhouse sites can be attributed to the indoor spraying of pesticides. The cropping system plays a significant role in shaping the atmospheric pesticides patterns. Further research is warranted to identify key factors influencing atmospheric pesticides distribution and to deepen our understanding of their environmental impact.

3.4. Occurrence and distribution patterns of atmospheric pesticides

To explore the co-occurrence of targeted pesticides across Quzhou, correlation plots utilizing Spearman's correlation coefficients (Corr) were generated to investigate the strength and direction of correlations between pesticide concentrations (see Fig. 4). Strong positive correlations ($R_s > 0.6$) were identified within three clusters of pesticides, including a cluster of fungicide combinations (trifloxystrobin + dimethomorph + propamocarb + tebuconazole) and two clusters of insecticide/fungicide combinations (metalaxyl + azoxystrobin + difenoconazole + fipronil, and pyraclostrobin + chlorantraniliprole + chlorothalonil).

Several factors contribute to the presence of pesticides mixtures in the atmosphere, such as chemical volatility, pesticides stability in the environment, and the formulation of multiple active ingredients in plant protection products (Bedos et al., 2002; Das and Hageman, 2020). In this study, a positive correlation was observed among individual pesticide in the ambient air of Quzhou, with no significant negative clusters identified. The strong positive correlation between dimethomorph, propamocarb, and tebuconazole, with detection frequencies exceeding 47 %, suggests that farmers may employ these pesticides simultaneously to address common fungal pathogens. Fipronil is frequently applied in cotton and fruit fields during warm seasons for pest control, overlaps with the pesticides application period of metalaxyl and tebuconazole. Pyraclostrobin and chlorothalonil are commonly used together in several crop systems. Additionally, the use of pesticides mixtures can broaden the spectrum of targeted pathogens and prevent ineffective spraying due to individual resistance issue. Consequently, the simultaneous application of multiple pesticides contributes to a positive correlation among pesticides in the ambient air.

3.5. Health risk of inhalation exposure to residents and wildlife

Hazard quotients (HQ) associated with non-carcinogenic chronic health hazards of pesticides to residents and the ratio (R) of the maximum inhalation dose to the toxicity endpoint to wildlife are presented in Table S9. The results showed that all HQ values for individual pesticide were well below "1″, ranging from 1.08×10^{-8} to 2.26×10^{-3}, suggesting that the inhalation of individual pesticide is unlikely to cause chronic, non-cancerous health issues. Chlorpyrifos exhibited the highest HQ value of 2.26×10^{-3}, followed by dichlorvos and fipronil at 4.71×10^{-4} and 1.37×10^{-4}, respectively, while the HQ values for the remaining quantified pesticides were below 10^{-4}.

The HQ values indicate that individual pesticide present in the ambient air of Quzhou pose negligible risks to residents. This finding aligns with risk assessments conducted in the United States (9.3×10^{-14} to 5.8×10^{-3}) (Murphy and Haith, 2007), France (1.11×10^{-7} to 1.92×10^{-2}) (Coscolla et al., 2017), and South China (7.93×10^{-4} to 1.54×10^{-3}) (Li et al., 2014), where individual pesticide was deemed unlikely to pose threats to residents, even to infants with the highest inhalation-to-body weight ratio.

The hazard index (HI) for residents was calculated using the concentration-addition method as a conservative approach. Although spatial and seasonal variations in HI values were observed, no values exceeded "1″, indicating that current atmospheric pesticide concentrations are relatively safe for residents (see Fig. 5). Though all risk values observed in current study were below the toxicological thresholds of "1", it should be noted that two values greater than 0.01 were found in HQX (0.015 in summer) and HC (0.014 in spring) exhibiting relatively higher risks than other sites, primarily due to high concentrations of chlorpyrifos during those periods. Considering the significant influence of season and cropping systems on the presence of atmospheric pesticides, the risk of inhalation exposure of residents around cash crops during the warm season needs to be emphasized. Organophosphorus pesticides (OPPs), including chlorpyrifos (73.8 %), dichlorvos (15.4 %), omethoate (1.9 %), and diazinon (1.7 %), were identified as the main contributors to inhalation risks posed by atmospheric pesticides to residents, collectively accounting for 92.8 % of the HI (refer to Table S9).

To estimate the worst-case health risk for the population, a conservative approach was employed by cumulating individual hazard quotients through the concentration-addition method, assuming pesticides caused the same types of health hazards. This approach helps avoid unpredictable negative effects resulting from unknown hazard stacking (Backhaus, 2016; Spilsbury et al., 2020). Both concentrations and toxicity of pesticides play direct roles in determining health risks. Regarding the risk source of atmospheric pesticides in Quzhou, the presence of organophosphorus pesticides in the ambient air accounts for 53.8–99.1 % of the human health risk. As these pesticides are gradually banned in China, the health risk associated with atmospheric pesticides in Quzhou is expected to decrease significantly.

It should be noted that the absence of pesticide concentrations in the particle-phase limits our assessment and overlooks some potential exposure pathways, such as dust ingestion (Wang et al., 2018a). Consequently, the health risk value is underestimated for pesticides with low vapor pressure primarily distributed in the particle-phase, leading to a certain bias (Degrendele et al., 2016). Therefore, it is imperative to improve sampling techniques or utilize predictive models for gas-particle partitioning of semi-volatile organic compounds to calculate pesticide concentrations in the particle-phase, thereby obtaining more reliable health risk assessment outcomes.

The results obtained from the STIR model provide a screening-level evaluation of the need for further characterization of inhalation risks to animals associated with atmospheric pesticides. As shown in Table S9, the ratio of the maximum inhalation dose to the toxicity endpoint for quantified pesticides across Quzhou was considerably lower than the threshold value of "0.1". The range for avian species was 8.97×10^{-17} to 9.63×10^{-9} (median = 3.94×10^{-13}), while for mammalian species, it was 3.71×10^{-18} to 3.29×10^{-10} (median = 1.95×10^{-14}), indicating that the primary acute risk of the detected pesticides to avian and mammalian was acceptable. Existing studies evaluating inhalation exposure risks associated with atmospheric pesticides for wildlife are scarce, making it unreachable to compare our results with other researches. To our best knowledge, this is the first report to use field data for conducting inhalation risk assessment for wildlife. Considering the proven harm of pesticides pose to wildlife, we strongly recommend that more relevant research should be conducted to support wildlife conservation. Furthermore, the STIR model only performs for primary risk assessments, more accurate assessment results should be obtained

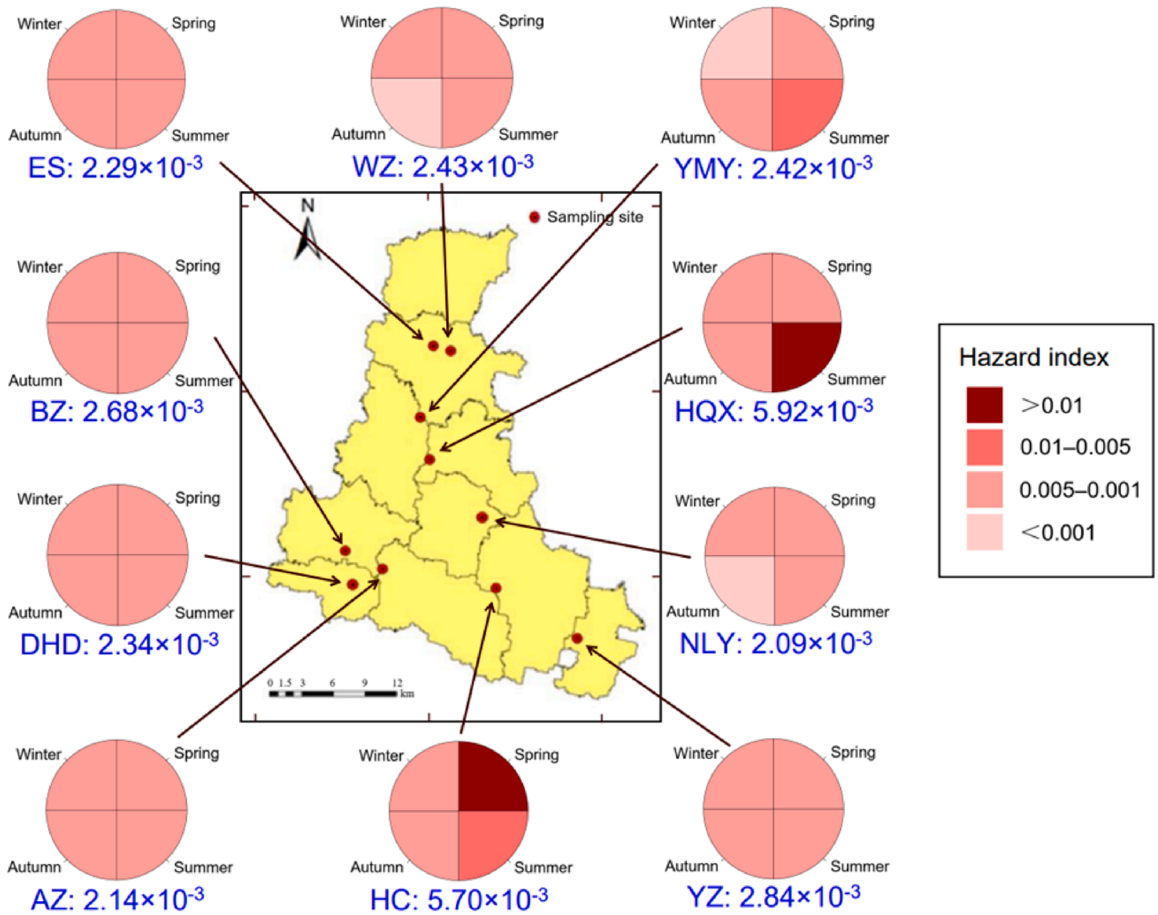

Fig. 5. Hazard index for the cumulative health risk of the atmospheric pesticides in different seasons at each sampling site. The annual average HI of each sampling site is presented below the corresponding pie chart. Different colors indicate different HI values.

through field investigations and toxicology experiments.

4. Conclusions

This study investigated the spatial and temporal distribution of atmospheric pesticides for a whole year in the rural region of Quzhou county, the North China Plain, an important agricultural region in China. Our monitoring work unveiled noteworthy contrasts in concentrations of atmospheric pesticide between the warm and cold seasons, alongside pronounced disparities across different cropping systems. Notably, cash crop sites exhibited significantly higher concentrations compared to other cropping systems. These findings raise pertinent concerns regarding potential exposure to composite atmospheric pesticide mixture during specific temporal and spatial contexts. Moreover, passive air sampling techniques are deemed suitable for monitoring atmospheric pesticides on a regional scale. Multi-site observation networks can be set up in other agricultural areas, such as grain production regions in Northeast China, rice production regions in South China, and tobacco/flower production regions in Southwest China, which are able to monitor atmospheric pesticides in different regions of China and to assess the efficacy of pollution control measures within the agricultural sector.

Interestingly, no values above toxicological thresholds were found in the results of the model-based risk assessment, suggesting that prevailing atmospheric pesticides levels are unlikely to pose imminent risks to human and mammalian. However, in the current study, only the parent compounds of pesticides were detected and their metabolites in the atmosphere were not investigated, which may be more or less toxic compared to the parent pesticides. Therefore, potential risks may still remain. In future work, laboratory smog chamber experiments could be conducted to study the environmental fate (i.e. oxidation process) of pesticides in the atmosphere, and related metabolites can be identified based on high-resolution mass spectrometry. In addition, active air samplers can be employed to determine concentrations of pesticides in both gas and particle phases. This information is crucial for assessing the health risks of atmospheric pesticides associated with different exposure routes. The study emphasizes the need for continuous atmospheric pesticide monitoring to understand their dynamic distribution in the ambient air. Additionally, accurate risk assessment of human and ecosystem to hazardous agrochemicals and their metabolites in the environment remains an imperative undertaking.

CRediT authorship contribution statement

Mingyu Zhao: Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft. **Junxue Wu:** Resources, Supervision, Writing – review & editing. **Daniel M. Figueiredo:** Formal analysis, Validation, Writing – review & editing. **Yun Zhang:** Writing – review & editing. **Ziyu Zou:** Investigation, Software, Visualization. **Yuxuan Cao:** Investigation. **Jingjing Li:** Investigation. **Xue Chen:** Investigation. **Shuping Shi:** Investigation. **Zhiyun Wei:** Writing – review & editing. **Jindong Li:** Writing – review & editing. **Hongyan Zhang:** Supervision, Writing – review & editing. **Ercheng Zhao:** Resources, Supervision, Writing – review & editing. **Violette Geissen:** Supervision, Writing – review & editing. **Coen J. Ritsema:** Supervision, Writing – review & editing. **Xuejun Liu:** Resources, Supervision, Writing – review & editing. **Jiajun Han:** Supervision, Writing – review & editing. **Kai Wang:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 42207125 and No. 42107002); The State Key Laboratory of Loess and Quaternary Geology is affiliated with the Institute of Earth Environment in the Chinese Academy of Sciences (SKLLQG214); Professor station of China Agricultural University at Xinzhou Center for Disease Control and Prevention; the High-level Team Project of China Agricultural University; Yunnan Provincial Major Science and Technology Special Project (202102AE090030); the China Scholarship Council (No. 201913043).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2023.108342.

References

Ahrens, L., Harner, T., Shoeib, M., Koblizkova, M., Reiner, E.J., 2013. Characterization of Two Passive Air Samplers for Per- and Polyfluoroalkyl Substances. Environ. Sci. Technol. 47, 14024–14033. https://doi.org/10.1021/es4048945.
Backhaus, T., 2016. Environmental Risk Assessment of Pharmaceutical Mixtures: Demands, Gaps, and Possible Bridges. Aaps J. 18, 804–813. https://doi.org/10.1208/s12248-016-9907-0.
Bedos, C., Cellier, P., Calvet, R., Barriuso, E., Gabrielle, B., 2002. Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview. Agronomie 22, 21–33. https://doi.org/10.1051/agro:2001003.
Beketov, M.A., Kefford, B.J., Schafer, R.B., Liess, M., 2013. Pesticides reduce regional biodiversity of stream invertebrates. P. Natl. Acad. Sci. U.S.A. 110, 11039–11043. https://doi.org/10.1073/pnas.1305618110.
Boxall, A.B.A., Sinclair, C.J., Fenner, K., Kolpin, D., Maud, S.J., 2004. When synthetic chemicals degrade in the environment. Environ. Sci. Technol. 38, 368A–375A. https://doi.org/10.1021/es040624v.
Climent, M.J., Coscolla, C., Lopez, A., Barra, R., Urrutia, R., 2019. Legacy and current-use pesticides (CUPs) in the atmosphere of a rural area in central Chile, using passive air samplers. Sci. Total Environ. 662, 646–654. https://doi.org/10.1016/j.scitotenv.2019.01.302.
Coscolla, C., Yusa, V., Marti, P., Pastor, A., 2008. Analysis of currently used pesticides in fine airborne particulate matter (PM 2.5) by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1200, 100–107. https://doi.org/10.1016/j.chroma.2008.05.075.
Coscolla, C., Lopez, A., Yahyaoui, A., Colin, P., Robin, C., Poinsignon, Q., Yusa, V., 2017. Human exposure and risk assessment to airborne pesticides in a rural French community. Sci. Total Environ. 584, 856–868. https://doi.org/10.1016/j.scitotenv.2017.01.132.
Das, S., Hageman, K.J., 2020. Influence of Adjuvants on Pesticide Soil-Air Partition Coefficients: Laboratory Measurements and Predicted Effects on Volatilization. Environ. Sci. Technol. 54, 7302–7308. https://doi.org/10.1021/acs.est.0c00964.
Degrendele, C., Okonski, K., Melymuk, L., Landlova, L., Kukucka, P., Audy, O., Kohoutek, J., Cupr, P., Klanova, J., 2016. Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides. Atmospheric Chem. Phys. 16, 1531–1544. https://doi.org/10.5194/acp-16-1531-2016.
Dekeyser, D., Foque, D., Duga, A.T., Verboven, P., Hendrickx, N., Nuyttens, D., 2014. Spray deposition assessment using different application techniques in artificial orchard trees. Crop Prot. 64, 187–197. https://doi.org/10.1016/j.cropro.2014.06.008.
Estellano, V.H., Pozo, K., Efstathiou, C., Pozo, K., Corsolini, S., Focardi, S., 2015. Assessing levels and seasonal variations of current-use pesticides (CUPs) in the Tuscan atmosphere, Italy, using polyurethane foam disks (PUF) passive air samplers. Environ. Pollut. 205, 52–59. https://doi.org/10.1016/j.envpol.2015.05.002.
FAO, 2021. FAOSTAT. https://wwwfaoorg/faostat/en/#data.
Figueiredo, D.M., Duyzer, J., Huss, A., Krop, E.J.M., Gerritsen-Ebben, M.G., Gooijer, Y., Vermeulen, R.C.H., 2021. Spatio-temporal variation of outdoor and indoor pesticide air concentrations in homes near agricultural fields. Atmospheric Environ. 262 https://doi.org/10.1016/j.atmosenv.2021.118612.
Francisco, A.P., Harner, T., Eng, A., 2017. Measurement of polyurethane foam-air partition coefficients for semivolatile organic compounds as a function of temperature: Application to passive air sampler monitoring. Chemosphere 174, 638–642. https://doi.org/10.1016/j.chemosPhere.2017.01.135.
Geissen, V., Silva, V., Lwanga, E.H., Beriot, N., Oostindie, K., Bin, Z.Q., Pyne, E., Busink, S., Zomer, P., Mol, H., Ritsema, C.J., 2021. Cocktails of pesticide residues in conventional and organic farming systems in Europe- Legacy of the past and turning point for the future*. Environ. Pollut. 278 https://doi.org/10.1016/j.envpol.2021.116827.
Huang, H.F., Ding, Y., Chen, W., Zhang, Y., Chen, W.W., Chen, Y.J., Mao, Y., Qi, S.H., 2019. Two-way long-range atmospheric transport of organochlorine pesticides (OCPs) between the Yellow River source and the Sichuan Basin. Western China. Sci. Total Environ. 651, 3230–3240. https://doi.org/10.1016/j.scitotenv.2018.10.133.
Jiao, L.P., Lao, Q.B., Chen, L.Q., Chen, F.J., Sun, X., Zhao, M.X., 2018. Concentration and Influence Factors of Organochlorine Pesticides in Atmospheric Particles in a Coastal Island in Fujian. Southeast China. Aerosol Air Qual. Res. 18, 2982–2996. https://doi.org/10.4209/aaqr.2018.04.0126.
Kolpin, D.W., Barbash, J.E., Gilliom, R.J., 1998. Occurrence of pesticides in shallow groundwater of the United States: Initial results from the National Water-Quality Assessment Program. Environ. Sci. Technol. 32, 558–566. https://doi.org/10.1021/es970412g.
Kumar, V., Kumari, A., Price, A.J., Bana, R.S., Singh, V., Bamboriya, S.D., 2023. Impact of Futuristic Climate Variables on Weed Biology and Herbicidal Efficacy: A Review. Agronomy-Basel 13. https://doi.org/10.3390/agronomy13020559.
Li, H.Z., Ma, H.Z., Lydy, M.J., You, J., 2014. Occurrence, seasonal variation and inhalation exposure of atmospheric organophosphate and pyrethroid pesticides in an urban community in South China. Chemosphere 95, 363–369. https://doi.org/10.1016/j.chemosphere.2013.09.046.
Loddo, D., Scarabel, L., Sattin, M., Pederzoli, A., Morsiani, C., Canestrale, R., Tommasini, M.G., 2020. Combination of Herbicide Band Application and Inter-Row Cultivation Provides Sustainable Weed Control in Maize. Agronomy-Basel 10. https://doi.org/10.3390/agronomy10010020.
Metcalf, R.L., 1980. Changing-Role of Insecticides in Crop Protetion. Annu. Rev. Entomol. 25, 219–256. https://doi.org/10.1146/annurev.en.25.010180.001251.
MOA, 2023. China Pesticide Information Network. http://wwwchinapesticideorgcn/eng/dataCenter.
Mu, H.Y., Zhang, J.C., Yang, X.M., Wang, K., Xu, W., Zhang, H.Y., Liu, X.J., 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. https://doi.org/10.1016/j.chemosphere.2022.135115.
Murphy, R.R., Haith, D.A., 2007. Inhalation health risk to golfers from turfgrass pesticides at three northeastern US sites. Environ. Sci. Technol. 41, 1038–1043. https://doi.org/10.1021/es060964b.
Oerke, E.C., 2006. Crop losses to pests. J. Agric. Sci. 144, 31–43. https://doi.org/10.1017/s0021859605005708.
Peck, A.M., Hornbuckle, K.C., 2005. Gas-phase concentrations of current-use pesticides in Iowa. Environ. Sci. Technol. 39, 2952–2959. https://doi.org/10.1021/es0486418.
Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: Results from the GAPS study. Environ. Sci. Technol. 40, 4867–4873. https://doi.org/10.1021/es060447t.
PPDB, 2023. Pesticide Properties DataBase. https://sitemhertsacuk/aeru/ppdb/.
Qu, C.K., Albanese, S., Lima, A., Hope, D., Pond, P., Fortelli, A., Romano, N., Cerino, P., Pizzoante, A., De Vivo, B., 2019. The occurrence of OCPs, PCBs, and PAHs in the soil, air, and bulk deposition of the Naples metropolitan area, southern Italy: Implications for sources and environmental processes. Environ. Int. 124, 89–97. https://doi.org/10.1016/j.envint.2018.12.031.
Racke, K.D., 1993. Environmental Fate of Chlorpyrifos. Rev. Environ. Contam. Toxicol. 131, 1–150.
Rani, L., Thapa, K., Kanojia, N., Sharma, N., Singh, S., Grewal, A.S., Srivastav, A.L., Kaushal, J., 2021. An extensive review on the consequences of chemical pesticides on human health and environment. J. Clean. Prod. 283 https://doi.org/10.1016/j.jclepro.2020.124657.
Rosenheim, J.A., Cass, B.N., Kahl, H., Steinmann, K.P., 2020. Variation in pesticide use across crops in California agriculture: Economic and ecological drivers. Sci. Total Environ. 733 https://doi.org/10.1016/j.scitotenv.2020.138683.
Sanchez-Bayo, F., 2014. The trouble with neonicotinoids. Science 346, 806–807. https://doi.org/10.1126/science.1259159.
Schuster, J.K., Harner, T., Eng, A., Rauert, C., Su, K., Hornbuckle, K.C., Johnson, C.W., 2021. Tracking POPs in Global Air from the First 10 Years of the GAPS Network (2005 to 2014). Environ. Sci. Technol. 55, 9479–9488. https://doi.org/10.1021/acs.est.1c01705.
Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils - A hidden reality unfolded. Sci. Total Environ. 653, 1532–1545. https://doi.org/10.1016/j.scitotenv.2018.10.441.
Spilsbury, F.D., Warne, M.S., Backhaus, T., 2020. Risk Assessment of Pesticide Mixtures in Australian Rivers Discharging to the Great Barrier Reef. Environ. Sci. Technol. 54, 14361–14371. https://doi.org/10.1021/acs.est.0c04066.
Tang, F.H.M., Lenzen, M., McBratney, A., Maggi, F., 2021. Risk of pesticide pollution at the global scale. Nat. Geosci. 14,206-+. https://doi.org/10.1038/s41561-021-00712-5.
Tubiello, F.N., Soussana, J.F., Howden, S.M., 2007. Crop and pasture response to climate change. P. Natl. Acad. Sci. U.S.A. 104, 19686–19690. https://doi.org/10.1073/pnas.0701728104.
USEPA, 2010a. Screening Tool for Inhalation Risk Version 1.0.

USEPA, 2010b. STIR Version 1.0 User's Guide for Pesticide Inhalation Risk.
USEPA, 2011. EPA's Exposure Factors Handbook.
USEPA, 2019. Guidelines for Human Exposure Assessment.
USEPA, 2023. ECOTOX Knowledgebase. https://cfpubepagov/ecotox/.
Veludo, A.F., Figueiredo, D.M., Degrendele, C., Masinyana, L., Curchod, L., Kohoutek, J., Kukucka, P., Martinik, J., Pribylova, P., Klanova, J., Dalvie, M.A., Roosli, M., Fuhrimann, S., 2022. Seasonal variations in air concentrations of 27 organochlorine pesticides (OCPs) and 25 current-use pesticides (CUPs) across three agricultural areas of South Africa. Chemosphere 289. https://doi.org/10.1016/j.chemosphere.2021.133162.
von Waldow, H., MacLeod, M., Scheringer, M., Hungerbuhler, K., 2010. Quantifying Remoteness from Emission Sources of Persistent Organic Pollutants on a Global Scale. Environ. Sci. Technol. 44, 2791–2796. https://doi.org/10.1021/es9030694.
Wang, C.L., Herbst, A., Zeng, A.J., Wongsuk, S., Qiao, B.Y., Qi, P., Bonds, J., Overbeck, V., Yang, Y., Gao, W.L., He, X.K., 2021a. Assessment of spray deposition, drift and mass balance from unmanned aerial vehicle sprayer using an artificial vineyard. Sci. Total Environ. 777 https://doi.org/10.1016/j.scitotenv.2021.146181.
Wang, J., Lin, K.D., Taylor, A., Gan, J., 2018a. In vitro assessment of pyrethroid bioaccessibility via particle ingestion. Environ. Int. 119, 125–132. https://doi.org/10.1016/j.envint.2018.05.043.
Wang, S.R., Salamova, A., Hites, R.A., Venier, M., 2018b. Spatial and Seasonal Distributions of Current Use Pesticides (CUPs) in the Atmospheric Particulate Phase in the Great Lakes Region. Environ. Sci. Technol. 52, 6177–6186. https://doi.org/10.1021/acs.est.8b00123.
Wang, S.R., Steiniche, T., Romanak, K.A., Johnson, E., Quiros, R., Mutegeki, R., Wasserman, M.D., Venier, M., 2019. Atmospheric Occurrence of Legacy Pesticides, Current Use Pesticides, and Flame Retardants in and around Protected Areas in Costa Rica and Uganda. Environ. Sci. Technol. 53, 6171–6181. https://doi.org/10.1021/acs.est.9b00649.
Wang, S.R., Salamova, A., Venier, M., 2021b. Occurrence, Spatial, and Seasonal Variations, and Gas-Particle Partitioning of Atmospheric Current-Use Pesticides (CUPs) in the Great Lakes Basin. Environ. Sci. Technol. 55, 3539–3548. https://doi.org/10.1021/acs.est.0c06470.
Wolters, A., Linnemann, V., van de Zande, J.C., Vereecken, H., 2008. Field experiment on spray drift: Deposition and airborne drift during application to a winter wheat crop. Sci. Total Environ. 405, 269–277. https://doi.org/10.1016/j.scitotenv.2008.06.060.
Yang, X.M., Van Der Zee, S., Gai, L.T., Wesseling, J.G., Ritsema, C.J., Geissen, V., 2016. Integration of transport concepts for risk assessment of pesticide erosion. Sci. Total Environ. 551, 563–570. https://doi.org/10.1016/j.scitotenv.2016.02.058.
Zaller, J.G., Kruse-Plass, M., Schlechtriemen, U., Gruber, E., Peer, M., Nadeem, I., Formayer, H., Hutter, H.P., Landler, L., 2022. Pesticides in ambient air, influenced by surrounding land use and weather, pose a potential threat to biodiversity and humans. Sci. Total Environ. 838 https://doi.org/10.1016/j.scitotenv.2022.156012.
Zhan, L., Cheng, H., Zhong, G., Sun, Y., Jiang, H., Zhao, S., Zhang, G., Wang, Z., 2021. Occurrence of atmospheric current-use and historic-use pesticides at a CAWNET background site in central China. Sci. Total Environ. 775 https://doi.org/10.1016/j.scitotenv.2021.145802.
Zhang, W., Ye, Y.B., Hu, D., Ou, L.B., Wang, X.J., 2010. Characteristics and transport of organochlorine pesticides in urban environment: air, dust, rain, canopy throughfall, and runoff. J. Environ. Monitor. 12, 2153–2160. https://doi.org/10.1039/c0em00110d.