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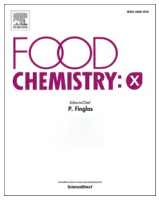

The fate and potential hazards of chlorfenapyr and one metabolite tralopyril in cabbages: A comprehensive investigation

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ABSTRACT

The potential hazards of chlorfenapyr warrant attention owing to its widespread application on vegetables. A comprehensive investigation of the fate of chlorfenapyr in the ecosystem is imperative. This paper presents a method for detecting chlorfenapyr and tralopyril in cabbages, which exhibits good linearity (determination coefficients $>$ 0.99) and satisfactory recoveries (82.50 %–108.03 %). Chlorfenapyr residues in cabbages demonstrate a positive correlation with its application dose and time. Tralopyril can inhibit the dissipation of chlorfenapyr, as evidenced by the half-lives of 5.67–11.14 d (chlorfenapyr) and 6.91–14.77 d (total chlorfenapyr). The results of terminal residues (<2.0 mg/kg) and dietary risk assessment (<100 %) suggest preharvest intervals of 14 d (greenhouse) and 10 d (open-field). Additionally, the uptake of chlorfenapyr in cabbages is limited (translocation factor $<$ 1), while the downward translocation predominantly occurs through phloem transport. The findings provide valuable insights for understanding the fate and potential risks of chlorfenapyr in cabbages.

Introduction

In addition to being a crucial source of vital vitamins, minerals, fiber, and essential amino acids (Ferrer, García-Reyes, Mezcua, Thurman, & Fernández-Alba, 2005), vegetables possess a diverse array of biologically active components, including potassium, folic acid, flavonoids, and other phenolic compounds (Walorczyk, 2008; Roberts & Moreau, 2016). Nevertheless, the vegetable cultivation and processing sectors suffer substantial reductions in output owing to insect pests (Farina, Abdullah, Bibi, & Khalik, 2017; Ofuya, Okunlola, & Mbata, 2023). The use of pesticides is widely recognized as a highly economical and effective method for mitigating the prevalence of pests and diseases as well as enhancing vegetable yields (Fan et al., 2013; Pan et al., 2019; Wang et al., 2021). However, the persistent application of diverse pesticide variants introduces them into the environment during the safeguarding of vegetables, leading to elevated levels of pesticide residues in agricultural commodities. Furthermore, the potential transmission of these residues through the food chain poses a potential hazard to consumer health (Liang, Li, Li, Wu, Zhou, & Liu, 2011; Zhang, Feng, et al., 2017; Pullagurala et al., 2018; Jia et al., 2021). Hence, understanding the pattern of pesticide accumulation, distribution, and translocation in vegetables is imperative for conducting safety risk assessments of pesticides in agricultural commodities.

Chlorfenapyr (Fig. S1A, Supporting Information) is currently extensively employed for the management of insect populations that exhibit resistance to carbamates, organophosphates, and pyrethroids in various crops, including vegetables (Cao, Yi, Huang, Hou, & Lu, 2006). The mode of action of this pesticide involves the demethylation of *N*-ethoxymethyl of chlorfenapyr by multifunctional oxidative enzymes within the mitochondria of insect cells, resulting in the formation of tralopyril, an active metabolite (Fig. S1B, Supporting information). Tralopyril disrupts the proton balance across the mitochondrial membrane, inhibits the conversion of adenosine diphosphate to adenosine triphosphate, and ultimately induces pest mortality through somatic cell failure (Yang et al., 2020; Chen et al., 2021). According to the FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization) (2018), chlorfenapyr and tralopyril have been reported to possess the potential to cause harm to environmental organisms. Therefore, the combined effects of chlorfenapyr and tralopyril must be considered while evaluating their risk. However, despite numerous previous studies that have focused on developing analytical methods and investigating the dissipation of chlorfenapyr in various

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crops (Ditya, Das, Sarkar, & Bhattacharyya, 2010; Rahman et al., 2012; Ghani & Abdallah, 2016; Shi, Li, Yuan, Li, & Liu, 2016; Patra, Ganguly, Barik, & Samanta, 2018; Li, Chen, & Hu, 2019; Badawy, Mahmoud, & Khattab, 2020), only Xu et al. (2022) have determined the residues of both analytes in tea. Unfortunately, there is still a lack of information regarding the fate of chlorfenapyr and tralopyril in vegetables.

This paper presents the development and validation of a straightforward analytical approach for quantifying the levels of chlorfenapyr and its metabolite tralopyril in various cabbage tissues (roots, stems, and leaves). Further, the dissipation and residues of chlorfenapyr and tralopyril were examined in cabbages subjected to different applications of pesticide doses and durations. Furthermore, the potential dietary intake risk of chlorfenapyr in cabbages was assessed for Chinese consumers using acute and chronic risk quotients (RQs). In addition, the accumulation, distribution, and translocation patterns of chlorfenapyr and tralopyril in cabbage plants were investigated using two application methods: foliar spraying and root irrigation. The research outcomes hold some notable implications for understanding the destiny and potential hazards of chlorfenapyr and tralopyril within cabbage ecosystems as well as for ensuring the appropriate and secure utilization of chlorfenapyr in vegetable cultivation.

Materials and methods

Chemical reagents and materials

The standards of chlorfenapyr (97 % purity) and tralopyril (98 % purity) were purchased from Ehrenstorfer GmbH (Augsburg, Germany) and Shanghai Yuanye Bio-technology Co., Ltd. (Shanghai, China), respectively. The formulation of chlorfenapyr (suspension concentrate (SC), 100 g/L) was bought from BASF Plant Protection (Jiangsu) Co., Ltd. (Nantong, China). Mass spectrometry (MS)-grade methanol and formic acid were obtained from Thermo Fisher Scientific (Waltham, USA). Acetonitrile, acetone, NaCl, and anhydrous $MgSO_4$ were provided by Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Primary secondary amine (PSA) was purchased from Bonna-Agela Technologies (Tianjin, China), and the nylon syringe filters (0.22 μm) were bought from Tianjin Navigator Lab Instrument Co., Ltd. (Tianjin, China).

Field trials

The cabbage seeds underwent a germination period of 10–15 d in a greenhouse; after which, they were transplanted into soil and cultivated for approximately 40 d. Multiple batches of seedlings exhibiting consistent growth patterns, with a root length of 9 cm and a shoot length of 11 cm, were prepared for subsequent experiments. To investigate the dissipation dynamics and terminal residues of chlorfenapyr and tralopyril in cabbages, a control group and four treatment groups were separately established under greenhouse and open-field conditions. The treatment groups comprised two application doses (105 and 157.5 g a.i./ha) and two application times (1 and 2) of chlorfenapyr via foliar spraying. Cabbage shoot samples were collected in triplicate ($n = 3$) at specific time points (0 [2 h], 1, 3, 5, 7, 10, 14, 21, 28, and 35 d) after the final application for each treatment. Among these samples, specific intervals (7, 10, 14, and 21 d) were chosen for determining the terminal residues. The evaluation of dietary intake risk involved determining the sum of chlorfenapyr and tralopyril residues (referred to as total chlorfenapyr) using the methods outlined in Table S1 (Supplementary Information), provided by the FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization) (2018). To investigate the accumulation, distribution, and translocation of chlorfenapyr and tralopyril in cabbage, a study was conducted using foliar spraying with two application doses (105 and 157.5 g a.i./ha) and a control group under soil-cultivated conditions (downward translocation). Additionally, root irrigation with two application doses (5.6 and 11.2 mg/L) and a control group were established under hydroponic conditions (upward translocation). The roots, stems, and leaves of cabbages were separately collected in triplicate ($n = 3$) at various time points (0 [2 h], 1, 2, 3, 5, 7, 10, 14, 21, and 28 d) after the application of chlorfenapyr. All the samples were stored at −20 °C before analysis.

Instrumentation and sample pretreatment

Instrumentation

The content of chlorfenapyr was detect via gas chromatography (GC) using a 7890 N gas chromatograph equipped with an electron capture detector (Agilent Technologies, CA, USA). The content of tralopyril was analyzed via an LC-20AD liquid chromatography (LC) system (Shimadzu Corporation, Kyoto, Japan) with a Sciex 4000 Q TRAP triple quadrupole MS/MS system (Applied Biosystems, Foster City, USA). Detailed analytical parameters are listed in the Supporting Information.

Sample pretreatment

First, 10 ± 0.02 g of a cabbage leaf (stem or root) sample was weighed into a 50-mL centrifuge tube. Then, 20 mL of acetonitrile, 4 g of anhydrous $MgSO_4$, and 2 g of NaCl were added to the tube. The resulting mixture was vortexed for 3 min at 2,500 rpm and centrifuged for 5 min at 6,000 rpm. To detect chlorfenapyr, 1 mL of the supernatant formed after vortexing was collected and subjected to evaporation at 40 °C. The resulting residues were then dissolved in 1 mL of acetone and subsequently transferred into a 2-mL centrifuge tube containing 100 mg of PSA. After vortexing for 30 s at a speed of 2,500 rpm and subsequent centrifugation for 2 min at 8,000 rpm, the liquid component was filtered through a 0.22-μm nylon syringe filter before GC analysis. To detect tralopyril, 1 mL of the extracted supernatant was transferred into a 2-mL centrifuge tube containing 100 mg of PSA. The resulting mixture was vortexed for 30 s at 2,500 rpm and centrifuged for 2 min at 8,000 rpm. Subsequently, the supernatant was filtered through a 0.22-μm nylon syringe filter before LC–MS/MS analysis.

Method optimization and validation

The quick, easy, cheap, effective, rugged, and safe (QuEChERS) method is commonly used in the pretreatment process of pesticide residue analysis. However, certain QuEChERS procedures may require optimization for specific analytes and crops (Bruzzoniti et al., 2014). This study focused on screening extraction solvents (ethyl acetate, acetone, hexane, acetontrile, acetontrile with 1 % of acetic acid) and purification sorbents (PSA and C18) for determining the content of chlorfenapyr and tralopyril in cabbage. Furthermore, the developed analytical methods were validated by calculating parameters such as linearity, matrix effect (ME), limit of detection (LOD), and limit of quantification (LOQ) (Rahman et al., 2012; Liu, Chen, Han, Chen, & Zhang, 2021). The linearity of the chlorfenapyr and tralopyril calibration curves was evaluated by plotting the curves using solvent and matrix-matched standards at seven concentrations (0.005, 0.05, 0.1, 0.5, 1, 5, and 10 μg/mL). The ME value was determined by dividing the slope of the solvent standard curve by the slope of the matrix-matched standard curve (Ghani & Abdallah, 2016). The LOD was calculated with a signal-to-noise (S/N) ration of 3, while the LOQ was determined as the lowest spiked level (Liu et al., 2021). The accuracy and precision of the developed methods were evaluated through the assessment of intraday ($n = 5$) and interday ($n = 15$) recoveries of chlorfenapyr and tralopyril in different tissues of cabbage, as well as the determination of relative standard deviations (RSDs) (Tsochatzis, Menkissoglu-Spiroudi, Karpouzas, & Tzimou-Tsitouridou, 2010; Zhang, Ding, et al., 2017). The spiked levels of the analytes in the roots, stems, and leaves of cabbages were set at 0.01, 0.1, and 1 mg/kg, respectively.

Data processing and statistical analysis

The dissipation dynamics of chlorfenapyr and tralopyril in cabbages

were evaluated using the first-order kinetic model (Badawy et al., 2020). The acute RQ (RQ_a) and chronic RQ (RQ_c) were used to evaluate the acute and chronic dietary intake risks, respectively (Chen, Ye, Liao, Wu, & Zhang, 2024), and were determined using the standard methods (FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization), 2011). The residual levels of chlorfenapyr and tralopyril in various parts of the cabbage—including roots, stems, and leaves—as well as the corresponding translocation factors (TFs) were used to examine the accumulation, distribution, and translocation patterns of these substances within the cabbage plant (Wang, Zhang, Huang, Zhao, & Lv, 2011). The detailed calculation procedures are shown in the Supporting information.

The experimental data were processed using Microsoft Office Excel 2016 (Microsoft Corporation, Washington, D.C., USA) and Origin 2022 (OriginLab Corporation, Massachusetts, USA). The statistical analysis was performed on SPSS Statistics software ver. 27 (IBM Corporation, New York, USA), and a one-way analysis of variance followed by Duncan's multiple range test ($P < 0.01$) was used for analyzing the differences among the treatments. All experimental data were expressed as the average value ± standard deviation (SD) ($n = 3$).

Results and discussion

Optimization and validation of the analytical methods

To enhance the efficacy of the extraction technique for identifying chlorfenapyr and tralopyril in cabbage samples, thorough evaluation and refinement of the extraction solvent and purification sorbent were conducted independently. A total of five extraction solvents, namely ethyl acetate, acetone, *n*-hexane, acetonitrile, and acetonitrile (1 % acetic acid), were carefully chosen for this study. The extraction efficiency data (Fig. S2, Supplementary Information) indicated that acetonitrile and acetonitrile (1 % acetic acid) exhibited significantly higher recoveries (81.82 %–106.94 %) for the two analytes in various cabbage samples compared with other extraction solvents ($P < 0.001$). Considering the goals of reducing consumption and streamlining the procedure, acetonitrile was ultimately selected as the optimal extraction solvent. Meanwhile, various purification sorbents, including 100-mg PSA, 50-mg PSA, 100-mg C18, 50-mg C18, and 50-mg PSA + 50-mg C18, were employed. In Fig. S3 (Supplementary Information), when PSA was selected, the recoveries were 91.58 %–99.16 % (100 mg) and 92.59 %–100.85 % (50 mg) for chlorfenapyr, and 90.59 %–95.02 % (100 mg) and 83.04 %–85.45 % (50 mg) for tralopyril, indicating that 100 mg of PSA provided better purification and extraction efficiency. When C18 were used, the recoveries were 91.37 %–109.68 % (100 mg) 84.71 %–91.94 % (50 mg) for chlorfenapyr, and 88.55 %–92.72 % (100 mg) and 76.38 %–87.68 % (50 mg) for tralopyril, showing that 100 mg of C18 was more suitable. The recovery efficiency of the combination of PSA and C18 was not as good as that of the single application with recoveries of 67.12 %–87.18 % for both analytes. From the extraction and purification efficiency, and cost savings, 100 mg of PSA was determined to be the optimal sorbent for the purification process.

After optimization of the pretreatment procedures, the analytical method was validated. The solvent and matrix-matched calibration curves of chlorfenapyr and tralopyril (Table 1) exhibited a strong linear relationship with R^2 values exceeding 0.99. Notably, the three types of cabbage tissues demonstrated a matrix suppression effect for chlorfenapyr (MEs < 1), while a matrix enhancement effect was observed for tralopyril (MEs > 1). These findings underscore the importance of using matrix-matched calibration curves for accurate residual calculation of both analytes. The LODs and LOQs of chlorfenapyr and tralopyril were both 0.003 and 0.01 mg/kg, respectively. The accuracy and precision of the analytical method were assessed by calculating the recoveries and RSDs of the two analytes in various cabbage tissues. Table 2 presents the intraday and interday recoveries of chlorfenapyr in cabbage roots, stems, and leaves, which ranged from 82.50 % to 98.76 % and from 90.47 % to 95.15 %, respectively. The intraday and interday RSDs for chlorfenapyr ranged from 1.52 % to 12.24 % and from 4.38 % to 8.70 %, respectively. Similarly, the intraday and interday recoveries of tralopyril were found to range from 85.10 % to 108.03 % and from 87.86 % to 104.48 %, respectively. The intraday and interday RSDs for tralopyril ranged from 1.13 % to 10.11 % and from 2.48 % to 8.48 %, respectively. The results indicate that the optimized extraction and detection methods are appropriate for quantifying the presence of chlorfenapyr and tralopyril residues in cabbage samples (European Commission, 2019).

Table 1
Linear equation, determination coefficient (R^2), limit of detection (LOD), limit of quantification (LOQ), and matrix effect (ME) of chlorfenapyr and tralopyril in solvent and matrices.

Analyte	Matrix	Linear equation	R^2	LOD (mg/kg)	LOQ (mg/kg)	ME
Chlorfenapyr	Acetonitrile	$y = 186{,}077x + 147$	0.9999	/	/	/
	Root	$y = 147{,}978x + 2{,}423$	0.9974	0.003	0.01	0.79
	Stem	$y = 181{,}698x + 18{,}958$	0.9947	0.003	0.01	0.97
	Leaf	$y = 172{,}947x + 11{,}449$	0.9979	0.003	0.01	0.92
Tralopyril	Acetonitrile	$y = 1{,}761{,}454x + 204{,}398$	0.9961	/	/	/
	Root	$y = 2{,}456{,}858x + 398{,}068$	0.9934	0.003	0.01	1.39
	Stem	$y = 2{,}667{,}728x + 439{,}400$	0.9925	0.003	0.01	1.51
	Leaf	$y = 2{,}630{,}077x + 507{,}133$	0.9910	0.003	0.01	1.49

Dissipation, terminal residues, and dietary intake risk of chlorfenapyr and tralopyril in cabbage

The concentrations of chlorfenapyr, tralopyril, and total chlorfenapyr in cabbage samples after various treatments under greenhouse and open-field conditions are shown in Fig. 1. In the case of chlorfenapyr, a positive correlation was observed between the concentrations and the application dose and time. For instance, under greenhouse conditions, the initial levels of chlorfenapyr increased from 3.36 mg/kg (low dose: 105 g a.i./ha) to 4.34 mg/kg (high dose: 157.5 g a.i./ha) after a single application. In open-field conditions, the initial levels of chlorfenapyr residues were 3.33 mg/kg at a low dose and 4.66 mg/kg at a high dose after a single application. Furthermore, when the application dose was 105 g a.i./ha, the initial concentrations of chlorfenapyr varied from 3.36 mg/kg (application time: once) to 5.35 mg/kg (application time: twice) in greenhouse-cultivated cabbage samples and from 3.33 mg/kg (once) to 5.34 mg/kg (twice) in open-field-cultivated cabbage samples. As the sampling intervals were extended, the concentrations of chlorfenapyr decreased and its dissipation percentages increased. Under greenhouse conditions, the dissipation percentages ultimately exceeded 90 % in the cabbage samples collected 35 d after the final application in all the four treatments (Fig. S4A and Fig. S4B, Supporting information), while the dissipation percentages were more than 90 % in the cabbage samples gathered 28 d after the last application in the four open-field treatments (Fig. S4C and Fig. S4D, Supporting information), indicating that chlorfenapyr dissipated faster in the cabbage samples under open-

Table 2
Recoveries and relative standard deviations (RSDs) of chlorfenapyr and tralopyril in different cabbage tissues.

Analyte	Matrix	Spiked level (mg/kg)	Intra-day recovery, RSD (%, $n = 5$)			Inter-day recovery, RSD (%, $n = 15$)
			Day 1	Day 2	Day 3	
Chlorfenapyr	Root	0.01	96.34, 5.08	95.41, 7.01	82.50, 1.78	91.42, 8.70
		0.1	97.60, 3.75	97.58, 3.42	91.67, 3.04	95.62, 4.38
		1	92.18, 6.49	92.02, 7.73	92.24, 4.60	92.15, 5.79
	Stem	0.01	96.12, 6.95	88.75, 5.30	87.94, 4.91	90.94, 6.89
		0.1	91.32, 9.21	92.24, 12.24	89.48, 3.58	91.01, 8.58
		1	95.85, 3.99	97.54, 1.52	90.42, 7.99	94.60, 5.75
	Leaf	0.01	96.59, 4.72	94.06, 4.87	91.35, 6.47	94.00, 5.51
		0.1	85.36, 6.61	92.84, 3.96	93.22, 6.27	90.47, 6.59
		1	92.82, 6.47	98.76, 9.05	90.65, 1.96	94.08, 7.26
Tralopyril	Root	0.01	94.49, 1.99	85.10, 7.82	88.44, 5.56	89.34, 6.79
		0.1	95.45, 1.78	99.16, 5.87	95.33, 3.45	96.64, 4.26
		1	98.82, 4.47	107.67, 4.05	103.48, 4.28	103.32, 5.35
	Stem	0.01	94.74, 1.19	92.64, 10.11	89.29, 6.51	91.89, 6.87
		0.1	98.18, 4.65	108.03, 3.00	107.22, 2.69	104.48, 5.47
		1	95.03, 2.43	99.30, 1.15	98.40, 1.13	97.57, 2.48
	Leaf	0.01	91.15, 6.66	91.05, 6.44	87.69, 12.63	89.96, 8.48
		0.1	90.11, 3.37	88.28, 3.91	85.19, 3.21	87.86, 4.04
		1	97.75, 4.58	87.09, 5.16	92.04, 9.79	92.29, 8.04

field conditions. This could be because the climate impactors (solar intensity, temperature, huminity, etc.) in open-field ecosystems were more complicated than those in greenhouse ecosystems (Rahman et al., 2012; Li et al., 2019). Under the greenhouse and open-field conditions, tralopyril was detected in the cabbage samples with all the treatments. The concentrations of tralopyril initially increased and then decreased with the dissipaiton of chlorfenapyr. For instance, the concentration of this metabolite increased from 0.0866 to 0.2462 mg/kg within the initial 7-d period, followed by a subsequent decrease to 0.0630 mg/kg over the subsequent 28-d period when chlorfenapyr was applied twice at a low dose under greenhouse conditions. In the same treatment under open-field conditions, tralopyril levels increased from 0.0908 (0 d) to 0.2674 mg/kg (7 d) and then decreased to 0.0172 mg/kg (35 d) with increasing duration. As the dosage and duration of application increased, higher levels of tralopyril were observed in cabbage samples. Analogous to chlorfenapyr, the cumulative data for total chlorfenapyr demonstrated a gradual decline in cabbage as the intervals between sampling events increased. The results of the correlation coefficient (r^2) analysis (Tables S2 and S3, Supporting information) show a strong relationship (greenhouse: 0.9270–0.9775; open field: 0.9786–0.9959) between the dissipation of chlorfenapyr in cabbage samples and the first-order kinetic model. The half-lives of chlorfenapyr were 11.14 and 6.56 d (low dose applied once), 11.02 and 6.22 d (low dose applied twice), 11.09 and 6.43 d (high dose applied once), and 10.10 and 5.67 d (high dose applied twice) in greenhouse- and open-field-cultivated cabbage samples, respectively, indicating the faster dissipation of chlorfenapyr under open-field conditions. Previous studies have documented the dissipation rates of chlorfenapyr in various crops, such as chili peppers (with a half-life of 2.9–3.0 d, Ditya et al., 2010), eggplants (with a half-life of 3.5–3.8 d, Shi et al., 2016), tomatoes (with a half-life of 5.1–6.2 d, Patra et al., 2018), leeks (with a half-life of 2.9–5.1 d, Li et al., 2019), and teas (with a half-life of 4.7–6.2 d, Yang et al., 2020). In addition to the specific physiological and biochemical characteristics of crops, multiple factors influence the dissipation rate of pesticides in crops, including cultivation methods, microbial degradation, and metabolic transformation (Di et al., 2021). The dissipation of pesticides in crops grown under greenhouse conditions was found to occur at a slower rate compared with that in the crops grown in open-field conditions, as demonstrated by Badawy et al. (2020) and Di et al. (2021). Our findings are consistent with those of previous research conducted by Ditya et al. (2010) and Patra et al. (2018), who reported half-lives of chlorfenapyr in cabbage grown under open-field conditions ranging from 5.8 to 9.3 d. These findings provide further evidence that the mode of cultivation can considerably affect the dissipation of chlorfenapyr in cabbage. The dissipation of total chlorfenapyr in cabbage samples exhibited conformity to the first-order kinetic model results, as evidenced by the r^2 values ranging from 0.9661 to 0.9825 (greenhouse) and from 0.9726 to 0.9892 (open field). Moreover, the half-lives of total chlorfenapyr in cabbage samples were found to be 12.20–14.77 d and 6.91–8.07 d under greenhouse and open-field conditions, respectively, surpassing those reported for chlorfenapyr. These results suggest that the presence of tralopyril could impede the dissipation of chlorfenapyr in crops, indicating that metabolic transformation may serve as an additional influential factor affecting the dissipation of chlorfenapyr in cabbage samples (Xu et al., 2022).

The determination of the maximum residue limit (MRL) serves as a crucial criterion for assessing the safety of food and establishing the appropriate preharvest intervals (PHI) for the usage of pesticides in agricultural crops (Dong et al., 2018). Notably, both China and Japan have established the MRL for chlorfenapyr in cabbage at a level of 2.00 mg/kg (The Japan Food Chemical Research Foundation. (2018), 2018; National Health and Family Planning Commission, Ministry of Agriculture and State Administration for Market Regulation of the People's Republic of China (2021)). In China, the residual definition of chlorfenapyr in crops was solely chlorfenapyr. The terminal residue data presented in Table S4 (Supporting information) revealed that the concentrations of chlorfenapyr ranged from 1.75 to 5.64 mg/kg, 1.30 to 3.45 mg/kg, 1.01 to 1.99 mg/kg, and 0.62 to 1.64 mg/kg in cabbage samples collected at 7, 10, 14, and 21 d, respectively, following the final application in four greenhouse treatments. Table S5 (Supporting information) demonstrated that the terminal residue levels of chlorfenapyr were 1.48–4.90 mg/kg (7 d), 0.96–3.27 mg/kg (10 d), 0.58–1.45 mg/kg (14 d), and 0.33–1.10 mg/kg (21 d) in open-field-cultivated cabbage samples. These findings suggest that a 7-d PHI can be recommended for chlorfenapyr in cabbage samples grown in greenhouse and open-field conditions, except for applying a high dose twice. However, the evaluation of the application safety of chlorfenapyr by FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization). (2018) involved the consideration of the combined sum of chlorfenapyr and tralopyril, referred to as total chlorfenapyr. To ensure more rigorous data, the levels of total chlorfenapyr were calculated and presented in Table S4 and Table S5 (Supporting information). Notably, the concentrations of total chlorfenapyr exceeded 2.00 mg/kg (greenhouse: 2.63–9.14 mg/kg; open field: 2.44–7.45 mg/kg) in cabbage samples collected at 7 d, indicating potential concerns regarding the suitability and safety of these samples for both consumers and the

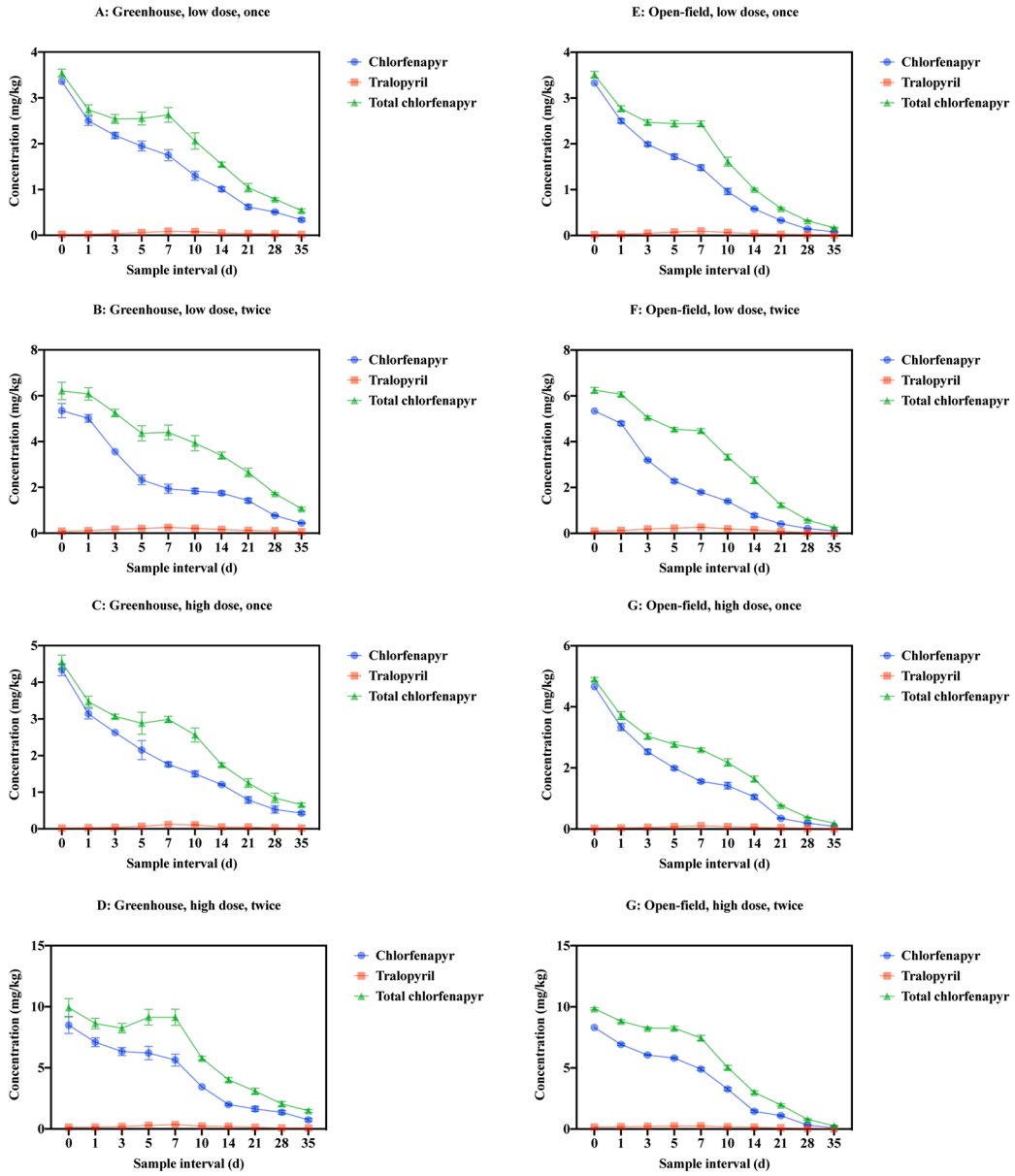

Fig. 1. Residual concentrations of chlorfenapyr, tralopyril, and total chlorfenapyr in cabbage samples collected at different (dissipation) intervals under greenhouse (**A**, **B**, **C** and **D**) and open-field conditions (**E**, **F**, **G** and **H**) (Low dose: 105 g a.i./ha, high dose: 157.5 g a.i./ha, $n = 3$).

environment. The cabbage samples collected over 14 d exhibited concentrations of total chlorfenapyr at 1.51 and 1.71 mg/kg, following a single application of a low dose and high dose, respectively. It is advised that a PHI of 14 d must be observed under greenhouse conditions, with the recommended application method involving a single application of chlorfenapyr at doses of 105 and 157.5 g a.i./ha. Under open-field conditions, the level of total chlorfenapyr was 1.61 mg/kg in cabbage samples collected at 10 d after applying chlorfenapyr once at a low dose, indicating that the recommended PHI was 10 d in cabbage under open-field conditions when the application was 105 g a.i./ha and the application time was once.

The assessment of dietary intake risk is an additional approach utilized to evaluate the safety of food for consumers after the application of pesticides in crops (FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization), 2011). In cabbage samples collected at four (terminal residue) intervals, HRs of total chlorfenapyr were 3.38–9.98 mg/kg (greenhouse) and 2.06–7.66 mg/kg (open field) and STMRs of total chlorfenapyr were 1.95–3.56 mg/kg (greenhouse) and 0.97–3.51 mg/kg (open field). In Fig. 2A, the RQ_a values of total chlorfenapyr in greenhouse-cultivated cabbage samples were found to range from 48.0 % to 115.4 % (7 d), 28.9 % to 69.4 % (10 d), 21.2 % to 51.0 % (14 d), and 16.3 % to 39.1 % (21 d). In Fig. 2B, the RQ_a values of total chlorfenapyr in open-field-cultivated cabbage samples were between 9.9 % and 88.6 % in all four intervals. These results indicate that the acute dietary intake risk of chlorfenapyr for Chinese consumers can be disregarded ($RQ_a < 100$ %) in cabbage samples collected 10 d (greenhouse) and 7 d (open field) after the last application in all four treatments (Dong et al., 2018), which may be related to the complex climate conditions in open-field trials. The RQ_c values (Fig. 2C and Fig. 2D) for total chlorfenapyr were 6.2 %–36.8 % in greenhouse-cultivated cabbage samples and 4.7 %–40.6 % in open-field-cultivated cabbage samples collected at 7, 10, 14, and 21 d after the final application in the four treatments. These findings suggest that the chronic dietary intake risk of chlorfenapyr ($RQ_c < 100$ %) for Chinese consumers in the 7-d cabbage samples under greenhouse and open-field conditions is acceptable (Chen et al., 2024). In conclusion, the recommended PHI of chlorfenapyr for cabbage samples was determined to be 14 d under greenhouse conditions with a single application at doses of

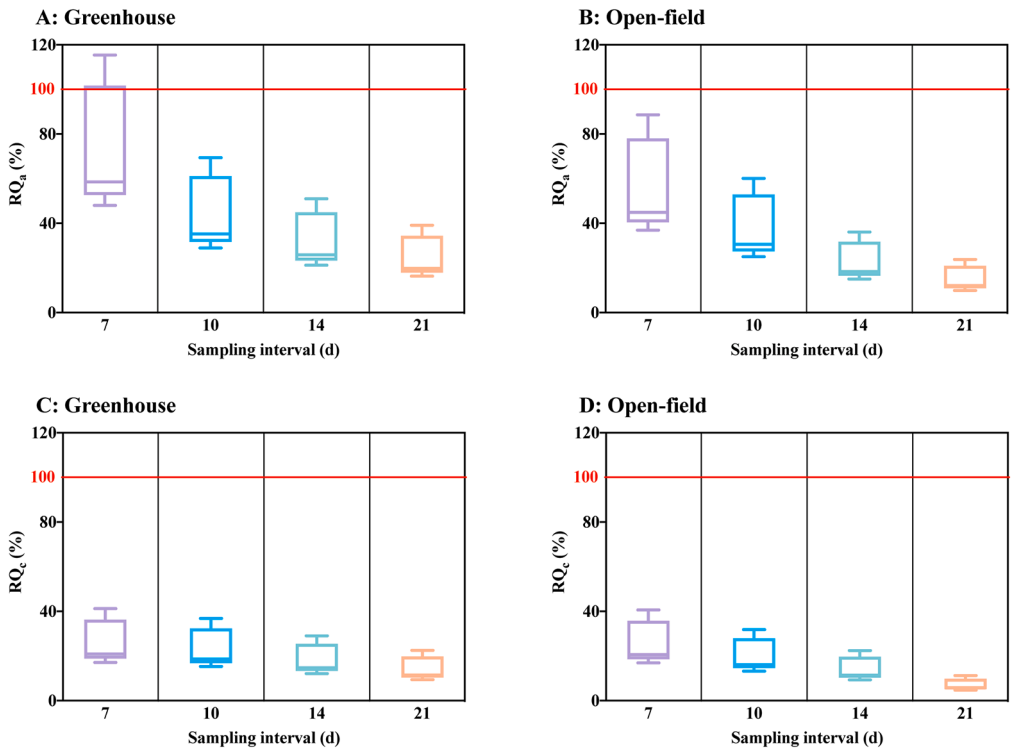

Fig. 2. Acute risk quotients (**A** and **B**) and chronic risk quotients (**C** and **D**) of chlorfenapyr in cabbage samples collected at four (terminal residue) intervals under greenhouse and open-field conditions for Chinese consumers.

105 and 157.5 g a.i./ha. When applying chlorfenapyr at 105 g a.i./ha once, the recommended PHI was 10 d for open-field-cultivated cabbage samples.

Accumulation, distribution, and translocation of chlorfenapyr and tralopyril in cabbage

In the upward translocation trials (Table S6, Supporting information), the concentrations of chlorfenapyr in the roots of cabbage rapidly increased from 0.42 to 27.40 mg/kg in case of the 5.6-mg/L treatment and from 1.82 to 51.99 mg/kg in case of the 11.2-mg/L treatment within 7 d, followed by a subsequent decrease ($P < 0.001$). In both the treatments, the levels of chlorfenapyr in the roots (ranging from 0.42 to 27.40 mg/kg in case of the 5.6-mg/L treatment and from 1.82 to 51.99 mg/kg in case of the 11.2-mg/L treatment) were found to be higher than the levels in the stems (ranging from 0.15 to 3.29 mg/kg in case of the 5.6-mg/L treatment and from 0.37 to 7.57 mg/kg in case of the 11.2-mg/L treatment) and leaves (ranging from 0.13 to 1.13 mg/kg in case of the 5.6-mg/L treatment and from 0.18 to 2.43 mg/kg in case of the 11.2-mg/L treatment). These findings suggest that cabbage roots can absorb chlorfenapyr from hydroponic solutions, leading to its accumulation primarily in the roots, with the residual amount being positively associated with the dosage applied (Zhang, Feng, et al., 2017). Previously, Huang and Sheng (2021) reported similar findings regarding lindane absorption in rice seedlings, where the roots of rice seedlings exhibited a higher capacity for lindane absorption compared with other parts of the seedlings. Similarly, the levels of chlorfenapyr in cabbage stems and leaves initially increase and then decrease after the application of chlorfenapyr, and the presence of the metabolite tralopyril in cabbage roots, stems, and leaves indicates the upward transportation of chlorfenapyr from the roots to the upper portions of the cabbage plant, accompanied by metabolic transformations. The concentrations of total chlorfenapyr in cabbage tissues were determined (Table S7, Supporting information). The levels of tralopyril were found to be below 0.12 mg/kg, resulting in a relatively modest increase in the levels of total chlorfenapyr, not exceeding 1.2 mg/kg. Additionally, the pattern of total chlorfenapyr residues exhibited a similar trend to that of chlorfenapyr in specific cabbage tissues, characterized by an initial increase followed by a subsequent decrease. Notably, the highest levels were observed in the roots on the seventh day, with higher concentrations observed in the higher dose treatment groups. The data presented in this study indicate that the impact of tralopyril on the adsorption and accumulation of chlorfenapyr in cabbage roots, stems, and leaves was not readily apparent. To assess the ability of cabbage roots to transport chlorfenapyr upwards, the researchers calculated and illustrated the TF values of chlorfenapyr, tralopyril, and total chlorfenapyr in Fig. 3. All TF values initially exhibited higher levels and subsequently decreased gradually as the sampling intervals increased. For instance, the $TF_{stem/root}$ values exhibited a significant decrease from 0.37 to 0.10 (chlorfenapyr), from 0.24 to 0.02 (tralopyril), and from 0.36 to 0.10 (total chlorfenapyr) ($P < 0.001$). Furthermore, all TF values were below 1, indicating that the ability of cabbage roots to transport chlorfenapyr to stems (or leaves) was restricted, diminished over time, and unaffected by the presence of tralopyril. One potential explanation for this phenomenon is the hydrophobic nature of chlorfenapyr, as indicated by its $\log K_{ow}$ value of 5.28 (FAO (Food and Agriculture Organization of the United Nations) and WHO (World Health Organization) (2018)). This characteristic facilitates its efficient uptake by plant roots, while impeding its movement upwards from the roots (Chen et al., 2024).

The concentrations of chlorfenapyr and tralopyril in cabbage tissues after foliar spraying are shown in Table S8 (Supporting information). In the 105-g a.i./ha treatment, the levels of chlorfenapyr in leaves decreased from 2.18 to 0.26 mg/kg during a trial period of 28 d, and increased from 0.10 to 0.93 mg/kg within 3 d, and subsequently decreased to 0.21 mg/kg in stems. Similarly, in roots, the levels of chlorfenapyr increased from 0.07 to 0.25 mg/kg within 3 d and then decreased to 0.08 mg/kg ($P < 0.001$). In the 157.5-g a.i./ha treatment, the levels of chlorfenapyr residues in leaves decreased from 3.64 to 0.27 mg/kg in 28 d, and increased from 0.17 to 1.99 mg/kg within a period of 3 d, and decreased to 0.19 mg/kg in stems. In addition, the levels of

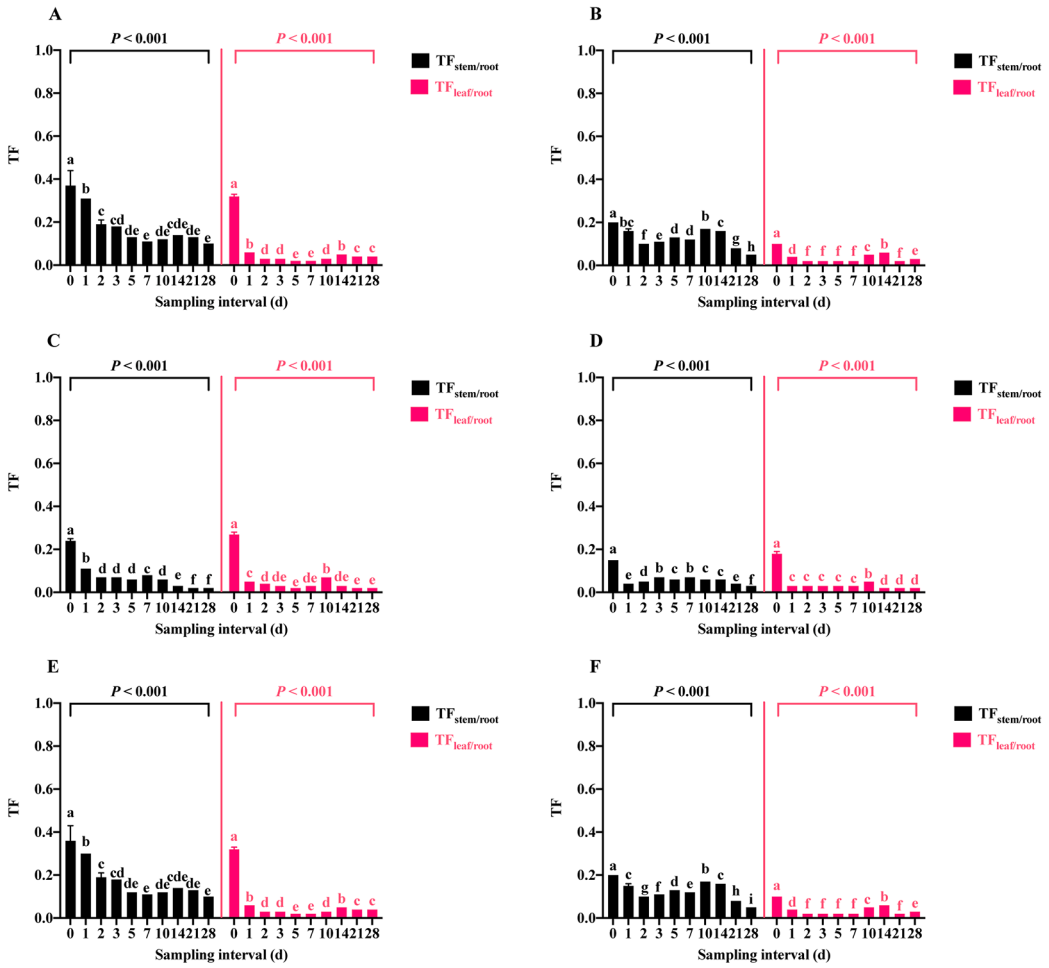

Fig. 3. Translocation factors (TFs) of chlorfenapyr and tralopyril among different tissues of cabbage after foliar spraying. **A** and **B** represent TFs of chlorfenapyr at the application dose of 105 g a.i./ha and 157.5 g a.i./ha, respectively. **C** and **D** represent TFs of tralopyril at the application dose of 105 g a.i./ha and 157.5 g a.i./ha, respectively. **E** and **F** represent TFs of total chlorfenapyr at the application dose of 105 g a.i./ha and 157.5 g a.i./ha, respectively. Different lower case letters indicate significant differences between different sampling intervals for each analyte ($P < 0.01$).

chlorfenapyr residues in roots increased from 0.08 to 0.24 mg/kg within 3 d and then decreased to 0.10 mg/kg. This observed trend was statistically significant ($P < 0.001$). Tralopyril was detected in all cabbage tissues, although its concentrations were relatively low (≤0.03 mg/kg). Hence, in comparison with chlorfenapyr, there was a slight increase in the concentration of total chlorfenapyr (≤0.3 mg/kg) (Table S9, Supporting information). These findings indicate that chlorfenapyr primarily accumulates in leaves (Wang et al., 2021), the dosage of application positively impacts the initial concentrations of chlorfenapyr (Pullagurala et al., 2018), the downward translocation and metabolic transformation of chlorfenapyr occur concurrently (Wang et al., 2011), and the influence of tralopyril on the accumulation of chlorfenapyr in the downward translocation experiments was not significant. The $TF_{stem/leaf}$ values for chlorfenapyr were observed to range from 0.04 to 1.08 and 0.05 to 2.11 in the treatments with 105 and 157.5 g a.i./ha, respectively (Fig. 4A and Fig. 4D). These values exhibited significant differences ($P < 0.001$). Conversely, the $TF_{root/leaf}$ values remained below 1 (ranging from 0.02 to 0.36) in both treatments. Phloem serves as a common pathway for the downward translocation of pesticides (Chen et al., 2024). The observed downward translocation of chlorfenapyr in cabbage suggests the occurrence of phloem transport in the leaf-to-stem translocation, while it does not readily occur in the leaf-to-root translocation (Jia et al., 2021). The TF values of tralopyril (Fig. 4B and E) exhibited a range of 0.10–0.57 (leaf-to-stem) and 0.05–0.49 (leaf-to-root), respectively, with significant differences ($P < 0.001$), indicating limited downward translocation and a tendency for preferential accumulation in leaves. In the 105-g a.i./ha treatment, the $TF_{stem/leaf}$ values for total chlorfenapyr ranged from 0.05 to 0.97, while in the 157.5-g a.i./ha treatment, the $TF_{stem/leaf}$ values ranged from 0.05 to 1.72 ($P < 0.001$). In addition, the $TF_{root/leaf}$ values for total chlorfenapyr ranged from 0.02 to 0.35 (Fig. 4C and F). These findings suggest that the presence of tralopyril may have a slight inhibitory effect on the translocation of chlorfenapyr from leaves to stems.

Conclusions

This study presents the development of a simple and viable analytical approach for quantifying residual levels of chlorfenapyr and its metabolite, tralopyril, in various cabbage tissues, namely roots, stems, and leaves. The validation of this method demonstrated a strong linear relationship ($R^2 > 0.99$) between the standard calibration of chlorfenapyr and tralopyril in both solvent and matrix. Furthermore, the recovery data (82.50 %–108.03 %) and RSDs (1.13 %–12.24 %) obtained from intraday and interday analyses indicated the satisfactory accuracy and precision of the established method for quantifying both analytes in cabbage samples. In the dissipation and terminal residue experiments, the concentrations of chlorfenapyr and tralopyril exhibited a positive correlation with both the application dose and time. Specifically, chlorfenapyr dissipated rapidly in cabbage samples with half-lives of 10.10–11.14 d and 5.67–6.56 d under greenhouse and open-field

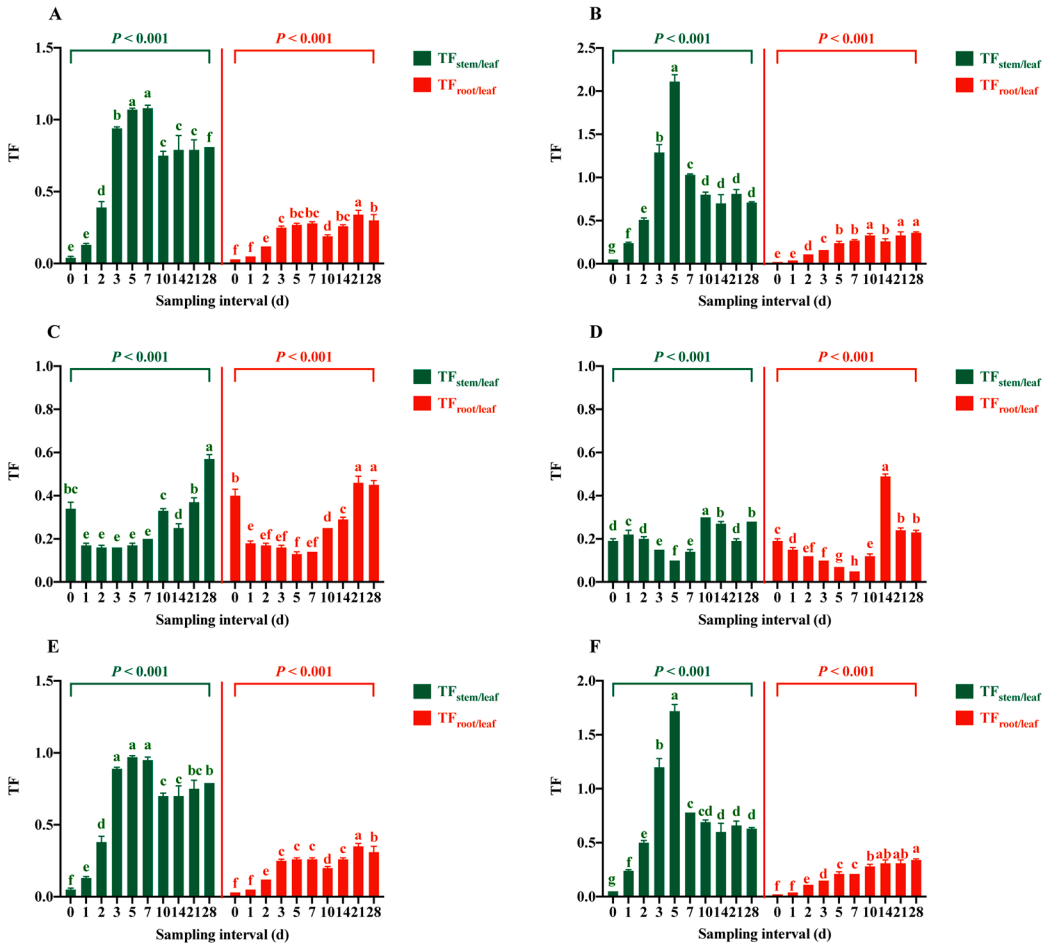

Fig. 4. Translocation factors (TFs) of chlorfenapyr and tralopyril among different tissues of cabbage after root irrigation. **A** and **B** represent TFs of chlorfenapyr at the application dose of 105 g a.i./ha and 157.5 g a.i./ha, respectively. **C** and **D** represent TFs of tralopyril at the application dose of 105 g a.i./ha and 157.5 g a.i./ha, respectively. **E** and **F** represent TFs of total chlorfenapyr at the application dose of 105 g a.i./ha and 157.5 g a.i./ha, respectively. Different lower case letters indicate significant differences between different sampling intervals for each analyte ($P < 0.01$).

conditions, respectively. Notably, tralopyril was detected during the trials and its presence may impede the dissipation of chlorfenapyr through metabolic transformation, which is evidenced by the fact that the half-lives of total chlorfenapyr decreased to 12.20–14.77 d and 6.91–8.07 d in greenhouse and open-field-cultivated cabbage samples, respectively. The concentration of residual chlorfenapyr in cabbage samples collected at 14 d (greenhouse) and 10 d (open field) was found to be below the MRL set by China and Japan, with values less than 2.0 mg/kg. Additionally, the RQ values (RQ_a and RQ_c) for total chlorfenapyr in 10-d (greenhouse) and 7-d (open field) cabbage samples were below 100 % for Chinese consumers. Based on these findings, PHIs of 14 d and 10 d are recommended for chlorfenapyr in greenhouse- and open-field-cultivated cabbage samples, respectively. Cabbage roots demonstrate a high capacity for absorbing chlorfenapyr from hydroponic solutions and accumulating it within their tissues. However, the upward translocation of chlorfenapyr is limited (TF < 1) due to the hydrophobic property of the analyte. Conversely, the downward translocation of chlorfenapyr from leaves to stems primarily occurs through phloem transport, as evidenced by a TF value greater than 1. Tralopyril is found in all cabbage tissues, but its influence on chlorfenapyr translocation is not deemed significant. This study can offer insights into the appropriate and secure application technique for chlorfenapyr in vegetables, as well as a comprehensive understanding of the distribution and behavior of chlorfenapyr and tralopyril within various cabbage tissues.

CRediT authorship contribution statement

Hao Zhang: Writing – original draft, Visualization, Methodology, Formal analysis. **Shilin Chen:** Investigation. **Shaotao Wu:** Software. **Ye You:** Validation. **Kankan Zhang:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.101287.

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