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Research article

Assessment of pesticide exposure to applicators during spraying in orchards with a stretcher-mounted sprayer

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A R T I C L E I N F O

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Risk assessment model

A B S T R A C T

Various health risk assessment models have been developed to evaluate occupational pesticide exposure in China. However, there has been limited investigation into the relationship between health risks and pesticide spraying in orchards. In this study, we analyzed pesticide exposure of applicators while spraying with a stretcher-mounted sprayer in orchards located in four different climatic regions. All garments' unit exposure (UE) demonstrated a right-skewed distribution, with gloves and shins accounting for the highest proportion of dermal pesticide exposure. We observed little difference in dermal and inhalation UE levels between apple and citrus orchards, except for pesticide exposure levels on wipes and faces. While 57% of the inhalation UE distribution variance was attributed to clustering and location effects, no significant differences were observed in dermal exposure levels. We evaluated the impact of different levels of protective clothing on pesticide exposure levels, according to applicators' working habits in China. Our findings revealed that improved levels of protection significantly reduced dermal exposure to pesticides, particularly when wearing gloves during spraying with a stretcher-mounted sprayer. Based on our empirical data, we utilized a simple random sampling model and an intercept-only lognormal mixed model to estimate dermal and inhalation exposure levels. The estimated dermal UE was accurate to within 3-fold with 95% confidence, and half of the estimated inhalation UE was acceptable according to the fold relative accuracy (fRA). Our established and verified statistics for dermal and inhalation UE can be utilized to evaluate the potential pesticide exposure to applicators during spraying in orchards with a stretcher-mounted sprayer.

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1. Introduction

Pesticides are essential agricultural inputs that protect agro-products from pests, insects, weeds, and fungi in order to achieve high productivity. China is the largest market in the world for pesticide production and consumption [1,2], using more than 30% of global pesticides, while China's cropland only accounts for 9% of that of the world [3].

However, the wide use of pesticides has caused great concern regarding pesticide-related environmental and human health risks. One primary way pesticides could threaten human health is via direct exposure to inhalation and dermal contact [4]. For instance, occupational workers are exposed to pesticides during pesticide production, and pesticide operators are exposed to pesticides during the use of pesticides. The adverse health effects associated with pesticide exposure include cancer [5], asthma [6], hormone disruption [7], hypersensitivity [8], and reproductive and developmental disorders [9]. Exposure to pesticides could be influenced by many factors, such as formulation type, target crop [10], operating equipment [11], the weather during pesticide application [12], and the habit of an operator during pesticide application [13,14]. Pesticide operator exposure is scenario-dependent.

Fruit plantation is one main area for pesticide application in China. China is the largest apple producer [15] and ranked third for citrus production globally [16]. Pesticides are crucial for fruit production; without pesticides, total fruit production may reduce due to disease and pest injury [17]. However, pesticide overuse is not uncommon in orchards, which can threaten human health [18]. To ensure human health, it is necessary to evaluate the potential exposure of pesticides to operators in orchard spraying scenarios. The operation equipment usually includes knapsack sprayers, handheld foggers, and stretcher-mounted sprayers. The latter is more frequently used in orchards in China for pests and weed control [19]. Xuehua An et al. reported that there are exposure risks to pesticide applicators when using stretcher-mounted sprayers and electric backpack sprayers in orchards [16]. However, the study had limited applicators and contained only one climatic region. To date, pesticide exposure due to using stretcher-mounted sprayers in orchards is not well investigated, and there is a lack of sufficient experimental data on exposure dosage.

There are two primary methods to evaluate the potential dermal exposure during orchard spraying: the patch method and the whole-body method [20]. The whole-body method is more convenient in practical use, as it overcomes the inherent problems (overestimation or underestimation) of the patch method [21]. In this study, the exposure data were collected from four different locations in China via the whole-body method and personal sampling pump, respectively. This study aimed to evaluate the pesticide exposure to operators during the use of stretcher-mounted sprayers in orchards and the effects of different orchards and climates on exposure, providing key data for the risk assessment of pesticide operators due to the use of stretcher-mounted sprayers in orchards.

2. Materials and methods

2.1. Chemicals

Cyetpyrafen (99.5% purity), a newly registered acaricide in China, and 30% cyetpyrafen suspension concentrate (SC) were purchased from Shenyang Sciencreat Chemicals Co., Ltd (Liaoning, China). Other chemical reagents used were: 0.01% Aerosol OT (AOT) detergent solution and sodium chloride (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), acetonitrile, and formic acid (Fisher Scientific, Pittsburgh, Pittsburgh, Pennsylvania, USA). Inner and outer clothes (white color, >70% cotton) and gauze were purchased from Beijing Biopute Technology Co., Ltd (Beijing, China). OVS tubes (Orbo-609) were purchased from Supelco Co. (St. Louis, Missouri, USA).

2.2. Design of field experiment

Field experiments were carried out in four different locations: Changping District in the city of Beijing (June 7, 2017), Zhuzhou in the Hunan Province (Sep. 9, 2017), Baoji in the Shanxi Province (July 13, 2017), and Hangzhou in the Zhejiang Province (Oct. 19, 2017). In each location, the pesticide spraying was conducted by at least seven applicators. At each spraying time, 30% cyetpyrafen SC was diluted with 3000-fold water and loaded by a separate person. The temperature ranged from 18 to 37 °C, the relative humidity ranged from 45% to 87%, and the wind velocity was less than 0.1 m/s in all locations.

Before pesticide spraying, the operators were dressed up as follows. The whole body was covered with two layers (inner layer and outer layer) of clothing made of cotton (Septwolves, China). Applicators' hands were covered with two layers of cotton gloves. Their faces and necks were covered with eight layers of gauze (10 × 10 cm). Their heads were covered with a cotton hat (>70% cotton) and eight layers of gauze (40 × 20 cm) under the hat. In addition, a battery-powered personal air pump (Giliair plus, Sensidyne LP, St. Petersburg, Florida, USA) was used along with a solid sorbent tube (OVS tube, XAD-2). The air pump was calibrated before the experiment and kept working through the whole pesticide spraying process with both flow rate and time recorded.

Pesticide spraying in both apple orchards (Beijing and Shanxi) and citrus orchards (Hunan and Zhejiang) was conducted by using a stretcher-mounted sprayer. A spraying area of 667 m^2 was adopted for each operator, and the consumption (in volumes) of pesticide and water (80–300 L, varied by location) was recorded. After pesticide spraying, all cloths were removed from the operator and were divided into six parts: front torso, rear torso, upper arms (right and left), lower arms (right and left), upper legs (right and left), and lower legs (right and left). The gloves, gauze, and OVS tubes were also removed from the operator. All samples were placed separately in labeled plastic bags and stored in a refrigerator (−20 °C) for future use. The operator's face and neck were wiped twice with separate gauzes (eight layers, 10cm × 10 cm) pre-wetted with 4 mL of 0.01% AOT. The gauzes were then placed in labeled plastic bags and stored in a refrigerator (−20 °C) for future use. The operator's hands were also washed with 0.01% AOT of 400 mL for the first time and 0.01% AOT of 100 mL for the second time. The hand washing liquid (a total volume of 500 mL) was placed in a labeled bottle and stored at 4 °C.

2.3. Sample pretreatment

Sample pretreatment procedures were carried out to extract pesticides (cyetpyrafen) from different samples. Cotton samples (cloths, gloves, and hats) and gauze samples were extracted by a certain volume of acetonitrile in a sonicator for 15 min. OVS tube samples were cut into small pieces, immersed in 20 mL acetonitrile in a 50 mL PP tube, and centrifuged at 4000 rpm for 5 min. The hand washing liquid of 10 mL was mixed with 5 g sodium chloride and 10 mL acetonitrile in a 50 mL PP tube and centrifuged at 4000 rpm for 5 min. The extracting solutions (acetonitrile) after sonication and centrifugation (supernatant part) were passed by a 0.22 μm membrane filter, further diluted or not diluted with acetonitrile, and analyzed by a liquid chromatography-tandem mass spectrometry (LC-MS/MS) method.

2.4. LC-MS/MS method

Quantification of cyetpyrafen in different samples was performed by the LC-MS/MS method. A Shimadzu LCMS-8050 system (Shimadzu, Japan) was used. Standard solutions of cyetpyrafen in acetonitrile with concentrations of 0.1–200 μg/L were prepared to establish the external calibration curve ($R^2 > 0.9998$). Separation of cyetpyrafen was achieved by using a Shim-pack XR-ODS II column (2.2 μm, 2.0 mm × 75 mm) kept at 40 °C. Isocratic elution was carried out using acetonitrile/0.1% formic acid in water (80:20, v/v) as the mobile phase at a flow rate of 0.3 mL/min. The injected volume was 5 μL. All samples were tested in triplicate.

The detection of cyetpyrafen was carried out by setting the MS detector at electrospray ionization in positive mode and performing data acquisition in multiple reaction monitoring (MRM) mode. A drying gas temperature of 300 °C with a gas flow of 5 L/min and a sheath gas temperature of 250 °C with a sheath gas flow of 11 L/min were used. Two pairs of MRM transitions, m/z 394.60 → 310.20 and m/z 394.60 → 109.10, were selected for qualification and 394.60 → 310.20 was selected for quantification.

The source cone voltage was set at 22 V, and the collision energies were set at 25eV for 394.60 → 310.20 and 50eV for 394.60 → 109.10. Other MS parameters were set to the recommended values for the instrument.

2.5. Method validation

The limit of detection (LOD) and limit of quantification (LOQ) were determined by diluting the standard solution of cyetpyrafen with acetonitrile (six replicates) and recording the peak height until a signal-to-noise ratio of 3 (for LOD) or 10 (for LOQ) was achieved. These criteria determined the LOD and LOQ values to be 0.01 μg/L and 0.02 μg/L, respectively. And the LOQ was verified with QC samples in each matrix.

Recovery of cyetpyrafen from various samples was also investigated. Standard cyetpyrafen solutions were added to the cotton samples at concentrations ranging from 0.002 mg/L to 0.2 mg/L, the gauze samples at concentrations of 0.0002 mg/L, 0.002 mg/L, and 0.02 mg/L, the OVS tube samples at concentrations of 0.0002 mg/L, 0.002 mg/L and 0.1 mg/L and the AOT samples at concentrations of 0.0002 mg/L, 0.002 mg/L and 0.15 mg/L. The spiked samples were subject to the sample pretreatment procedures mentioned above and analyzed by LC-MS/MS. The recovery values were in a range of 76.9–104.5% (RSD = 1.7–4.9%), 76.0–96.6% (RSD = 4.0–4.5%), 77.6–90.5% (RSD = 1.5–3.2%) and 81.0–105.0% (RSD = 1.7–2.3%) for the cotton, gauze, tube and AOT samples, respectively.

2.6. Statistical analysis

Experimental data were collected from a total of 32 spraying operators in 4 different orchards. For the exposure data below LOQ but above LOD, 50% LOQ was used [22,23]. For the exposure data below LOD, a value of 0.01 μg/sample was used [23]. The proportions of non-detects between LOD and LOQ is 44/672. The proportions of non-detects below LOD is 3/672. UE assay was adopted to describe the exposure level during pesticide application according to the U.S. Environmental Protection Agency (USEPA) guidelines [24]. UE is defined as the exposure dose (mg) over the active substance (cyetpyrafen) handled (kg). An air change rate of 21.9 L/min was used to assess inhalation (XAD-2) UE according to the respiratory rate of adults working at medium labor intensity in urban and rural China [25]. The air sampler's pumping rate was 2 L/min. A factor of 29.2/2 was multiplied for the calculation of inhalation UE.

Three levels of protection have been defined: level_a, level_b and level_c. The dermal exposure in level_a consisted of shins, forearms, inner_cap, cap, inner_gloves, gloves, inner_chest, inner_back, inner_thighs, inner_shins, inner_upper_arms, inner_forearms, face, mask, neck and wipes. Level_b did not include shins and foreams compared with level_a. Level_c did not include cap and gloves compared with level_b.

Detailed climatic data were extracted from the China meteorological forcing dataset (1979–2018) [26,27] based on geographic coordinates and time of field experiments to fully elucidate the effects of climatic conditions on inhalation UE. Stratified regression analysis was performed to investigate the associations among Ln (XAD_2), pressure (Pres), temperature (Temp), and downward shortwave radiation (Srad) by using SPSS 25.0.

Parameter estimation for UE was performed using a simple random sampling model (code "s") and an intercept-only lognormal mixed model (code "m"). Arithmetic means, geometric means, medians, and 75th percentile of UE were calculated using SAS (Version 9.3) in each statistical model. The software also provided relative accuracy and fold relative accuracy (*f*RA) values.

Shapiro-Wilk test was performed using R (4.1.3) and Rstudio (2022.02.1 Build 461), and the exposure data were not normally distributed. Mann-Whitney *U* test was utilized to compare the difference between apple and citrus orchards using Rstudio. Kruskal-Wallis H-test and Dunnett's T3 (SPSS 25.0) were used to determine the statistical significance among climate regions. The level of statistical significance was established at $P < 0.05$.

3. Results and discussion

3.1. Dermal and inhalation exposure during application

Exposure data of 32 applicators, each using a stretcher-mounted sprayer, was acquired from four provinces of China. Dermal exposure was evaluated using the measured residues on the body through the whole-body exposure method. Inhalation exposure was evaluated using a personal air sampler. As shown in Fig. 1A–E, the UE of all tested body parts showed a right-skewed distribution and contained some discrete values. Consistent with the previous work [16], the distribution ratio of exposure of gloves and shins was significantly higher than that of the other sections (as shown in Fig. 1F, ($P < 0.001$, $P < 0.001$)), indicating that gloves and long pants are of utmost importance when pesticide spraying in an orchard by a stretcher-mounted sprayer. As expected and consistent with previous reports [23,28], the total dermal exposure is log-normally distributed, and the inhalation exposure (XAD_2) is close to log-normally distributed (data not shown).

3.2. Difference between apple and citrus orchards

The UE of each garment in apple and citrus orchards is shown in Fig. 2A,B. We found that the exposure of most sections had no significant difference between apple and citrus orchards except for when it concerned faces and wipes ($P < 0.05$, $P < 0.001$). The UE of the faces accounted for an average of 0.05% and 0.04% of the total dermal exposure in citrus and apple orchards, respectively. Similarly, the exposure of wipes accounted for an average of 0.60% and 0.01% of the total dermal exposure in citrus and apple orchards, respectively. Additionally, there is no significant difference between the total dermal UE of applicators in the two kinds of orchards (data not shown). As such, since it is common practice to use closely linked surrogate data to evaluate the pesticide exposure of applicators [29], we concluded that it would be reasonable to merge the exposure data of apple and citrus orchards into one scenario. Our data could be used to assess the potential pesticide exposure of applicators when spraying with stretcher-mounted sprayers in many other fruit orchards or tea plantations.

3.3. Difference in climatic regions

We wondered whether climatic regions might also affect dermal and inhalation exposure, so the field experiments were performed in two northern regions and two southern regions in China. As shown in Fig. 3A,B, no significant difference existed among the four regions in the UE of dermal garments. Similarly, there was no significant difference (data not shown) in the total dermal UE of the four climatic regions. This is contrary to the findings of Zhikang Li et al., who reported that a difference existed in climatic regions when spraying with a hand-pumped knapsack sprayer in a maize field [30]. The different application methods may be the main reason for the opposite findings. In contrast, as shown in Fig. 3B, our results showed that the inhalation exposure was influenced by climatic regions ($P < 0.01$).

3.4. Difference among the level of protection

The average total dermal UE of applicators under different levels of protective clothing is shown in Fig. 4. Those in level_a wore short pants, short shirts, no gloves, no hats, and no masks. Those in level_b wore long pants, long shirts, no gloves, no hats, and no masks. Those in level_c wore long pants, long shirts, gloves, hats, and masks. Results for the three different levels of protective clothing showed that the total dermal UE was of a right-skewed distribution for all three levels of protection with some discrete values. The dermal exposure of level_c was significantly smaller than level_a and level_b ($P < 0.001$, $P < 0.01$). We found no significant difference between the average dermal exposure of level_b and level_a (reduced by 38.9%). The main reason may be that the standard deviations of the dermal UE for both levels of protection are rather substantial. However, when equipped with gloves, hats, and masks under level_c, the total dermal UE was reduced by 73.8% when compared with level_b, indicating that wearing gloves is highly recommended when spraying pesticides.

3.5. Parameter estimation of dermal and inhalation unit exposure

To predict the potential dermal and inhalation exposure of applicators when spraying with a stretcher-mounted sprayer in orchards, we developed two models: the simple random sampling model and the intercept-only lognormal mixed model. Table 1 presents the geometric mean (GM), arithmetic mean (AM), and 75th percentile (P75) estimates from the two models, together with *f*RA and parametric confidence intervals. A parametric bootstrap was utilized to compute confidence intervals. According to the USEPA document [31], the mixed model is better suited for modeling the data, so the parametric bootstrap simulations were all generated from the fitted lognormal mixed model (albeit some statistics were extracted from a simpler statistics model). As shown in Table 1, P75 statistics were the maximum under level_a and level_b, while GM statistics were the minimum in all estimations. *f*RA is a measure to evaluate how well a statistic can describe its population parameter [31]. In Agricultural Handler Exposure Task Force scenarios, 3-fold relative accuracy is a reasonable default for regulatory purposes [32]. All statistics' *f*RA of the dermal route was less than 3, so the statistics were accurate to within 3-fold with 95% confidence. Remarkably, AM's *f*RA in the inhalation route was larger than 3-fold, suggesting that perhaps these statistics were not a good choice for predicting inhalation exposure. However, certain scenarios with less accuracy and lower exposures could be tolerated [32], therefore, although certain inhalation UE estimations, such as P75s and P75 m, have less accuracy, they were still suitable for the application.

In addition, the medians of the UE were also calculated to compare with the GMs. As shown in Table 1, the medians of level_a, level_b, and level_c are all close to their corresponding GMs, indicating that the dermal UE realistically follows a log-normal distribution. We also found that the median of XAD_2 was not close to its corresponding GMs, demonstrating that the estimation method of the mixed model may be limited to predicting inhalation pesticide exposure.

Our study used the intercept-only model to estimate the intraclass correlation [33], which showed an estimate of 0.57 for the inhalation UE. Thus, 57% of the variance of the inhalation UE is at the clustering and location effects, consistent with Fig. 3B. To further elucidate the clustering and location effects, we analyzed climatic data from various locations and correlated them with inhalation UE. Stratified regression was used to analyze whether a gradual increase in Temp and Pres improves the level of prediction of Srad on Ln (XAD_2). As shown in Table 2, the final model (Model 3) incorporating the three variables (Srad, Temp, and Pres) showed statistically significant results with $R^2 = 0.536$, adjusted $R^2 = 0.486$, $F(3, 28) = 10.763$ ($P < 0.001$). Maria Pia Gatto et al. reported that climate change, such as global warming, influenced human exposure to pesticides during agricultural activities [34]. Our study suggests that climatic conditions may affect the inhalation exposure of applicators to pesticides during sprying. In contrast, the estimated intraclass correlation of dermal UE of the three levels of protection is 0.14, 0.01, and 0 for level_a, level_b, and level_c, respectively, which implies very little clustering and location differences in dermal exposure.

4. Conclusions

The dermal and inhalation exposure of applicators to pesticides was monitored using a whole-body garment method and a personal sampling pump during stretcher-mounted spraying in orchards in China. Our results indicated that the UE of all garments is of right-skewed distribution, and the UE of glovers and shins were two of the highest, indicating glovers and long pants are absolutely necessary when spraying. In addition, although the total dermal UE is not affected by orchard types and climatic regions, we found that climatic regions did have some influence on the inhalation UE. Moreover, 57% of the variance of the inhalation UE is at the clustering and location effects. Long pants and long shirts, gloves, masks, and caps during pesticide application can reduce dermal exposure by more than 80%. Two statistical models were fitted to the dermal and inhalation UE. All estimations of the dermal route are accurate with 3-fold with 95% confidence. These estimations could be used to predict potential pesticide exposure to applicators during pesticide spraying with a stretcher-mounted sprayer in orchards.

Declarations

According to the Ethical Review of Life Sciences and Medical Research Involving Human Subjects in China, review and approval by an ethics committee was not needed for this study because this study was not involving interacting with or observation of people, and/or the use of peoples' data. This study only collected the protective equipment worn by applicators, such as clothing, trousers, masks, hats, etc., and did not collect any biological samples from applicators. Applicators were all local farmers with experience in pesticide spraying and in good health. They volunteered to participate in the project and wore the necessary protective equipment. Prior to participation in the study, a signed informed consent form was obtained from each applicator.

Data availability statement

The data are available from the corresponding author on reasonable request.

CRediT authorship contribution statement

Tao Chuanjiang: Supervision, Project administration, Methodology, Conceptualization. **Mei Chenghan:** Writing – original draft, Formal analysis, Data curation. **Zhang Liying:** Visualization, Investigation. **Li Shuang:** Methodology. **Yan Yizhou:** Methodology. **She Dongmei:** Methodology. **An Xuehua:** Methodology. **Fu Qiang:** Methodology. **Pu Entang:** Methodology. **Tao Lingmei:** Supervision. **Liu Ran:** Validation. **Zhang Hongjun:** Validation. **Huang Xiuzhu:** Writing – review & editing, Resources, Funding acquisition.

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.

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Appendices.

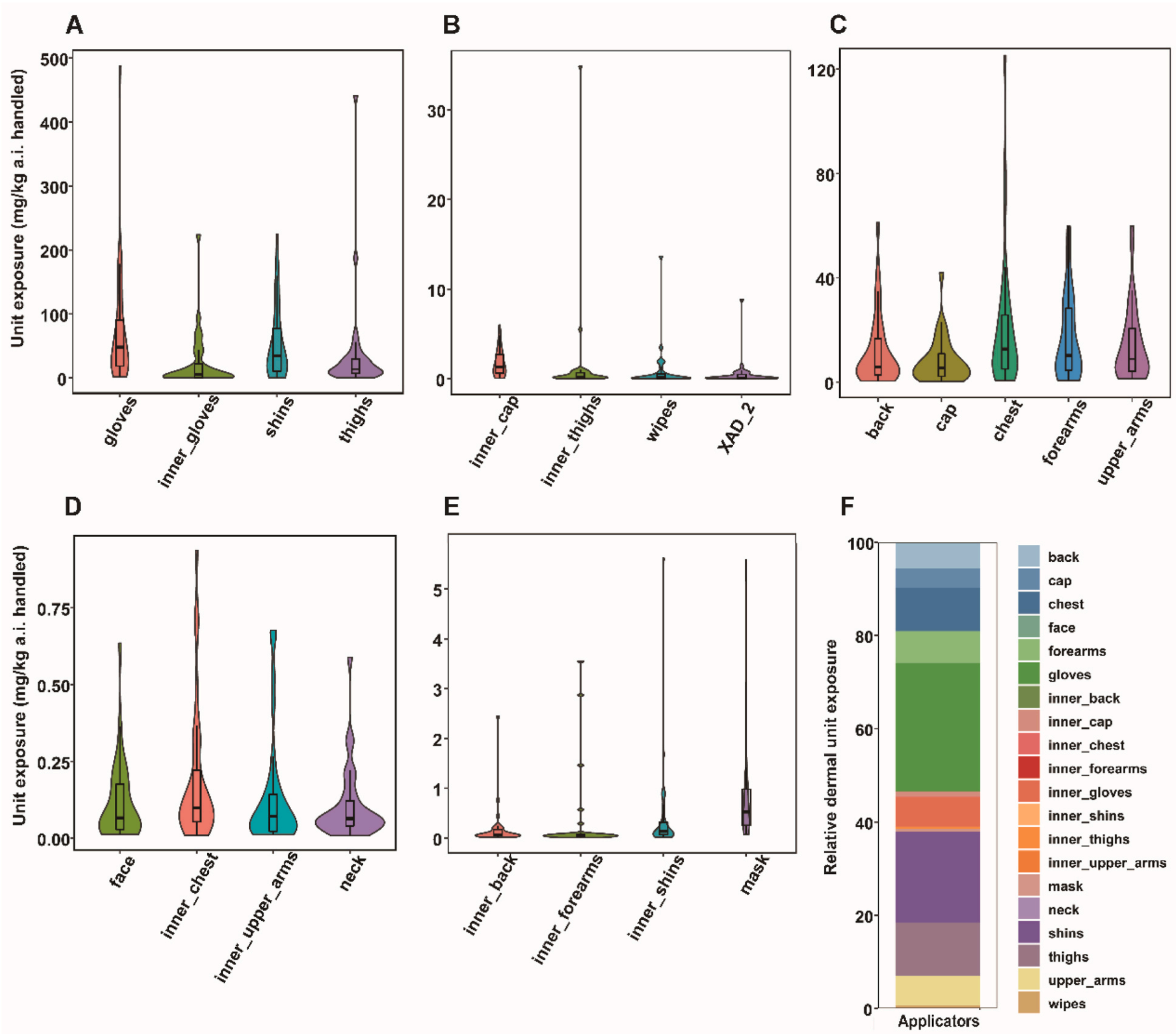

Fig. 1. Exposure to applicators during spraying by a stretcher-mounted sprayer. A whole-body method was performed to evaluate the dermal exposure to applicators. Inhalation exposure was monitored through an air pump and OVS tube. The unit exposure for the different parts of the applicators' bodies is right-skewed distribution (A-E). Data are presented in the violin plot. Relative dermal unit exposure of applicators after spraying in four orchards (F). The dermal unit exposure of different body parts of each applicator was normalised to their total dermal unit exposure and then averaged for each garment.

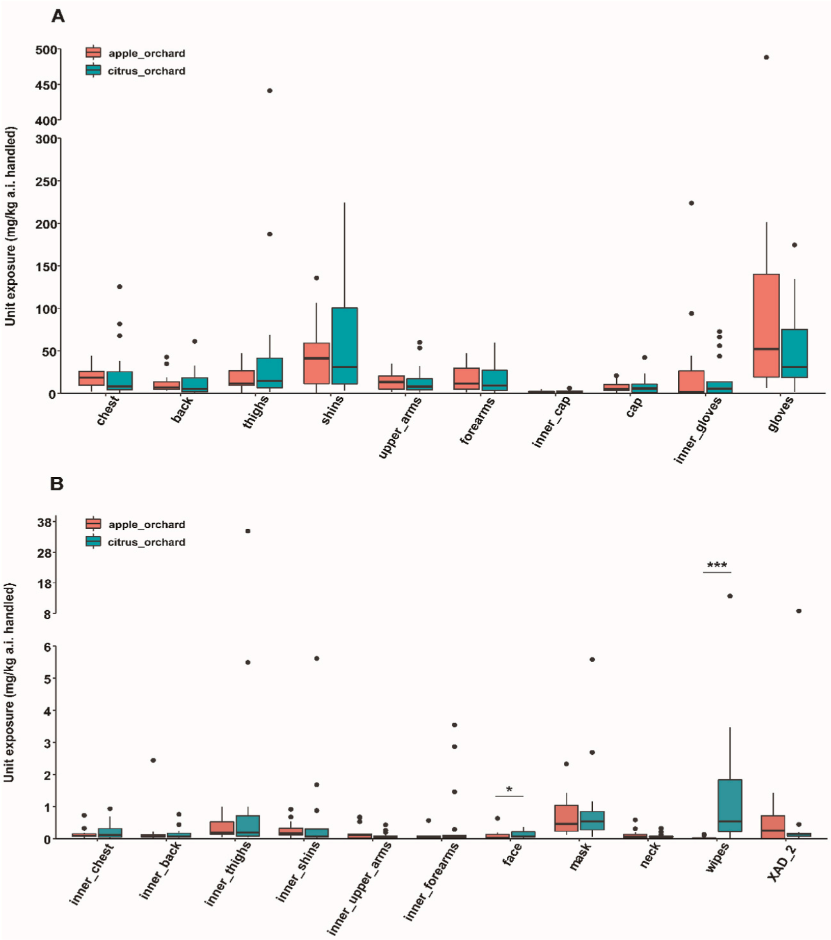

Fig. 2. Distribution of pesticide exposure during spraying in apple and citrus orchards. Data are presented in box plots (A-B). *$P < 0.05$, ***$P < 0.001$ compared with the apple_orchard group.

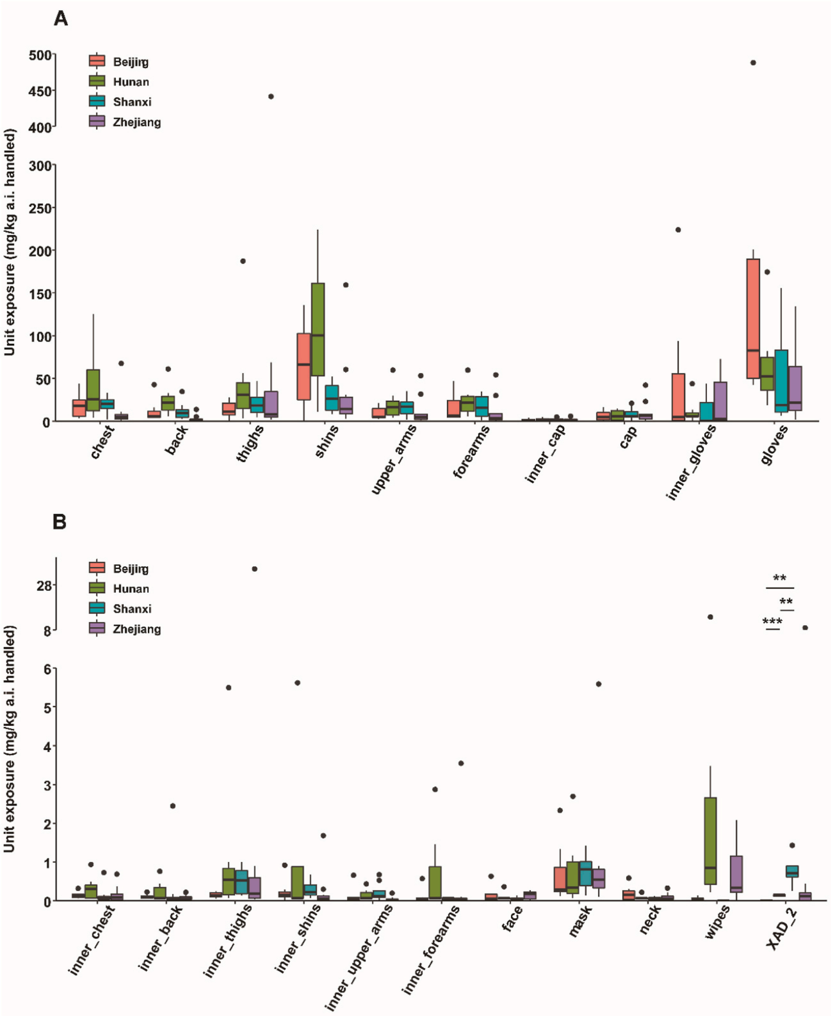

Fig. 3. Distribution of pesticide exposure during spraying in different climatic regions. Data are presented in box plots (A-B). **$P < 0.01$, ***$P < 0.001$ compared with the specific group.

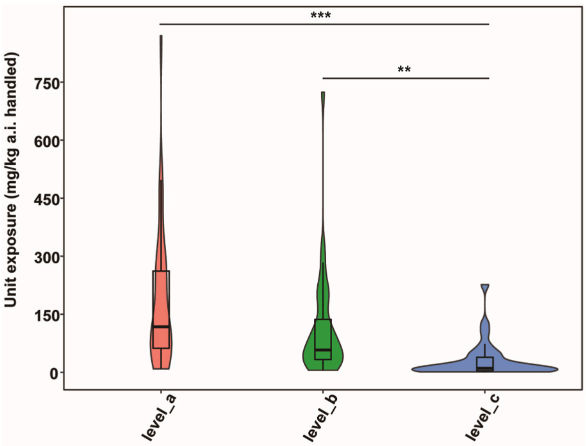

Fig. 4. Total dermal exposure under various levels of protection. Data are presented in violin plots. Level_a) short pants, short shirts, no gloves, no hat, no mask; level_b) long pants, long shirts, no gloves, no hat, no mask; level_c) long pants, long shirts, gloves, hat, mask. **$P < 0.01$, ***$P < 0.001$ compared with the level_c group.

Table 1
The estimated dermal and inhalation unit exposure.

Statistic	Dermal and inhalation route	Unit Exposure Esitimated (mg/kg ai)	95% Cl		*f*RA
			Lower	Upper	
P75s	Level_a	263.60	144.09	396.29	1.83
	Level_b	171.17	81.08	235.94	2.11
	Level_c	41.80	15.47	59.52	2.70
	XAD-2	0.53	0.12	1.91	4.32
P75 m	Level_a	247.01	155.88	364.62	1.58
	Level_b	141.21	88.21	214.56	1.60
	Level_c	30.05	17.30	52.58	1.75
	XAD-2	0.45	0.15	1.47	3.28
GMs	Level_a	115.50	78.90	169.62	1.47
	Level_b	64.46	43.28	96.65	1.50
	Level_c	11.56	7.00	19.08	1.65
	XAD-2	0.07	0.02	0.18	2.78
GMm	Level_a	119.64	78.69	169.62	1.52
	Level_b	65.90	43.13	96.72	1.53
	Level_c	11.56	7.00	19.08	1.65
	XAD-2	0.06	0.02	0.19	2.94
AMs	Level_a	185.07	124.59	329.63	1.78
	Level_b	113.08	71.23	202.13	1.79
	Level_c	29.58	14.72	65.27	2.21
	XAD-2	0.54	0.27	22.33	41.68
AMm	Level_a	212.99	129.24	338.66	1.65
	Level_b	124.65	74.03	207.61	1.68
	Level_c	31.46	16.17	66.60	2.12
	XAD-2	4.35	0.55	63.45	14.58
Medians	Level_a	117.64	72.50	183.35	1.62
	Level_b	57.58	39.50	105.17	1.83
	Level_c	10.48	6.24	21.69	2.07
	XAD-2	0.16	0.02	0.23	8.12

Lognormal miexed model: Y = LnGM + Cluster + Error. LnGM is the log of the geometric mean.
P75s = 75 percentile of UE.
P75 m = Variance component model-based 75 percentile of UE = exp(LnGM+0.675*standard deviation of Y).
AMs = Arithmetic mean of UE.
AMm = exp(LnGm)exp(1/2*(standard deviation of Y)^2).
GMs = exp(average of ln(UE)).
GMm = variance component model-based geometric mean = exp(LnGM).
*f*RA = Max (95% Cl_upper/UE estimated, UE estimated/95% Cl_lower).

Table 2
Stratifiec regression analysis results.

Variates	Model 1		Model 2		Model 3	
	Unstandardized Coefficients	Standardized Coefficients	Unstandardized Coefficients	Standardized Coefficients	Unstandardized Coefficients	Standardized Coefficients
Constant	−2.560**	/	−84.220**	/	100.466	/
Srad	−0.001	−0.035	−0.008	−0.376	−0.016***	−0.715
Temp	/	/	0.279**	0.640	0.001	0.003
Pres	/	/	/	/	−1.027**	−0.996
R^2	0.001	/	0.294	/	0.536	/
F	0.037	/	6.045**	/	10.763***	/
$\triangle R^2$	0.001	/	0.293	/	0.241	/
$\triangle F$	0.037	/	12.039**	/	14.550**	/

Note: N = 32, *$P < 0.05$, **$P < 0.01$, ***$P < 0.001$.

References

[1] A. Shattuck, Generic, growing, green?: the changing political economy of the global pesticide complex, J. Peasant Stud. 48 (2) (2021) 231–253.
[2] A. Sharma, et al., Worldwide pesticide usage and its impacts on ecosystem, SN Appl. Sci. 1 (11) (2019) 1446.
[3] Y. Wu, et al., Policy distortions, farm size, and the overuse of agricultural chemicals in China, Proc. Natl. Acad. Sci. U.S.A. 115 (27) (2018) 7010–7015.
[4] J. Ohlander, et al., Systematic review of methods used to assess exposure to pesticides in occupational epidemiology studies, 1993–2017, Occup. Environ. Med. 77 (6) (2020) 357.
[5] A.M. Lewis-Mikhael, et al., Occupational exposure to pesticides and prostate cancer: a systematic review and meta-analysis, Occup. Environ. Med. 73 (2) (2016) 134–144.

[6] N. Le Moual, et al., Update of an occupational asthma-specific job exposure matrix to assess exposure to 30 specific agents, Occup. Environ. Med. 75 (7) (2018) 507–514.
[7] M. Leemans, et al., Pesticides with potential thyroid hormone-disrupting effects: a review of recent data, Front. Endocrinol. 10 (2019).
[8] T.S. Ferreira, A.P.S. Carneiro, E.V. Mancuzo, Occupational exposure to pesticides and chronic hypersensitivity pneumonia: a case report, Rev Bras Med Trab 19 (2) (2021) 249–252.
[9] S. Gangemi, et al., Occupational exposure to pesticides as a possible risk factor for the development of chronic diseases in humans (Review), Mol. Med. Rep. 14 (5) (2016) 4475–4488.
[10] H. Choi, J.-K. Moon, J.-H. Kim, Assessment of the exposure of workers to the insecticide imidacloprid during application on various field crops by a hand-held power sprayer, J. Agric. Food Chem. 61 (45) (2013) 10642–10648.
[11] D. Nuyttens, et al., Potential dermal pesticide exposure affected by greenhouse spray application technique, Pest Manag. Sci. 65 (7) (2009) 781–790.
[12] C.A. Damalas, I.G. Eleftherohorinos, Pesticide exposure, safety issues, and risk assessment indicators, Int. J. Environ. Res. Publ. Health 8 (5) (2011).
[13] I. Baldi, et al., Levels and determinants of pesticide exposure in operators involved in treatment of vineyards: results of the PESTEXPO Study, J. Expo. Sci. Environ. Epidemiol. 22 (6) (2012) 593.
[14] E.A. Hughes, et al., Analytical method for assessing potential dermal exposure to captan, using whole body dosimetry, in small vegetable production units in Argentina, Pest Manag. Sci. 62 (9) (2006) 811–818.
[15] G.-D. Suo, et al., Long-term effects of different surface mulching techniques on soil water and fruit yield in an apple orchard on the Loess Plateau of China, SCI HORTIC-AMSTERDAM 246 (2019) 643–651.
[16] X. An, et al., Exposure risks to pesticide applicators posed by the use of electric backpack sprayers and stretcher-mounted sprayers in orchards, Hum. Ecol. Risk Assess. 26 (8) (2020) 2288–2301.
[17] M. Tudi, et al., Agriculture development, pesticide application and its impact on the environment, Int. J. Environ. Res. Publ. Health 18 (3) (2021) 1112.
[18] J. Cai, et al., Pesticide overuse in apple production and its socioeconomic determinants: evidence from Shaanxi and Shandong provinces, China, J. Clean. Prod. 315 (2021) 128179.
[19] Y. Lu, W. Yi, H. Tuo, Present state and trends of orchard sprayer, Journal of Chinese Agricultural Mechanization 39 (1) (2018) 36–41.
[20] E. Kim, et al., Exposure and risk assessment of insecticide methomyl for applicator during treatment on apple orchard, J KOREAN SOC APPL BI 55 (1) (2012) 95–100.
[21] B. Gao, et al., Measurement of operator exposure to chlorpyrifos, Pest Manag. Sci. 70 (4) (2014) 636–641.
[22] R.W. Hornung, L.D. Reed, Estimation of average concentration in the presence of nondetectable values, Appl. Occup. Environ. Hyg 5 (1) (1990) 46–51.
[23] C. Großkopf, et al., Joint development of a new agricultural operator exposure model [cited 2020 12 May]; Available from: https://www.bfr.bund.de/cm/350/joint-development-of-a-new-agricultural-operator-exposure-model.pdf, 2013.
[24] U.S.E.P. Agency, Standard operating procedures for residential pesticide exposure assessment [cited 2020 12 March]; Available from: https://www.epa.gov/sites/production/files/2015-08/documents/usepa-opp-hed_residential_sops_oct2012.pdf, 2012.
[25] X. Duan, Highlights of the Chinese Exposure Factors Handbook, Academic Press, Beijing, 2015.
[26] J. He, et al., The first high-resolution meteorological forcing dataset for land process studies over China, Sci. Data 7 (1) (2020) 25.
[27] K. Yang, et al., On downward shortwave and longwave radiations over high altitude regions: observation and modeling in the Tibetan Plateau, Agric. For. Meteorol. 150 (1) (2010) 38–46.
[28] I.C. Chen, S.J. Bertke, B.D. Curwin, Quantile regression for exposure data with repeated measures in the presence of non-detects, J. Expo. Sci. Environ. Epidemiol. 31 (6) (2021) 1057–1066.
[29] H.L. Wong, et al., Assessment of exposure of professional agricultural operators to pesticides, Sci. Total Environ. 619 (2018) 874–882.
[30] Z. Li, et al., Effect of spraying direction on the exposure to handlers with hand-pumped knapsack sprayer in maize field, Ecotoxicol. Environ. Saf. 170 (2019) 107–111.
[31] U.S.E.P. Agency, AEATF Wipe Study Using Ready-To-Use Wipes Statistical Review for HSRB, 2011 [cited 2020 13 March]; Available from: https://archive.epa.gov/osa/hsrb/web/pdf/2-appendix-a-statistical-review-aeatf-wipe-trigger-spray.pdf.
[32] E.D. Bruce, Agricultural handler exposure Task Force: a technical overview of agricultural handler exposure data development, in: Data Generation for Regulatory Agencies: A Collaborative Approach, ACS Publications, 2021, pp. 111–167.
[33] J.J. Hox, M. Moerbeek, R. Van de Schoot, Multilevel Analysis: Techniques and Applications, Routledge, New York, 2017.
[34] M.P. Gatto, R. Cabella, M. Gherardi, Climate change: the potential impact on occupational exposure to pesticides, Annali dell'Istituto superiore di sanita 52 (3) (2016) 374–385.