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Dissipation kinetics, residue level, and risk assessment of chlorantraniliprole in *Rosa roxburghii* and its residue removal using household decontamination technique

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ORIGINAL ARTICLE

Abstract

Rosa roxburghii (*R. roxburghii*) is edible and medicinal fruit rich in vitamin C. Residues and potentially ecological risks of chlorantraniliprole (CAP) in the *R. roxburghii* orchard have aroused concern considering its extensive use for controlling oriental fruit moth, aphid, and whitefly of *R. roxburghii*. In this study, an effective UPLC–MS/MS method was developed for quantitation of CAP in *R. roxburghii* and soil using modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) dispersive solid-phase extraction with average recoveries of 73.89–96.63% and a relative standard deviation of <15%. Dissipation dynamics and terminal residue trials under the field conditions in 2021 and 2022 showed that half-lives of CAP in *R. roxburghii* (2.64–2.70 days) were shorter than those in soil (3.58–3.80 days), and its terminal residues in *R. roxburghii* and soil were 0.034–0.818 mg kg^{-1} and 0.003–0.015 mg kg^{-1}, respectively. Long-term dietary and soil ecological risk assessments indicated that the risk quotient was significantly less than 100%, meaning that the use of CAP on *R. roxburghii* at the recommended dosage was safe to consumers and soil ecology system, and that maximum residue limits (MRLs) and safe pre-harvest intervals of CAP in *R. roxburghii* were recommended as 0.7 mg kg^{-1} and 14 days, respectively. Removal experiments of CAP residues from *R. roxburghii* using simple household processing approaches exhibit that 2% baking soda water had the highest removal efficiency (56.04–60.33%). This study provides the basic data for establishing MRL, the safe and rational use of CAP in *R. roxburghii* production as well as the household decontamination prior to consumption of *R. roxburghii* fruits.

Keywords: chlorantraniliprole; *Rosa roxburghii*; soil; dissipation; risk assessment; residue removal; UPLC–MS/MS

Introduction

Rosa roxburghii (*R. roxburghii*) is a fruit of the family Rosaceae, and it is a wild plant common in southwest China (Liu *et al*., 2016; Wang *et al*., 2023; Zhao *et al*., 2022). It is also an emerging healthy and typical representative of the third-generation fruit that contains a large number of active substances beneficial for human body, such as vitamin C, superoxide dismutase (SOD), amino acids, flavonoids (Li *et al*., 2021a, 2022a; Zhang *et al*., 2022a). Many pharmacological studies have demonstrated that *R. roxburghii* possesses various beneficial functions, such as enhancing body immunity, decreasing blood pressure, and regulating the digestive system as

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well as antioxidant, anti-aging, and anti-radiation effects (Luo *et al*., 2023; Wang *et al*., 2019; Zhang *et al*., 2022b). Early studies have shown that *R. roxburghii* juice promotes the formation of foam cells, reduce the accumulation of cholesterol in cells, and thus reduce the incidence of atherosclerosis (Zhang *et al*., 2001). As one of the 12 major industries of Guizhou Province in China, *R. roxburghii* has developed rapidly in recent years because of its high nutritional, medicinal, and economic value.

However, with the expansion of *R. roxburghii* cultivation, many insect pests, such as fruit moth, aphid, and whitefly, became increasingly severe. The yield and quality of *R. roxburghii* declined drastically due to the attacks of these insect pests every year (Li *et al*., 2021b). In order to reduce the yield loss caused by insect pests, the cultivators often use chlorantraniliprole (CAP) as a control insecticide during production of *R. roxburghii*. CAP is a novel diamide insecticide, which has a novel insecticidal principle compared to other insecticides and can activate the ryanodine receptor of insects as well as improve the cells to release excessive calcium ions, and cause paralysis and death of insects (Cordova *et al*., 2006; Lahm *et al*., 2009). In China, since its introduction, CAP has been used widely for controlling lepidopteran and whitefly insect pests (Li *et al*., 2022b). After spraying CAP, its residue may remain in the fruit and soil ecosystem, and humans and soil invertebrates (such as earthworms and arthropods) may be poisoned through dietary intake. However, to date, no pesticides are indicated for the fruit moth, aphid, and whitefly of *R. roxburghii*, and little is known about the rationality and safety use of this insecticide in production of *R. roxburghii*. Therefore, an urgent need is felt for appropriate guidelines for the application of CAP in production of *R. roxburghii*.

In order to improve the yield and quality of agricultural products, the intensive use of pesticides leads to the presence of pesticide residues in agricultural products, especially in fruits and vegetables in various countries (Ahlawat *et al*., 2019; Donkor *et al*., 2016; Vijayasree *et al*., 2015; Winter, 2012). Many studies have shown that the combined toxicity of multiple pesticides to organisms has synergistic effects, and lower doses of pesticides could cause potential risks for the edible safety of fruits and vegetables (Vijayasree *et al*., 2015; Winter, 2012). Peeling and cooking have been demonstrated to remove some pesticide residues from fruits and vegetables (Soliman, 2001; Yang *et al*., 2012). However, peeling and cooking are not possible in case of some fruits and vegetables, such as strawberry and cherry. Therefore, cleaning has become a popular method for consumers to remove pesticide residues from fruits and vegetables. Like strawberry and cherry, the effects of different cleaning methods to remove CAP residues in *R. roxburghii* need to be investigated.

In recent years, the pretreatment methods of fruit and vegetable samples mainly include solid–liquid–solid dispersive extraction and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) dispersive solid-phase extraction (dSEP) (Saidi *et al*., 2017; Ueno *et al*., 2003; Wu *et al*., 2017; Yu *et al*., 2017). The main detection technologies include gas chromatography (GC), high-performance liquid chromatography (LC), gas chromatography–mass spectrometer (GC-MS), ultra-high liquid chromatography–tandem mass spectrometry (UPLC−MS/MS) (Ahlawat *et al*., 2019; Dong *et al*., 2023; Kuang *et al*., 2022; Varghese *et al*., 2015; Zhang *et al*., 2013). Among these, the QuEChERS extraction method has been distinguished as the official method of the Association of Official Analytical Chemists (AOAC) International (Lehotay, 2007). It is used as a pretreatment method because of its QuEChERS advantages. UPLC−MS/MS technology has the advantages of having strong separation ability, high sensitivity, strong selectivity, and high accuracy, and therefore used to detect pesticide residues. Currently, the QuEChERS sample preparation method combined with UPLC−MS/MS detection is widely used for the residual detection of pesticides (e.g., insecticides, fungicides, and herbicides) in plant fruits (Chen *et al*., 2021; Li *et al*., 2022c; Yan *et al*., 2016). However, *R. roxburghii* is more complex than many fruit matrices because it contains high vitamin, amino acid, and SOD contents. Therefore, it is necessary to improve the classical QuEChERS method to make it suitable for the analysis of CAP in *R. roxburghii*, and is important for ensuring both product quality and public safety.

So far, no study has been conducted on the residual behavior of CAP on *R. roxburghii*, and it is not discovered whether CAP is safe in the production of *R. roxburghii*. Therefore, it is necessary to study the dynamics and final residue of CAP in *R. roxburghii*. The aims of this work were to establish and validate an efficient quantitation method of CAP residues in *R. roxburghii* fruit and soil, to investigate dissipation dynamics and terminal residues of CAP in *R. roxburghii* fruit and soil, to assess the risk of CAP residual levels in *R. roxburghii* (dietary) and soil (soil ecosystems), and to determine the removal efficiency (RE) of CAP residues from *R. roxburghii* fruit using simple household processing methods. This work aimed to provide references for further management plans regarding the acceptable maximum residue limit (MRL) and safe pre-harvest interval (*PHI*) of CAP for producing *R. roxburghii*.

Materials and Methods

Reagents and chemicals

The commercial formulation 200 gL^{-1} CAP suspension concentrate (SC) was obtained from FMC Corporation

(Shanghai, China). The analytical-grade CAP (95% purity) was obtained from Aladdin (Shanghai, China). Formic acid and chromatographic-grade acetonitrile (ACN) were provided by Merck KGaA (Darmstadt, Germany) and Macklin (Shanghai, China), respectively. Analytical-grade ACN, anhydrous magnesium sulfate (AMS), sodium chloride (NaCl), 28% ammonia, dichloromethane, glacial acetic acid, ethyl acetate, methanol, and acetone were obtained from Tianjin Kermel Chemical Reagent Co. Ltd (Tianjin, China). Florisil was acquired from Shanghai Sinopharm Chemical Reagent Co. Ltd, China, and graphite carbon black (GCB) was obtained from XFNANO (Nanjing, China). Both C_{18} and primary secondary amine (PSA) were acquired from Bonna-Agela Technologies Co. Ltd. (Tianjin China). Baking soda was obtained from Macklin (Shanghai, China). Nylon syringe filter (0.22 µm, organic) and polypropylene centrifuge tube were obtained from Biosharp (Anhui, China). A miniaturized high-speed centrifuge (1-16) was from Sigma (Marburg, Germany). Centrifuge (BY-400B) was acquired from Beijing Baiyang Medical Instruments Co. Ltd (Beijing, China). Vortex oscillator was from Hangzhou Ruicheng Instruments Co. Ltd (Zhejiang, China). Autosampler glass vial was obtained from Guangzhou Bixiluo Technology Co. Ltd (Guangdong, China).

Field trial and sampling

The field trials were performed during 2021 and 2022 (August to October) in the orchard of *R. roxburghii*, called "Guinong No. 5" in Guizhou Province (Chaxiang Village, Gujiao Town, Longli County, Qiannan City, 26.56°N, 106.96°E, and 1430 m above sea level). During field experiments, weather temperature ranged from 18°C to 31°C and 18°C to 33°C in 2021 and 2022, respectively. The soil was of yellow-brown type, and its pH, organic matter, moisture, and cation exchange capacity values were 6.75, 1.72%, 45.70%, and 8.61 cmol kg^{-1}, respectively.

In order to investigate dissipation dynamics of CAP in *R. roxburghii* and soil, 200 gL^{-1} CAP suspension concentrate was sprayed on *R. roxburghii* plants and nearby soil with 90-mg active ingredient per liter (mg a.i. L^{-1}) using the 3WBJ-18B electrostatic sprayer (Guizhou Qianlin Agricultural Development Co. Ltd, China) in 2021 and 2022. The control plots were treated by the same amount of clean water. Each field trial plot had six *R. roxburghii* plants (in triplicate). The collection of soil samples (2.0 kg) at a depth of 0–10 cm and fruit samples (2.0 kg) was carried out using the five-point sampling method at different time intervals (after 2 h and 1–28 days of spraying).

In order to investigate the terminal residues of CAP in *R. roxburghii* orchards, 200 gL^{-1} CAP suspension concentrate was sprayed on *R. roxburghii* plants using an electrostatic sprayer at two doses (60 mg a.i. L^{-1} and 90 mg a.i. L^{-1}) in 2021 and 2022. Every treatment group was sprayed with each dose twice or thrice with 7-day intervals. According to the recommendations of Food and Agriculture Organization (FAO) as well as World Health Organization (WHO) in 2017, soil samples (2.0 kg) and *R. roxburghii* fruit samples (2.0 kg) were collected from each plot at a *PHI* of 7, 14, 21, and 28 days after the last application. CAP was stored at 4°C in a refrigerator until use. Both *R. roxburghii* fruit and soil samples were also stored in a refrigerator at −20°C until analysis.

Sample pretreatment

In this study, the pretreatment method of samples was appropriately optimized on the basis of classical QuEChERS method (Christia *et al*., 2015). Reagent combinations were selected for having a high extraction and purification effect by orthogonal experimental design as extraction solvents and purification agents for the sample. The extraction solvents were ACN, 1% formic acid–ACN, 1% ammonia–ACN, acetone, ethyl acetate, and dichloromethane. The purification agents of *R. roxburghii* were C_{18}, PSA, florisil, GCB, and C_{18}+PSA. The purification agents of the soil were C_{18}, PSA, florisil, and C_{18}+PSA.

The samples were mashed, and 10.0-g fruit samples and 10.0-g soil samples were placed in a 50-mL polypropylene centrifuge tube containing 10-mL extraction solvent (the highest extraction effect in pretreatment optimization) and 5 mL of water, respectively, and oscillated for 10 min, followed by addition of 1.0-g NaCl and 4.0-g anhydrous magnesium sulfate and oscillation for 5 min and centrifugation for 5 min at 4,000 rpm. A total of 1.5-mL supernatant and purification agent (the highest purification effect in pretreatment optimization) were transferred into 2-mL polypropylene centrifuge tube, oscillated in the vortex oscillator for 3 min, centrifuged at 12,000 rpm for 3 min; 1.5-mL supernatant was absorbed by a nylon syringe, passed through 0.22-µm filter membrane, and finally added to a 2-mL autosampler glass vial for UPLC–MS/MS analysis.

Conditions of UPLC–MS/MS analyses

The residue analysis of CAP was done by an Agilent 1290 Infinity II UPLC system with an Agilent 6470A triple quadrupole mass spectrometer (UPLC–MS/MS) (electrospray ionization [ESI] source). Sample, 5 µL, was injected by an autosampler and the target substance was separated on Agilent ZORBAX Eclipse Plus C_{18} (2.1×50 mm, 1.8 µm) column at 30°C; (A) 0.1% formic acid and

(B) ACN were used as a mobile phase with the flow rate of 0.4 mL min^{-1}. The gradient elution conditions were as follows: 0–1 min (10% B), 1–3 min (10–90% B), and 3–5 min d(90–10% B). Mass spectrometry ion monitoring was multiple reaction monitoring (MRM) in a positive mode.

Other parameters of mass spectrometry include drying gas temperature of 300°C, drying gas flow of 5 L min^{-1}, capillary voltage of 3,500 V, cell acceleration voltage of 4 V, and nebulizer pressure of 45 psi. MRM parameters of CAP include 483.9-m z^{-1} precursor ion, 452.9-m z^{-1} quantitative product ion, 285.8-m z^{-1} qualitative product ion, 105-V fragmentor voltage, 8-eV and 16-eV collision energy, and ion ratio of 47.5. The gas was high-purity nitrogen (99.99%). Under these instrument conditions, the retention time for CAP was 2.091 ± 0.02 min, and the blank *R. roxburghii* and soil samples had no obvious interference in the ion channel and retention time of CAP (Figure 1).

Method validation

The detection of CAP was validated on the basis of SANTE guidelines (European Commission Directorate General for Health and Food Safety [SANTE], 2021), including limit of quantification (LOQ) and limit of detection (LOD), as well as standard curve, accuracy, precision, and matrix effect (ME). The evaluation of linearity was conducted by matrix-matched calibration curve for the six concentrations of 0.001, 0.01, 0.05, 0.10, 1.00 and 5.00 mg L^{-1} in matrix blank extraction and ACN. CAP standard curves were drawn with mass concentration as the abscissa (x-axis) and peak area as the ordinate (y-axis). The accuracy was assessed by recovery (70–120%) tests by spiking blank samples at four additional levels of 0.003, 0.03, 0.30, and 3.00 mg kg^{-1}. Five parallel repeats were set for each spiking level. These samples were pretreated and tested according to the above-mentioned procedure. The average recovery of spiked samples and relative standard deviation (RSD) were calculated, which served to assess the precision of this method. The matrix effect was calculated using Equation (1) (Sakthiselvi *et al.*, 2020; Tang *et al.*, 2023; Yu *et al.*, 2017):

$$ME = \left(\frac{B}{A} - 1\right) \times 100\% \tag{1}$$

where A and B are the slopes of standard curves in ACN and *R. roxburghii* or soil matrix, respectively.

LOD and LOQ in soil and *R. roxburghii* fruit matrix were appraised based on the CAP concentrations that correspond to the signal-to-noise ratios of 3 and 10, respectively; these were used to assess the analytical method sensitivity.

Residue and dissipation kinetics

The dissipation dynamics of CAP in soil and *R. roxburghii* fruit samples was equaled using Equation (2), and half-lives were calculated by Equation (3) (Han *et al.*, 2022; Luo *et al.*, 2022):

$$C_t = C_0 \cdot e^{-kt} \tag{2}$$

$$T_{1/2} = \frac{\ln 2}{k} \tag{3}$$

where C_t is the CAP residue (mg kg^{-1}), C_0 is the initial CAP residue after the last spraying (mg kg^{-1}), k is the degradation rate constant of CAP in the field, and t is the collection time of samples after the last spraying (day).

Risk assessment

Long-term dietary risk assessment

The chronic dietary risk quotient (RQ_c) was evaluated according to the risk quotient method by following recent studies. The $RQ_c \leq 100\%$ indicated an acceptable risk and $RQ_c > 100\%$ revealed an unacceptable risk with adverse effects on human health (Yu *et al.*, 2017). The national estimated daily intake (NEDI) and RQ_c values were calculated using Equations (4) and (5) (Qin *et al.*, 2023; Yu *et al.*, 2017), respectively.

$$NEDI = \frac{\sum\left[F_i \times STMR_i(MRL_i)\right]}{bw} \tag{4}$$

$$RQ_c = \frac{NEDI}{ADI} \times 100\% \tag{5}$$

where $STMR_i$ (mg kg^{-1}) is the supervised trial median residue; *bw* (kg) is the average body weight (63 kg in China); and F_i is the reference food intake (kg).

Soil ecological risk assessment

The soil ecological risk quotient (RQ_s) was assessed by following the risk assessment procedures described by European Communities (2003). Acute 14-d LR_{50} (600 mg kg^{-1}) value from other arthropods (*Aphidius colemani*, adult) and LC_{50} (625 mg kg^{-1}) value from earthworms (*Eisenia foetida*) were considered for the determination of RQ_s (Agriculture and Environment Research Unit [AERU], University of Horticulture, 2022; Lewis *et al.*, 2016). The values of predicted no effect concentration (PNEC) were evaluated by dividing the corresponding toxicity values by the assessment factor, which was 1,000 in this case (Paramasivam, 2021). RQ_s for arthropods and earthworms were calculated using Equation (6):

$$RQ_s = \frac{EC}{PNEC} \tag{6}$$

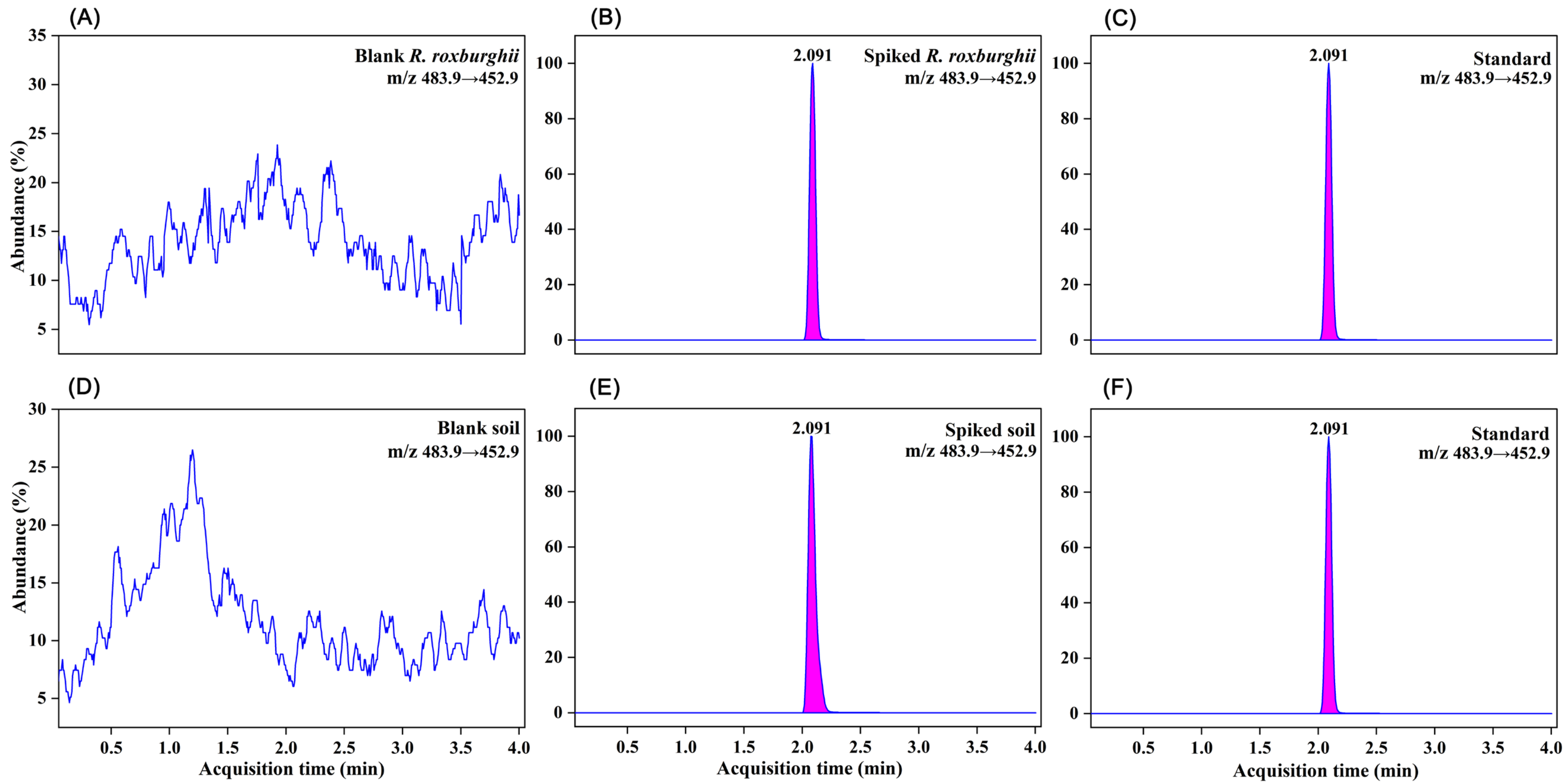

Figure 1. Representative UPLC-MS/MS chromatograms of chlorantraniliprole (CAP) in standard solution (1 mg L^{-1}), blank and spiked *R. roxburghii* samples (1 mg kg^{-1}), blank and spiked soil samples (1 mg kg^{-1}).

where PNEC is the predicted no effect concentration, and *EC* is the effective concentration.

Determination of removal of residues from fruit

Samples of *R. roxburghii* fruit were randomly sampled at 7 and 14 days after the last application of CAP in terminal residual plots (dose: 90 mg a.i.L^{-1}; spraying: 3 times) to compare and analyze the effects of differently simple household processing approaches on the removal of residual CAP from *R. roxburghii* fruit. Samples of *R. roxburghii* fruit were divided into six groups with three replicates, including control (untreated), baking soda water (2%), salt water (2%), washing water of rice, ordinary temperature tap water, and hot (40°C) tap water for washing. The fruit was immersed in the above-mentioned 1-L washing water of rice for about 1 min and gently stirred manually. The fruits was then placed on a filter paper for moisture absorbance, and air-dried. The air-dried fruit samples of *R. roxburghii* were treated using the above-mentioned sample pretreatment method, and the residue of CAP in *R. roxburghii* fruits were determined by UPLC–MS/MS analyses. The removal efficiency was calculated using Equation (7):

$$RE = \frac{C_0 - C}{C_0} \tag{7}$$

where C_0 and C are the residues of CAP (mg kg^{-1}) in *R. roxburghii* fruit prior to and after washing treatment, respectively.

Results and Discussion

Optimization of extraction solvent and purification agent

The commonly used extraction solvents mainly included ACN, acetone, and dichloromethane. Purification agents mainly included PSA, GCB, C_{18}, and florisil (Anastassiades *et al.*, 2003; Qin *et al.*, 2016; Zhang *et al.*, 2012). The sample preparation method to analyze CAP in both matrices was optimized by changing extraction solvents and purification agents, and comparing extraction and purification effects based on the classical QuEChERS method. The extraction and purification effects of different reagent combinations are shown in Figures 2A and 2B. The combination of ACN+PSA had the highest recovery rate (92.06%) of CAP in *R. roxburghii*, and the combination of ACN+PSA+C_{18} had the highest recovery rate (94.08%) of CAP in soil. Therefore, ACN was used as extraction solvent for the pretreatment of *R. roxburghii* and soil samples, and PSA and PSA+C_{18} were used as purification agents for *R. roxburghii* and soil samples, respectively.

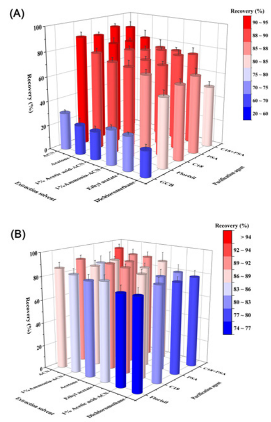

Figure 2. The choice of extraction solvents and purification agents for (A) *R. roxburghii* fruit and (B) soil samples.

Validation of analytical method

Accuracy and precision

The recovery and RSD of four spiking levels are shown in Table 1. The results demonstrated that the average recoveries of CAP in *R. roxburghii* and soil were 74.44–95.64% and 73.89–96.63%, with intraday RSDs of 3.64–13.10% and 4.12–12.60%, respectively. Moreover, the interday RSDs (n = 15) of CAP in the two substrates ranged from 2.10% to 11.21%. Obviously, the analytical method established here had satisfactory accuracy and precision, meeting the requirements of the SANTE guidelines and settling within the recovery range of 70–120% and RSD of less than 20% (European Commission Directorate General for Health and Food Safety [SANTE], 2021). Hence, the analytical method demonstrated good specificity and robustness.

Sensitivity, linearity, and matrix effect

In the concentration range of 0.001–5 μg mL^{-1}, the method had a good linear relationship (Table 1), and the determination coefficient (R^2) for CAP in *R. roxburghii* fruit and soil matrix was 0.9990 and 0.9933, respectively. In this study, the matrix effect of CAP in *R. roxburghii* fruit and soil samples was -19.68% and -22.04%, respectively, which showed a matrix suppression effect in *R. roxburghii* fruit and soil. Hence, in order to eliminate matrix effect in this study, the matrix matching standard curve was used to quantify residues of this insecticide in *R. roxburghii* fruit and soil samples. Based on the above-mentioned extraction and purification conditions, the LOD and LOQ of CAP in *R. roxburghii* fruit and soil matrix was 1.00 μg kg^{-1} and 3.33 μg kg^{-1}, respectively. Thus, the established method was accurate, sensitive, and appropriate for detecting the residues of CAP in *R. roxburghii* fruit and soil samples.

Table 1. Recoveries with RSD, linear equation with R^2, LOD, LOQ, and ME of chlorantraniliprole (CAP) in *R. roxburghii* fruit and soil.

Matrix	Spiked level (mg kg^{-1})	Intra-day (n = 5) Average recoveries (RSD[a]) (%)			Inter-day RSD (n = 15) (%)	Linear equation (R^2)	LOD[b] (μg kg^{-1})	LOQ[c] (μg kg^{-1})	ME[d] (%)
		Day 1	Day 2	Day 3					
R. roxburghii	0.003	75.91 (11.81)	78.80 (13.10)	74.44 (10.73)	11.21	y = 20390x + 353.82 (0.9990)	1.00	3.33	-19.68
	0.03	86.40 (5.73)	85.73 (5.21)	87.13 (6.12)	7.03				
	0.30	82.70 (6.53)	84.51 (7.11)	85.33 (6.82)	6.81				
	3.00	92.07 (3.64)	95.64 (4.71)	93.71 (4.24)	2.10				
Soil	0.003	77.24 (10.92)	73.89 (12.60)	75.42 (10.20)	10.32	y = 19791x - 2376.38 (0.9933)			-22.04
	0.03	86.82 (6.36)	82.61 (7.43)	85.44 (6.83)	7.50				
	0.30	88.51 (4.90)	85.70 (5.91)	83.91 (6.23)	3.83				
	3.00	96.63 (5.39)	93.28 (4.84)	93.93 (4.12)	2.54				
Solvent	-	-	-	-	-	y = 25385x + 410.96 (0.9955)	-	-	-

[a]RSD: relative standard deviation; [b]LOD: limit of detection; [c]LOQ: limit of quantification; [d]ME: matrix effect.

Dissipation of CAP in *R. roxburghii* fruit and soil samples

The dissipation equations of CAP for *R. roxburghii* fruit and soil samples in Guizhou province are shown in Table 2. The dissipation of CAP in *R. roxburghii* fruit and soil samples conformed well to the first-order kinetic equation ($R^2 > 0.97$) during the continuous two-year field experiments. The initial deposition of CAP in *R. roxburghii* fruit and soil samples were 1.073–1.158 mg kg^{-1} and 3.047–3.144 mg kg^{-1}, respectively. The half-lives of CAP in *R. roxburghii* fruit and soil samples were 2.64–2.70 days and 3.58–3.80 days, respectively. Owing to similar climatic conditions in 2021 and 2022, no significant differences were discovered between the half-lives of CAP for *R. roxburghii* fruit and soil at the same dose. During the experiment, the average temperatures in 2021 and 2022 were 24.5°C and 25.5 °C, respectively, and the total precipitation was 73.02 mm and 70.14 mm, respectively. The reported dissipation half-lives of CAP were 2.70 days for grapes (Malhat, 2012), 3.15 days for peach (Žeach *et al.*, 2019), 8.0–12.2 days for lychee (Liu *et al.*, 2023), and 2.2–4.7 days for tea (Xu *et al.*, 2022). The half-life of this insecticide in soil presented here was consistent with that reported by Malhat *et al.*, (2012) but not in agreement with that reported by Paramasivam (2021), which could be due to differences in climatic conditions and soil physicochemical properties. The above-mentioned results indicated that the half-lives of the same pesticide in case of various crops were different, which could be due to differences between substrates resulted from differences in original residues and degradation rates (Han *et al.*, 2022). Meanwhile, the environmental factors and soil properties can also affect significantly the dissipation behavior of pesticides (Guo *et al.*, 2021).

Terminal residues of CAP in *R. roxburghii* fruit and soil samples

The terminal residues of CAP in *R. roxburghii* fruit and soil samples in 2021 and 2022 are summarized in Figure 3 and Table 3. It was observed that the terminal residual levels of CAP in *R. roxburghii* fruit and soil samples exhibited a decreasing trend with increase in time, and the decreasing trend was significant. At doses of 60 mg a.i. L^{-1} and 90 mg a.i. L^{-1}, the terminal residues of CAP in *R. roxburghii* fruit (Figure 3) and soil (Table 3) samples were 0.034–0.818 mg kg^{-1} and 0.003–0.015 mg kg^{-1}, respectively. At 21 days after the last application of CAP, the residual levels of CAP in *R. roxburghii* fruit samples were <0.5 mg kg^{-1}. The *R. roxburghii* plant is a kernel fruit. To date, no MRL has been established for CAP residues in *R. roxburghii* fruit. However, MRL for kernel fruits (0.5 mg kg^{-1}) has been established by the European Union (European Commission 2021). The findings

Table 2. The degradation kinetic parameters of chlorantraniliprole (CAP) in *R. roxburghii* and soil.

Year	Matrix	Dissipation equation	Initial deposition (mg kg^{-1}) ± SD	R^2	Half-lives (day)
2021	*R. roxburghii*	$Ct = 1.1697e^{-0.2630t}$	1.158 ± 0.103	0.9796	2.64
	Soil	$Ct = 3.0140e^{-0.1934t}$	3.047 ± 0.246	0.9864	3.58
2022	*R. roxburghii*	$Ct = 1.0827e^{-0.2571t}$	1.073 ± 0.112	0.9779	2.70
	Soil	$Ct = 3.0933e^{-0.1824t}$	3.144 ± 0.222	0.9864	3.80

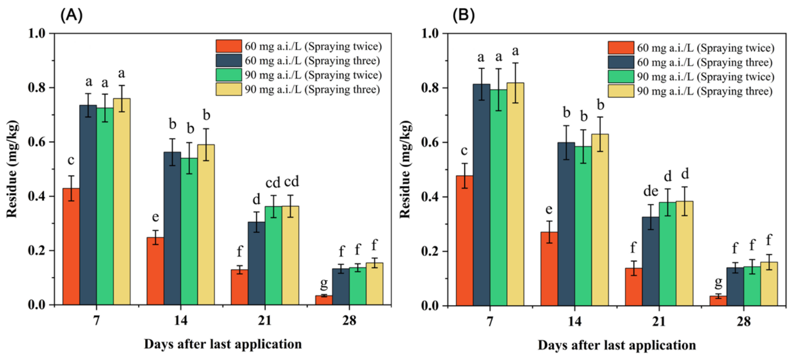

Figure 3. Terminal residues of chlorantraniliprole (CAP) in *R. roxburghii* in (A) 2021 and (B) 2022.

presented here provided data for the Chinese government to establish MRLs for the residual levels of CAP in *R. roxburghii* production.

Risk assessment

Chronic dietary risk assessment of CAP

According to the principle of maximum dietary risk, the default assumption was that all registered crops were treated with CAP (Lin *et al*., 2019). For assessing the chronic dietary risk of CAP, MRLs for relevant registered crops are used. The NEDI values were calculated by using the highest MRL in each food group. Since no MRLs are assigned for CAP in case of *R. roxburghii* fruits, a national chronic dietary risk assessment was carried out with STMR as a reference residue limit. STMR for *R. roxburghii* fruits and MRL values for sugarcane, rice, cabbage, chili, corn, and sweet potato were used to calculate NEDI values. The acceptable daily intake (ADI) value of CAP is specified as 2 mg kg·bw^{-1} in the latest Chinese standards of the Ministry of Agriculture and Rural Affairs of the People's Republic of China (2021). The calculated results are shown in Table 4. RQ_c was 3.02–3.04%, which was less than 100%, indicating that eating *R. roxburghii* fruits will not cause unacceptable risk to the health of the general population.

Table 3. The residue and ecological risk assessment of chlorantraniliprole (CAP) in soil.

Dosage (mg a.i.L^{-1})	Spraying time	Sampling interval (d)	Residue (mg kg^{-1})[a]	HR (mg kg^{-1})[b]	PNEC[c]		RQs[d]	
					Earthworms	Arthropods	Earthworms	Arthropods
60	2	7	0.010	0.012	0.625	0.600	0.019	0.020
		14	0.007	0.009			0.014	0.015
		21	0.003	0.003			0.005	0.005
		28	<LOQ	-			-	-
	3	7	0.010	0.013			0.021	0.022
		14	0.008	0.009			0.014	0.015
		21	0.003	0.004			0.006	0.007
		28	<LOQ	-			-	-
90	2	7	0.014	0.017			0.027	0.028
		14	0.009	0.010			0.016	0.017
		21	0.003	0.004			0.006	0.007
		28	<LOQ	-			-	-
	3	7	0.015	0.018			0.029	0.030
		14	0.009	0.011			0.018	0.018
		21	0.004	0.004			0.006	0.007
		28	<LOQ	-			-	-

[a]Residues were the average of 2-year experiments; [b]HR: the highest residue obtained from field experiments; [c]PNEC: predicted no effect concentration; [d]RQ_S: the soil ecological risk quotient.

Table 4. The chronic dietary risk assessment of chlorantraniliprole (CAP) based on the Chinese dietary pattern.

Crops	Food classification	F_i (kg)[a]	MRLs (mg kg^{-1})	Sources[b]	NEDI (mg kg·bw^{-1})	RQ_c (%)
Sugarcane	Sugar and starch	0.004	0.05	China	3.49×10^{-6}	2.00×10^{-4}
Rice	Rice and its product	0.240	0.50	China	1.90×10^{-3}	0.10
Cabbage	Light vegetable	0.184	20.00	EU	5.83×10^{-2}	2.92
Chilli	Dark vegetable	0.092	0.02	EU	2.91×10^{-5}	1.00×10^{-3}
Corn	other grain	0.023	0.02	China	7.40×10^{-6}	4.00×10^{-4}
Sweet potato	Tuber	0.050	0.02	EU	1.57×10^{-5}	1.00×10^{-3}
R. roxburghii	Fruit	0.046	0.73 (7 d)	$STMR_7$	5.30×10^{-4}	0.03
			0.55 (14 d)	$STMR_{14}$	3.99×10^{-4}	0.02
			0.33 (21 d)	$STMR_{21}$	2.39×10^{-4}	0.01
			0.14 (28 d)	$STMR_{28}$	1.02×10^{-4}	0.01
Total		0.684	-	-	6.08×10^{-2}	3.04
					6.07×10^{-2}	3.03
					6.05×10^{-2}	3.03
					6.04×10^{-2}	3.02

[a]F_i is the dietary intake for a certain kind of food of healthy Chinese people.
[b]$STMR_7$, $STMR_{14}$, $STMR_{21}$, and $STMR_{28}$ are the supervised experiments median residue of CAP in *R. roxburghii* with the pre-harvest interval (PHI) of 7, 14, 21, 28 d, respectively.

Soil ecological risk assessment

The soil ecological risk of CAP to earthworms and arthropods was predicted by calculating RQ_s. The calculated results are shown in Table 3; the PNEC values of earthworms and arthropods at the doses of 60 mg a.i.L^{-1} and 90 mg a.i.L^{-1} were 0.625 and 0.600, respectively, and the RQ_s values for earthworms and arthropods were in the range of 0.005–0.029 (low risk) and 0.005–0.030 (low risk), respectively. These results demonstrated that the use of CAP in *R. roxburghii* orchards presented an acceptable risk to earthworms and arthropods. Previously, the application of CAP in okra and tomato fields was reported as safe for both earthworms and arthropods (Mariappan and Kaithamalai, 2022; Paramasivam, 2021), which is consistent with the findings of this study.

MRLs and PHIs for CAP in *R. roxburghii* fruit samples

The referral of MRLs for residues of CAP in *R. roxburghii* fruit was conducted by following its highest residue (HR), PHI, and dietary risk assessment results under good agricultural practices (GAP). In view of the growth period of this fruit and the registration data of CAP in many other fruits, MRLs for residues of CAP in *R. roxburghii* fruits were recommended using the field trial data of 14 days PHI. When the PHI was 14 days, the HR of CAP was 0.658 mg kg^{-1} and the RQ_c was 3.03%. Therefore, the MRL for CAP residues in *R. roxburghii* fruit was recommended as 0.7 mg kg^{-1} based on its HR and dietary exposure assessment results. Taken together, the recommended MRLs of CAP in *R. roxburghii* fruits are reasonable and reliable for ordinary consumers, and provide safe and appropriate guidelines for the application of CAP in *R. roxburghii* production.

Removal of CAP residues from *R. roxburghii* fruit samples

After the application of pesticides, they tend to remain on fruit cuticles, and consumers use household decontamination methods to wash them off prior to consumption. The removal efficiency of CAP residues (90 mg a.i.L^{-1}, spraying thrice) from *R. roxburghii* fruits by different household decontamination methods is listed in Table 5. After the last application for 7- and 14-day treatments, the residues of untreated *R. roxburghii* fruits were significantly higher than that after five removal methods. Among these removal methods, the residues of untreated fruits, tap water-, salt water-, baking soda water-, washing water of rice-, and hot water-treated fruits were 0.517–0.724 mg kg^{-1}, 0.446–0.607 mg kg^{-1}, 0.288–0.376 mg kg^{-1}, 0.227–0.288 mg kg^{-1}, 0.261–0.347 mg kg^{-1}, and 0.343–0.480 mg kg^{-1}, respectively. By comparing these removal methods, it was observed that 2% baking soda water had an outstanding removal efficiency (56.04–60.33%), followed by washing with water of rice (49.52–52.02%), 2% salt water (44.21–48.10%), hot water (33.71–33.73%), and tap water (13.80–16.21%); significant differences were observed in removal efficiencies among these five removal methods. The present results are similar to those reported by other studies

Table 5. Removal efficiency (RE) of CAP residues from *R. roxburghii* fruit.

Processed fraction	DALA[a] 7		DALA 14	
	Residue (mg kg^{-1}) ± SD	RE (%)	Residue (mg kg^{-1}) ± SD	RE (%)
Untreated (control)	0.724 ± 0.064a	-	0.517 ± 0.043a	-
Tap water	0.607 ± 0.044b	16.21 ± 0.458e	0.446 ± 0.032b	13.80 ± 0.723e
Salt water (2%)	0.376 ± 0.032d	48.10 ± 1.498c	0.288 ± 0.027d	44.21 ± 0.851c
Baking soda water (2%)	0.288 ± 0.024e	60.33 ± 1.124a	0.227 ± 0.012e	56.04 ± 1.493a
Washing water of rice	0.347 ± 0.019de	52.02 ± 1.250b	0.261 ± 0.028de	49.52 ± 1.518b
Hot water	0.480 ± 0.040c	33.71 ± 0.625d	0.343 ± 0.022c	33.73 ± 0.379d

[a]DALA: days after last application; [b]CAP: chlorantraniliprole.

(Ahlawat *et al*., 2019; Vijayasree *et al*., 2015), who evaluated the removal methods of CAP from okra, *Capsicum annum*, and brinjal by using tap water, 2% salt water, and hot water. Thus, *R. roxburghii* fruit polluted by CAP was recommended to be decontaminated by 2% baking soda water or washing with water of rice prior to consumption.

Conclusions

In this study, an efficient method for quantifying CAP in *R. roxburghii* and soil samples was established based on the combination of the modified QuEChERS method and UPLC–MS/MS technology. Compared to soil dissipation, a shorter persistence of CAP in *R. roxburghii* fruits was observed during the 2-year field experiments. Our findings showed that the recommended dose of CAP could be applied in *R. roxburghii* production, and the risk factor for humans and soil animals was acceptable and safe. MRLs of 0.7 mg kg^{-1} and PHI of 14 days for residues of CAP in *R. roxburghii* fruits were recommended following the terminal residue and dietary risk assessment data. For residue removal of CAP from *R. roxburghii* fruits, 2% baking soda water could be used as a simple household processing method. This study provides basic data for the establishment of MRLs, the reasonable use of CAP in *R. roxburghii* production, and its household decontamination prior to consumption. However, the authentication and analysis of metabolites as well as the degradation mechanism of CAP in *R. roxburghii* were not involved in the present study. Therefore, further studies were needed to evaluate the safety of CAP metabolites in *R. roxburghii*.

Author Contributions

Xuefei Zhang: software, validation, writing of original draft, formal analysis, data curation, investigation, and visualization. Zhaochun Jiang: investigation, visualization, supervision, methodology, project administration, writing-review, and editing. Lei Han: software, validation, writing of original draft, formal analysis, and investigation. Xiaomao Wu: resources, conceptualization, methodology, project administration, fund acquisition, writing-review, and editing.

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Conflicts of Interest

The authors declared no conflict of interest.

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