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Pesticide residues risk assessment and quality evaluation of four characteristic fruits in Zhejiang Province, China

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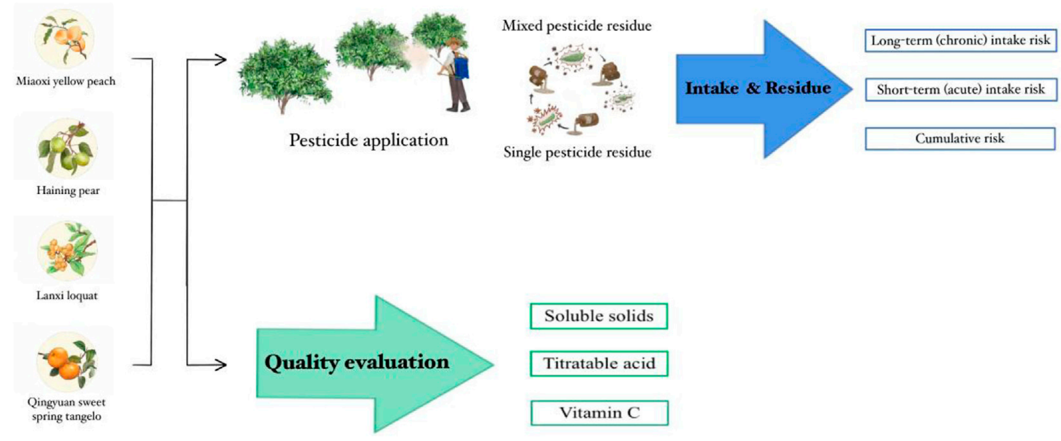
Miaoxi yellow peach, lanxi loquat, qingyuan sweet spring tangelo and haining pear are characteristic fruits in Zhejiang Province, China. This study investigated the levels of pesticides in these fruits in Zhengjiang Province, China, along with the associated risk of dietary exposure for consumer. In total, 25 pesticides were detected in the 68 samples. The pesticide detection rate of the samples was 95.59%, and the level of prochloraz in a pear sample was found to be higher than the maximum residue limit (MRL) in China. Overall, the pesticide residues were very low, and residue levels ranged from 0.001 to 1.06 mg/kg, of which 80.88% simultaneously occurred with 2–8 mixed residues. Acetamiprid (54.55%), carbendazim (64.71%), prochloraz (94.74%) and pyraclostrobin (85.71%) had the highest detection rate in the four fruits, respectively. A risk assessment of human exposure to pesticides *via* the intake of the four fruit types was performed, and the chronic intake risk (HQ_c) and acute intake risk (HQ_a) of a single pesticide and the hazard index (HI) of the mixture of pesticides for adults and children from the four fruit types were found to be less than 1, the exposure assessment showed that the levels of pesticides in the four fruit types were safe for human consumption. In addition, the quality of the four fruit types was analyzed and found to be not stable enough. We suggest strengthening standardized planting and management technology to improve product quality and safety, in particular, cultivators should use pesticides reasonably and control the pre-harvest interval (PHI) in order to better protect consumer health.

KEYWORDS

characteristic fruits, pesticide residues, exposure assessment, fruit quality, consumer health

Highlights

1) Risk assessment of pesticides in four characteristic fruits of Zhejiang Province, China.
2) 25 pesticides were detected in 68 (95.59%) samples.
3) The levels of prochloraz in a pear sample were found to be higher than the maximum residue limit (MRL) of China.
4) The exposure assessment showed that the levels of pesticides in four fruits were safe for human consumption.
5) The contents of soluble solids, titratable acid and vitamin C in the targeted fruits were analyzed.



GRAPHICAL ABSTRACT

1 Introduction

It is well known that fruits are an indispensable part of a balanced diet as they contain vitamins, minerals and dietary fiber (Mebdoua et al., 2017; Qin et al., 2021). Miaoxi yellow peach, lanxi loquat, qingyuan sweet spring tangelo and haining pear are characteristic fruits in Zhejiang Province, China. They have obtained the certification of geographical indication products, are popular with consumers and are widely planted, nowadays and the cultivated area of four fruits were 367 hm^2, 1,466 hm^2, 1,021 hm^2, and 920 hm^2, respectively. These regional characteristic fruits have gradually become the leading local cash crop in Zhejiang province. Certification of "three products and one standard" (pollution-free agricultural products, green food, organic food, geographical indications) for agricultural products is an important work to ensure safety and quality of edible agricultural products in China. Now it has gradually developed into a new concept of "breeding good varieties, improving product quality, building famous brands and standardized production". Focusing on the new concept of "three products and one standard", Zhejiang province establishes agricultural product brands by promoting products with geographical indications, so as to increase farmers' income.

Unlike the other three widespread planting of fruits, sweet spring tangelo is not commonly planted. Sweet spring tangelo, a late-mature hybrid citrus of satsuma mandrain (*Citrus unshiu* Marc.) and hassaku orange (*Citrus hassaku* hort. ex Tanaka), mainly planted in Qingyuan County, Zhejiang Province, is highly appreciated by Chinese consumers. In recent years, sweet spring tangelo has been widely planted owing to the advantages of good storability, stable yield, high quality and easy cultivation.

During cultivation, fruits are infested with insect pests, such as pear fruit borers, aphids, longicorn beetles and leafhoppers, as well as anthrax, brown rot and black spot. In modern agriculture, the use of pesticides is inevitable to control weeds, pests and fungal diseases and improve crop yield (Fu et al., 2017; L´opez-Fern´andez et al., 2012; van Bruggen et al., 2021). In addition to the benefits of drugs utilization, the non-standard use of drugs result in the accumulation of residues, increased pathogen resistance, leads to the reduction of biodiversity and the destruction of biological ecosystems (Mahdavi et al., 2022; Dai et al., 2023). The study of pyrethroid residues by Emert et al. (2023) showed that the judicious use of pesticides was are essential for biodiversity of agricultural ecosystems. Pesticide residues in agricultural products can be harmful to human health, as residues may transfer to, accumulate in, or deposit on fruit tissues (Jeong et al., 2012). In Spain where 84 pesticides in vegetable and fruit samples, such as peach, citrus fruit, pears and tomato, were measured, pesticide residues were detected in 63% of the samples, and five fruit samples exceeded the maximum residue limits (MRLs) established by law (Quijano et al., 2016). Mahdavi et al. (2022) investigated 85 pesticides in 50 fruit samples in Iran; apples (68%) and grapes (28%) were positive for pesticide residues, among which iprodione exceeded the allowable limit. It should not be ignored that the stimulation of pesticides can trigger the active substances produced by plants themselves, which is of great significance in the bioremediation of pesticides (Bhatt et al., 2019). Pyrethroid-degrading hydrolases have been previously reported from five plants (Yao et al., 2019). Enzymatic bioremediation is potentially a rapid method for the biodegradation of pesticides. Mahmood et al. (2014) reported that pesticides like many other pollutants initiate the development of ROS in the cells, the plants have many control measures against these ROS stresses, which include enzymatic antioxidants and non-enzymatic antioxidants. The antioxidant defense can result in an increase of thiobarbituric acid reactive substances (TBARS). Yin et al. (2008) found in the pesticide test on wheat that TBARS concentration increased under the exposure of pesticide (20 mg/kg), indicating stress.

It is to be expected that fruits will contain higher pesticide residues than other commodities of plant origin such as cereals, because the short interval between harvesting and the market and the fact that they are frequently consumed raw or semi-processed (Claeys et al., 2011; Bempah et al., 2016; Quijano et al., 2016; Li et al., 2020). It is worth mentioning that continuous exposure to pesticides, even in trace amounts, may lead to health problems due to accumulation in body tissues (Khazaal et al., 2022). The adverse effects of pesticide intake include allergies, birth defects, damage to reproductive organs, metabolic disorders and cancer (Mostafalou and Abdollahi, 2013; Valcke et al., 2017; Zhang et al., 2019). In addition to pesticide residues, fruit quality is among the

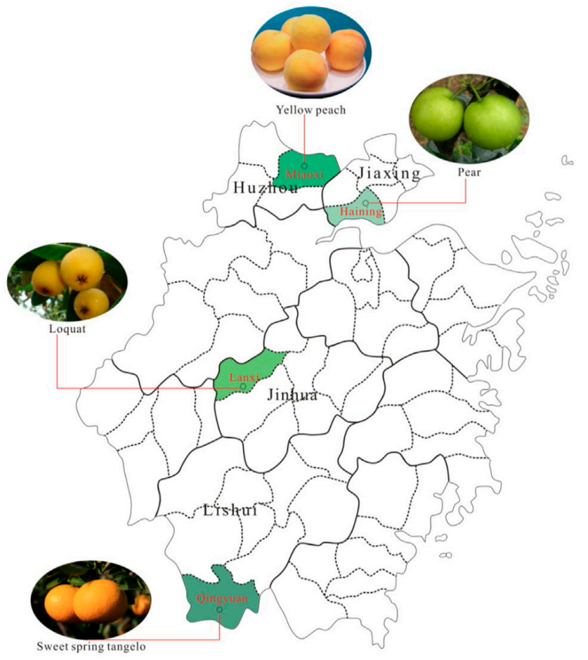


FIGURE 1
Sample collection from the four production areas in Zhejiang Province, China (n = 68).

core elements influencing the commerciality of the fruit, and its quality such as the sugar and acid contents, sugar acid ratio and vitamin C content are important indicators of fruit quality (Wang et al., 2022). The purchase frequency may decrease when consumers' expectations for the quality of fruit are not met, thus affecting the sales volume of fruit (Harker et al., 2008). There have been many studies on the levels of pesticide residues and quality in various food products. However, little is known about the risk of pesticide residues and quality in the four characteristic fruits in Zhejiang Province.

The main purpose of this work was to monitor 68 pesticides commonly used in four characteristic fruits in Zhejiang Province in China from 2020 to 2021 and to assess the health hazards of pesticides to consumers. Simultaneously, quality of four fruits was tested. This study provides useful data for relevant government departments as a reference for future monitoring. This study aimed to 1) determine pesticide residues in the four fruits grown in Zhejiang Province in China, 2) assess whether pesticide residues pose a health risk to the general population and children, and 3) analyze the quality of four characteristics of fruits, i.e., soluble solids (SS), titratable acid (TA), vitamin C (Vc) and maturation index (MI), which is SS/TA ratio.

2 Material and methods

2.1 Sample collection

A total of 68 samples were collected between 2020 and 2021 from the main production areas in Zhejiang Province, China (11 yellow peach samples from Miaoxi, 119°51′E, 30°36′N; 17 loquat samples from Lanxi, 119°45′E, 29°20′N; 19 sweet spring tangelo samples from Qingyuan, 119°06′E, 27°61′N; and 21 pear samples from Haining, and 120°68′E, 30°50′N) (Figure 1). Each sample was at least 3 kg in weight and classified quartering.

2.2 Detection of pesticides

Sample extraction and purification were performed as described by Sun et al. (2015). The fruit samples were naturally defrosted from −20°C and homogenized for extraction. In short, a 15 g homogenized fruit sample was accurately weighed into a 50-mL centrifuge tube. Then, 15 mL chromatographic-grade acetonitrile was added, and the tube was shaken by a vortex mixer (Talboys, United States) at 2000 r/min for 2 min in order to achieve well mixed. Then, 1.5 g anhydrous sodium acetate and 6 g anhydrous magnesiumsulfate were added to the centrifuge tube, and the tube was shaken by vortex mixer for 3 min. The mixture was centrifuged for 5 min at 5,000 r/min and prepared for purification. Then, 1.5 mL supernatant extract was transferred to a disposable plastic tube, and Cleanert MAS-Q (50 mg C_{18}, 50 mg PSA, and 150 mg $MgSO_4$) was added, vortexed for 1 min and then centrifuged at 8,000 r/min for 3 min. A clean extract was filtered through a 0.22 μm filter and transferred to a sample vial for analysis.

The pesticide multi-residues were measured using ultra-high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS, LCMS 8050, Shimadzu, Japan). 68 pesticide residues were tested in four fruits. Chromatographic and mass spectrometric conditions were set based on a report by Xu et al. (2021). The retention time and the multiple reaction monitoring parameters of each analyte were used according to Multi-residue Determination of 334 Pesticides in Vegetable by GC/MS and LC/MS (Ministry of Agriculture of the People's Republic of China, 2007). A list of the 68 pesticides screened is provided in Supplementary Table S1.

The analytical method was validated according to its linearity, precision, accuracy, limit of detection (LOD), and limit of quantification (LOQ). Standard solutions were prepared and analyzed for the linearity validation at four concentration levels ranging from 0.01 to 10 mg/L. Matrix effects (Me) were evaluated by the slope ratios between the calibration curves obtained in matrix and in solvent. The accuracy was determined as the average recovery by using spiked blank samples. To this end, blank fruit samples were spiked with the 68 pesticides at three different levels (0.05, 0.5, and 1.0 mg/kg). Precision was expressed by the relative standard deviation (RSD) of five replicates. The limit of detection (LOD) of the proposed method was calculated at signal-to-noise ratios (S/N) of 3. The limit of quantification (LOQ) was the lowest spiked level of the validation meeting the method performance acceptability criteria of recoveries within 70%–120% and RSD ≤ 20%.

2.3 Determination of SS and TA content

The content of SS was measured by a digital sugar meter (PAL-1, Atago, Tokyo, Japan), specific method according to Refractometric method for determination of total soluble solids in fruits and vegetables (Ministry of Agriculture and Rural Affairs of the People's Republic of China, 2014). The TA content was measured by an automatic titrator (877 Titrino plus, Metrohm, Herisau, Switzerland), specific method according to the National Food Safety Standard-Determination of Total Acid in Food (National Health Commission of the People's Republic of China, 2021). The results were expressed as a percentage of (%).

2.4 Determination of Vc content

The content of Vc was measured according to Shan et al. (2017). The content of Vc was expressed as mg/100 g FW.

2.5 Statistical analysis

The mean ± SE values were calculated. Statistical calculations were performed by one-way analysis of variance (ANOVA) using SPSS software version 22 (SPSS, Inc., Chicago, IL, United States). Multiple comparisons among treatments of significant differences were conducted by using LSD (least significant difference) ($p < 0.05$).

3.6 Health risk assessment of pesticides

The exposure risk of pesticides, chronic and acute risk assessments were conducted according to the following equations (Lv et al., 2022; Kuang et al., 2023).

2.6.1 Long-term (chronic) intake risk assessment

Long-term (chronic) intake risk assessment was calculated according to the following equations:

$$NEDI = \frac{RL_i \times F_i}{bw} \tag{1}$$

$$HQ_c = \frac{NEDI}{ADI} \tag{2}$$

where NEDI is the national estimated daily intake (mg/kg bw), bw is the body weight (kg), RL_i is the average residue level in the fruit (mg/kg), F_i is the consumption of the fruit (kg/d), HQ_c is the chronic exposure risk, and ADI is the acceptable daily intake (mg/kg bw). HQ_c indicates an unacceptable risk if it is higher than 1, and a higher value represents a higher risk. When $HQ_c < 1$, the risk is considered acceptable and does not constitute health threat in the long term. The average fruit consumption for children and adults were 0.0804 and 0.064 kg/d, respectively. The average body weights for children and adults were set to 32.7 and 55.9 kg, respectively (Zheng et al., 2007; Li et al., 2021). The ADIs of pesticides were summarized and used according to the National Food Safety Standard-MRLs for Pesticides in Food (Ministry of Agriculture and Rural Affairs of the People's Republic of China, 2021).

2.6.2 Short-term (acute) intake risk assessment

Short-term (acute) intake risk assessment was calculated according to the following equations:

$$NESTI = \frac{HR \times LP}{bw} \tag{3}$$

$$HQ_a = \frac{NESTI}{ARfD} \tag{4}$$

where HR is the highest residue (mg/kg) in available samples, and LP indicates a large portion, referring to the highest daily amount of fruit intake (kg/d). The maximum recommended intake of fruits were 0.15 kg and 0.35 kg for children and adults, respectively (Lv et al., 2022). HQ_a is the acute exposure risk, and ARfD is the acute reference dose (mg/kg bw). ARfDs were obtained from the EU Pesticides database. Values of $HQ_a < 1$ are considered acceptable and do not constitute a health threat in the short term, while values of $HQ_a > 1$ pose an unacceptable risk. The higher the HQ_a value, the greater the acute risk exposure.

2.6.3 Cumulative risk assessment

To assess the cumulative effect of pesticides, the hazard index (HI) was calculated according to the following equation:

$$HI = \sum HQ_C \tag{5}$$

When the hazard index (HI) > 1, the fruit should be considered a risk to consumers, but if the HI < 1, the fruit is considered acceptable.

3 Results

3.1 Pesticide residues in fruit samples

In this study, we analyzed 68 pesticides, of which 25 pesticides were detected in the 68 samples. The frequencies, concentration ranges and identities of pesticides in the analyzed samples are listed in Table 1. Amongst 68 pesticides, residues of 16 pesticides (23.53%) were found in the yellow peach samples: difenoconazole, acetamiprid, pyrimethanil, chlorbenzuron, carbendazim, imidacloprid, emamectinbenzoate, chlorfluazuron, chlorfenapyr, paclobutrazol, pyraclostrobin, chlorothalonil, chlorantraniliprole, cypermethrin, deltamethrin and cyfluthrin. Residues of nine pesticides (13.24%) were detected in the loquat samples: cyhalothrin, imidacloprid, pyrimethanil, difenoconazole, pyrimethanil, carbendazim, pyraclostrobin, acetamiprid and cypermethrin. Residues of ten pesticides (14.71%) were detected in the sweet spring tangelo samples: cypermethrin, acetamiprid, pyridaben, carbendazim, prochloraz, pyraclostrobin, difenoconazole, fenpropathrin, imidacloprid and dichlorvos. Residues of 16 pesticides (23.53%) were detected in the pear samples: fenvalerate, cyhalothrin, deltamethrin, bifenthrin, difenoconazole, chlorfenapyr, acetamiprid, chlorbenzuron, carbendazim, emamectinbenzoate, pyrimethanil, prochloraz, paclobutrazol, pyraclostrobin, chlorantraniliprole and abamectin.

Out of the 68 analyzed samples, three samples (4.41%) were found to be free of pesticides (two loquats and one sweet spring tangelo), and 65 samples (95.59%) were found to contain one or more pesticide residues with levels ranging from 0.001 mg/kg to 1.06 mg/kg. The maximum frequency of contaminated yellow peaches was 54.55%, i.e., with acetamiprid, followed by carbendazim (45.45%), pyraclostrobin (45.45%) and chlorfluazuron (36.36%). Carbendazim (64.71%) and cyhalothrin (52.94%) were the most frequently detected

TABLE 1 Frequencies and detection concentrations of pesticides in yellow peach, loquat, sweet spring tangelo and pear samples.

Pesticides	Yellow peach (11)[a]				Loquat (17)[a]				Sweet spring tangelo (19)[a]				Pear (21)[a]			
	D.R (%)	Detection concentration (mg/kg)			D.R (%)	Detection concentration (mg/kg)			D.R (%)	Detection concentration (mg/kg)			D.R (%)	Detection concentration (mg/kg)		
		Min-Max	Mean ± SD	Median		Min-Max	Mean ± SD	Median		Min-Max	Mean ± SD	Median		Min-Max	Mean ± SD	Median
Difenoconazole	9.09	0.031[b]	0.031[b]	0.031[b]	5.88	0.003[b]	0.003[b]	0.003[b]	31.58	0.014–0.061	0.034 ± 0.019	0.030	28.57	0.013–0.100	0.053 ± 0.034	0.056
Acetamiprid	54.55	0.002–0.054	0.0213 ± 0.018	0.018	17.65	0.001–0.006	0.002 ± 0.002	0.002	63.16	0.004–0.130	0.034 ± 0.037	0.024	33.33	0.003–0.020	0.010 ± 0.006	0.008
Pyrimethanil	27.27	0.002–0.088	0.053 ± 0.045	0.068	5.88	0.011[b]	0.011[b]	0.011[b]	ND	ND	ND	ND	9.52	0.014–0.031	0.023 ± 0.012	0.023
Chlorbenzuron	18.18	0.005–0.012	0.008 ± 0.005	0.008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbendazim	45.45	0.002–0.037	0.010 ± 0.015	0.004	64.71	0.001–0.214	0.049 ± 0.061	0.037	31.58	0.001–0.009	0.003 ± 0.003	0.002	42.86	0.002–0.160	0.023 ± 0.052	0.003
Imidacloprid	18.18	0.006–0.079	0.043 ± 0.051	0.043	5.88	0.025[b]	0.025[b]	0.025[b]	5.26	0.008[b]	0.008[b]	0.008[b]	ND	ND	ND	ND
Emamectin benzoate	18.18	0.002–0.003	0.002 ± 0.001	0.002	ND	ND	ND	ND	ND	ND	ND	ND	4.76	0.003[b]	0.003[b]	0.003[b]
Chlorfluazuron	36.36	0.006–0.024	0.016 ± 0.008	0.018	ND	ND	ND	ND	ND	ND	ND	ND	42.86	0.005–0.180	0.031 ± 0.056	0.013
Chlorfenapyr	18.18	0.027–0.035	0.031 ± 0.006	0.031	ND	ND	ND	ND	ND	ND	ND	ND	4.76	0.2[b]	0.2[b]	0.2[b]
Paclobutrazol	27.27	0.004–0.160	0.067 ± 0.082	0.037	ND	ND	ND	ND	ND	ND	ND	ND	14.29	0.003–0.046	0.004 ± 0.001	0.0041
Pyraclostrobin	45.45	0.001–0.070	0.023 ± 0.029	0.008	17.65	0.011–0.021	0.014 ± 0.006	0.011	63.16	0.003–0.052	0.025 ± 0.018	0.026	85.71	0.0017–0.220	0.026 ± 0.050	0.014
Chlorothalonil	9.09	0.013[b]	0.013[b]	0.013[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorantraniliprole	9.09	0.012[b]	0.012[b]	0.012[b]	ND	ND	ND	ND	ND	ND	ND	ND	71.43	0.002–0.110	0.033 ± 0.026	0.031
Cypermethrin	9.09	0.033[b]	0.033[b]	0.033[b]	5.88	0.016[b]	0.016[b]	0.016[b]	10.53	0.005–0.024	0.015 ± 0.013	0.015	ND	ND	ND	ND
Deltamethrin	9.09	0.017[b]	0.017[b]	0.017[d]	ND	ND	ND	ND	ND	ND	ND	ND	14.29	0.015–0.023	0.02 ± 0.004	0.022
Cyfluthrin	9.09	0.013[b]	0.013[b]	0.013[d]	ND	ND	ND	ND	ND	ND	ND	ND				
Cyhalothrin	ND	ND	ND	ND	52.94	0.012–0.130	0.044 ± 0.035	0.037	ND	ND	ND	ND	33.33	0.010–0.054	0.022 ± 0.016	0.014

(Continued on following page)

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TABLE 1 (*Continued*) Frequencies and detection concentrations of pesticides in yellow peach, loquat, sweet spring tangelo and pear samples.

Pesticides	Yellow peach (11)[a]				Loquat (17)[a]				Sweet spring tangelo (19)[a]				Pear (21)[a]			
	D.R (%)	Detection concentration (mg/kg)			D.R (%)	Detection concentration (mg/kg)			D.R (%)	Detection concentration (mg/kg)			D.R (%)	Detection concentration (mg/kg)		
		Min-Max	Mean ± SD	Median		Min-Max	Mean ± SD	Median		Min-Max	Mean ± SD	Median		Min-Max	Mean ± SD	Median
Thiamethoxam	ND	ND	ND	ND	23.53	0.013–0.154	0.073 ± 0.068	0.063	ND	ND	ND	ND	ND	ND	ND	ND
Pyridaben	ND	ND	ND	ND	ND	ND	ND	ND	5.26	0.004[b]	0.004[b]	0.004[b]				
Prochloraz	ND	ND	ND	ND	ND	ND	ND	ND	94.74	0.003–1.060	0.326 ± 0.332	0.400	9.52	0.100–0.210	0.155 ± 0.078	0.155
Fenpropathrin	ND	ND	ND	ND	ND	ND	ND	ND	5.26	0.170[b]	0.170[b]	0.170[b]	ND	ND	ND	ND
Dichlorvos	ND	ND	ND	ND	ND	ND	ND	ND	5.26	0.012[b]	0.012[b]	0.012[b]	ND	ND	ND	ND
Fenvalerate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	14.29	0.012–0.068	0.045 ± 0.029	0.054
Bifenthrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.76	0.065[b]	0.065[b]	0.065[b]
Abamectin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.76	0.010[b]	0.010[b]	0.010[b]

[a]The figures in square brackets denote the numbers of fruit samples.
[b]The corresponding pesticide was only detected in one sample.
D.R: detection rate % = number of samples with pesticide residue/total samples number.
ND: no detected.

TABLE 2 Long- and short-term risk assessment of pesticide residues in the four fruit types.

Pesticides	ADI (mg/kg bw.d)	ARfD (mg/kg bw.d)	Yellow peach				Loquat				Sweet spring tangelo				Pear			
			HQ_c		HQ_a		HQ_c		HQ_a		HQ_c		HQ_a		HQ_c		HQ_a	
			Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Difenoconazole	0.01	0.16	4.46E-03	6.07E-03	1.21E-03	8.89E-04	4.32E-04	5.87E-04	1.17E-04	8.60E-05	4.89E-03	6.65E-03	2.39E-03	1.75E-03	7.62E-03	1.04E-02	3.91E-03	2.87E-03
Acetamiprid	0.07	0.025	4.38E-04	5.96E-04	1.35E-02	9.91E-03	4.11E-05	5.59E-05	1.50E-03	1.10E-03	6.99E-04	9.51E-04	3.26E-02	2.39E-02	2.06E-04	2.80E-04	5.01E-03	3.67E-03
Pyrimethanil	0.2	—	3.81E-04	5.19E-04	—	—	7.91E-05	1.08E-04	—	—	ND	ND	ND	ND	ND	ND	ND	ND
Chlorbenzuron	1.25	—	9.21E-06	1.25E-05	—	—	ND	ND	ND	ND	ND	ND	ND	ND	4.46E-03	6.07E-03	1.21E-03	8.89E-04
Carbendazim	0.03	0.02	4.79E-04	6.52E-04	1.16E-02	8.49E-03	2.35E-03	3.20E-03	6.70E-02	4.91E-02	1.44E-04	1.96E-04	2.82E-03	2.06E-03	4.38E-04	5.96E-04	1.35E-02	9.91E-03
Imidacloprid	0.06	0.08	1.03E-03	1.40E-03	6.18E-03	4.53E-03	5.99E-04	8.16E-04	1.96E-03	1.43E-03	1.92E-04	2.61E-04	6.26E-04	4.59E-04	ND	ND	ND	ND
Emamectin benzoate	0.0005	—	5.75E-03	7.83E-03	—	—	ND	ND	ND	ND	ND	ND	ND	ND	3.81E-04	5.19E-04	—	—
Chlorfluazuron	0.005	—	4.60E-03	6.26E-03	—	—	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorfenapyr	0.03	0.015	1.49E-03	2.02E-03	1.46E-02	1.07E-02	ND	ND	ND	ND	ND	ND	ND	ND	9.59E-03	1.31E-02	8.35E-02	6.12E-02
Paclobutrazol	0.1	0.1	9.64E-04	1.31E-03	1.00E-02	7.34E-03	ND	ND	ND	ND	ND	ND	ND	ND	1.03E-03	1.40E-03	6.18E-03	4.53E-03
Pyraclostrobin	0.03	0.03	1.10E-03	1.50E-03	1.46E-02	1.07E-02	6.71E-04	9.13E-04	4.38E-03	3.21E-03	1.20E-03	1.63E-03	1.09E-02	7.95E-03	5.75E-03	7.83E-03	—	—
Chlorothalonil	0.02	0.05	9.35E-04	1.27E-03	1.63E-03	1.19E-03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorantraniliprole	2	—	8.63E-06	1.17E-05	—	—	ND	ND	ND	ND	ND	ND	ND	ND	4.60E-03	6.26E-03	—	—
Cypermethrin	0.02	0.005	2.37E-03	3.23E-03	4.13E-02	3.03E-02	1.15E-03	1.57E-03	2.00E-02	1.47E-02	1.08E-03	1.47E-03	3.01E-02	2.20E-02	ND	ND	ND	ND
Deltamethrin	0.01	0.01	2.45E-03	3.33E-03	1.06E-02	7.80E-03	ND	ND	ND	ND	ND	ND	ND	ND	2.88E-03	3.91E-03	1.44E-02	1.06E-02
Cyfluthrin	0.04	0.02	4.67E-04	6.36E-04	4.07E-03	2.98E-03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyhalothrin	0.02	—	ND	ND	ND	ND	3.16E-03	4.31E-03	—	—	ND	ND	ND	ND	1.58E-03	2.15E-03	—	—
Thiamethoxam	0.08	0.5	ND	ND	ND	ND	1.31E-03	1.79E-03	1.93E-03	1.41E-03	ND	ND	ND	ND	9.21E-06	1.25E-05	—	—
Pyridaben	0.01	0.05	ND	ND	ND	ND	ND	ND	ND	ND	5.75E-04	7.83E-04	5.13E-04	3.76E-04	ND	ND	ND	ND
Prochloraz	0.01	0.025	ND	ND	ND	ND	ND	ND	ND	ND	4.69E-02	6.38E-02	2.66E-01	1.95E-01	4.79E-04	6.52E-04	1.16E-02	8.49E-03
Fenpropathrin	0.03	0.03	ND	ND	ND	ND	ND	ND	ND	ND	8.15E-03	1.11E-02	3.55E-02	2.60E-02	ND	ND	ND	ND
Dichlorvos	0.004	0.002	ND	ND	ND	ND	ND	ND	ND	ND	4.32E-03	5.87E-03	3.76E-02	2.75E-02	ND	ND	ND	ND
Fenvalerate	0.02	—	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.24E-03	4.40E-03	—	—
Bifenthrin	0.01	0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	9.35E-03	1.27E-02	1.36E-02	9.94E-03

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TABLE 2 (*Continued*) Long- and short-term risk assessment of pesticide residues in the four fruit types.

Pesticides	ADI (mg/kg bw.d)	ARfD (mg/kg bw.d)	Yellow peach				Loquat				Sweet spring tangelo				Pear			
			HQ_c		HQ_a		HQ_c		HQ_a		HQ_c		HQ_a		HQ_c		HQ_a	
			Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Abamectin	0.001	0.005	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.49E-03	2.02E-03	1.46E-02	1.07E-02

ADI: acceptable daily intake.
ARfD: acute reference dose.
HQ_c: Long-term (chronic) intake risk assessment.
HQ_a: Short-term (acute) intake risk assessment.
ND: no detected.
—: there is no comparative ARfD value.

pesticides in the loquat samples. Prochloraz (94.74%), acetamiprid (63.16%) and pyraclostrobin (63.16%) were the most frequently detected pesticides in the sweet spring tangelo samples. Further, pyraclostrobin (85.71%), chlorantraniliprole (71.43%), carbendazim (42.86%), chlorbenzuron (42.86%), acetamiprid (33.33%) and cyhalothrin (33.33%) were the most frequently detected pesticides in the pear samples. It is noteworthy that acetamiprid, carbendazim, difenoconazole and pyriclostrobin were detected in the four fruit types, and carbendazim was the most frequently detected pesticide (45.59% of the overall samples). Carbendazim, as a broad-spectrum fungicide with low toxicity and high efficiency, is widely used in the prevention and treatment of plant fungal infections (Xu et al., 2018). These results indicate that these frequently detected pesticides are widely used in China for fruit planting. Our results are consistent with previous studies in China and other countries (Quijano et al., 2016; Li et al., 2018; Bibi et al., 2022). The remaining undetected pesticides are not shown in Table 1.

3.2 Risk assessment

3.2.1 Long-term consumer exposure to pesticides

In previous studies, the median residue data for pesticides are often used for long-term risk analysis (Lemos et al., 2016). In this study, because the average concentration (most data) was higher, the average concentration was used instead of the median concentration to assume the worst case. A long-term intake risk assessment of pesticide residues on the targeted fruits was conducted for both children and adults (Table 2). For chronic exposure risk assessment, HQ_c was evaluated by comparing the exposure with the toxicological reference value (ADI) (Sharma et al., 2022). To follow the principle of maximum risk, the four fruits intake were based on the maximum recommended intake of fruits (0.15 kg for children and 0.35 kg for adults) (Chen et al., 2021). The NEDI values were notably lower than the ADI values, which indicates that chronic risk from pesticide exposure *via* the consumption of the four fruit types can be ignored. As evident from the data (Table 2), among the four fruit types investigated, the HQ_c value (C corresponding to the average concentration in the available samples) of children and adults was less than 1. Among the fruits investigated, sweet spring tangelo had the highest HQ_c value (4.69E-02 for adults and 6.38E-02 for children), followed by pear (1.44E-02 for adults and 1.96E-02 for children), yellow peach (5.75E-03 for adults and 7.83E-03 for children) and loquat (3.16E-03 for adults and 4.31E-03 for children).

As depicted in Table 2, the chronic risk value for children was higher than that for adults due to their lower body weight. The highest HQc in sweet spring tangelo was 4.69E-02 due to the high residual value (1.06 mg/kg) of prochloraz.

3.2.2 Short-term consumer exposure to pesticides

As seasonal fruits, yellow peach, loquat, sweet spring tangelo and pear are largely consumed by consumers at certain times of the year, which may lead to high acute exposure to pesticides. Therefore, we also conducted an acute dietary exposure assessment of pesticides in these four fruit types to assess the risk to consumers. To minimize consumer risk, the estimated daily intakes of pesticides *via* fruits were determined by multiplying the maximum pesticide concentration in a fruit by the maximum fruit consumption. Acute exposure risk assessment could not be performed for chlorfluazuron, pyrimethanil, fenvalerate, cyhalothrin,

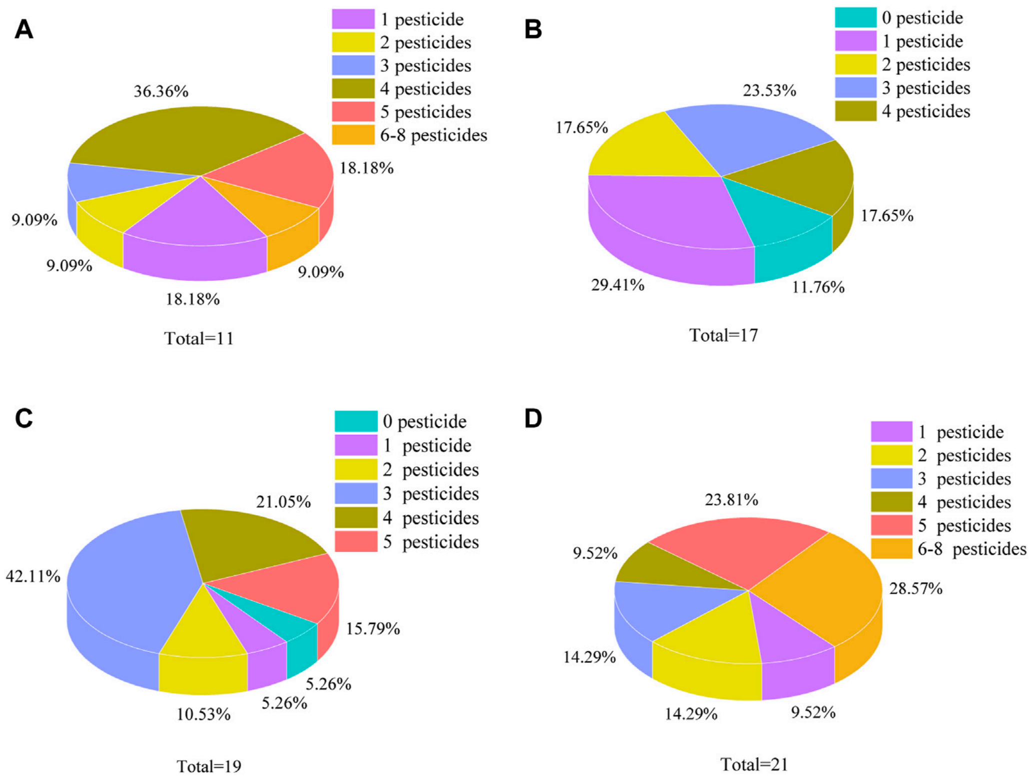

FIGURE 2
Proportion of pesticide residues in samples of yellow peach **(A)**, loquat **(B)**, sweet spring tangelo **(C)** and pear **(D)**.

chlorbenzuron, emamectinbenzoate and chlorantraniliprole as their ARfD values were not listed in the EU Pesticides database. The ARfD values of the other 18 pesticides are listed in Table 2, along with the corresponding acute hazard quotient (HQ_a). The maximum residue concentration and consumption of the four fruit types were used for the calculation of a worst-case scenario. Among the four fruit types analyzed, the HQ_a values of adults and children ranged from 1.17E-04 to 2.66E-01 and from 8.60E-05 to 1.95E-01, respectively, and were therefore well below 1 and within the acceptable range.

3.2.3 Cumulative dietary risk assessment of pesticides

As we all know, the use of a single pesticide may cause resistance to the target (Fan and Li., 2022). Agricultural producers use mixed pesticides to save time and improve pesticide effectiveness, which makes the mixed use of pesticides a common phenomenon (Kuang et al., 2023). In this study, most of the fruit samples tested contained multiple pesticide residues (Figure 2). Among the 68 samples, pesticides were detected in 65 samples, and the sample with the most detected pesticides contained eight kinds of pesticides. The HI of a mixture of pesticides is the sum of the HQ_c values, which are calculated as the ratio of the national estimated daily pesticide intake to the acceptable daily intake (Tripathy et al., 2022). As illustrated in Figure 3, the respective cumulative highest HI values for all detected pesticides in adults and children were calculated as 1.40E-03 and 1.80E-02 in yellow peach, 3.23E-02 and 4.40E-02 in pear, 1.54E-02 and 2.10E-02 in loquat and 1.53E-01 and 2.08E-01 in the sweet spring tangelo samples.

3.3 Quality of the four fruit types

Among basic tastes, SS, TA, and SS/TA ratio (MI) are the prominent eating quality attributes in fruit, which directly affect the grade and the commodity value of the fruit (Huang et al., 2021). SS, TA, the SS/TA ratio and the Vc content, shown in Figure 4, had a significant ($p < 0.05$) variation among the types of fruits. The mean values for the SS, TA and SS/TA ratio for the fruits ranged from 11.01% to 12.01%, 0.08%–0.38% and 33.76 to 139.02, respectively. The fruit with the highest Vc content was sweet spring tangelo, with the highest detection value reaching 29.2 mg/100 g.

4 Discussion

In this study, a total of 68 fruit samples from four main production were analyzed for 68 pesticides. The pesticide residues ranged from 0.001 to 1.06 mg/kg. The use of different types of pesticides to protect fruits against different pests or diseases may result in multiple residues in a sample (Lozowicka et al., 2012). The detection rates of three or more pesticides were 72.73% for yellow peaches, 41.18% for loquats, 78.95% for sweet spring tangelos

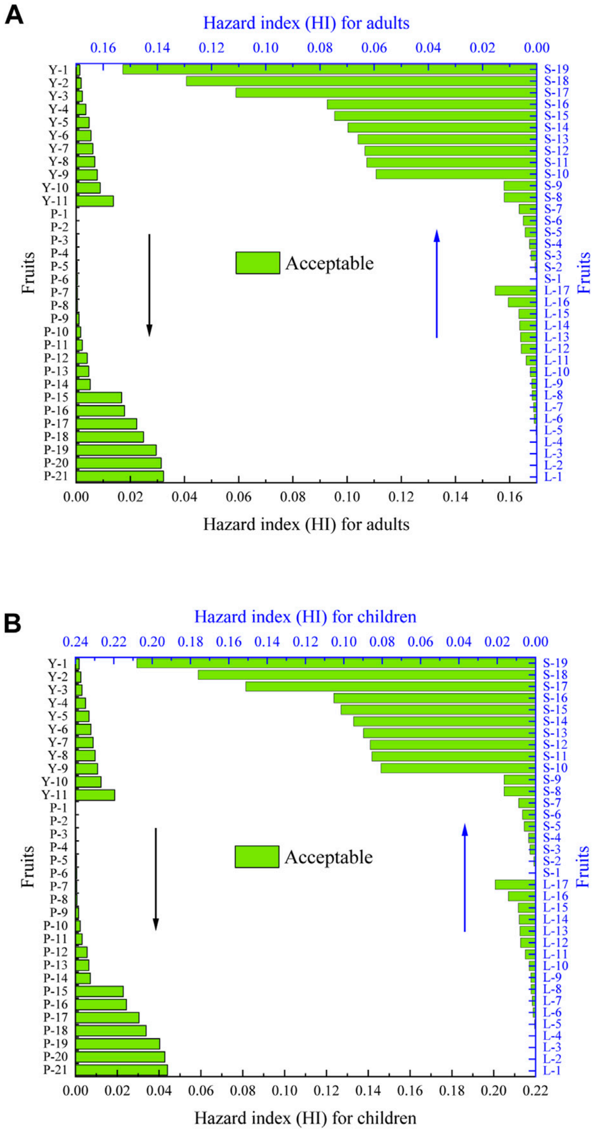

FIGURE 3
The estimated hazard index (HI) of pesticides for adults **(A)** and children **(B)** based on the consumption of the four fruit types. Letters refer to the different fruits: Y represents yellow peach, P represents pear, L represents loquat and S represents sweet spring tangelo.

and 76.19% for pears, indicating that a portion of the plants may have been exposed to a combination of pesticides (Figure 5, 2). In this study, except for imidacloprid and cypermethrin, 13 unregistered pesticides were detected in the yellow peach samples; eight unregistered pesticides were detected in the loquat samples (except cyhalothrin); and 10 pesticides were detected in sweet spring tangelo that have been registered for citrus. Among the 16 pesticides detected in pears, 10 pesticides were not registered, and pyriclostrobin had a very high detection rate of 85.71%. It should be noted that the detection of these pesticides could not fully prove the direct use of chemical pesticides because some pesticides may come from the environment or be transferred from other places and then be absorbed by plants (Wu et al., 2022). Producers and government regulators should pay more attention to the multi-residue problems of unregistered pesticides. Previous studies from the recent few years have also reported multiple residues of different pesticides in most fruit. Eslami et al. (2022) reported on the multiple residue assessment of 57 pesticides in 35 barberry samples, of which 48.5% of the samples contained pesticide residues and 37% of the samples contained multiple residues (more than two pesticides). Wang et al. (2022) monitored 37 pesticide residues in 268 litchi samples; up to 11 pesticides were positive simultaneously, and 96.6% of the samples contained at least two pesticides. It is well known that half-life is an important indicator of pesticide safety evaluation; Patra et al. (2022) reported that indefencarb degrades rapidly in cabbage and tomato, with a half-life ranging between 1.55 and 2.76 days, and can be safely consumed after spraying for 1 day. The half-life of bifenazate was fitted as 34.04 days in citrus (Wang et al., 2023). In order to further confirm the safety of pesticides, dietary risk assessment is very necessary.

The non-detected pesticides were excluded from the exposure estimates and risk assessment. We detected that prochloraz in a pear sample exceeded the MRLs set by the Chinese government in 68 fruit samples. Based on a comparison of the MRLs of pesticides formulated by the European Union (EU) (European Commission, 2022), Japan (Japan, 2022) and Codex Alimentarius Commission (CAC, 2022), some pesticides detected in the four types of fruits exceeded the MRLs (imidacloprid, chlordimefon and paclobutrazol in peach samples; imidacloprid in loquat samples; prochloraz in sweet spring tangelo samples; and prochloraz in pear samples) (Supplementary Table S2). The over-limit ratio of the 25 pesticides in the 68 samples based on the established MRLs in EU (27.94%) was higher than the MRLs of China (1.47%), Japan (2.94%) and CAC (0%), and this indicated that the limits for pesticides in the EU was much stricter than other countries and organizations. The residue data was further analyzed to assess the dietary risks associated with four fruits consumption. The HQ_c values for four fruits were found to vary from 8.63E-06 to 4.69E-02 for adults and from 1.17E-05 to 6.38E-02 for children (Table 2). For the long-term (chronic) risk assessment, the HQ_c values were all lower than 1. The present results demonstrate that the long-term dietary intake of the four fruit types is unlikely to present a public health concern for Chinese consumers. Although our research results indicate that the risk of exposure through the consumption of these four types of fruits can be ignored, and in order to reduce the total risk of exposure to these chemicals from various foods, we should take special precautions (Jeong et al., 2012).

The HQ_a values for four fruits were found to vary from 1.17E-04 to 2.66E-01 for adults and from 8.60E-05 to 1.95E-01 for children (Figure 5), and were therefore well below 1 and within the acceptable range. The dietary risk assessment of pesticide residues in the four fruit types revealed that HQ_a for all pesticides did not exceed the unit value ($HQ_a < 1$). Therefore, the pesticide residues in these fruits do not pose a risk and hence can be considered safe for human consumption. Moser et al. (2005) pointed out that the adverse effects of cumulative exposure to multiple pesticide residues are much more serious than any single exposure. HI method is usually used to calculate the cumulative dietary risk of pesticides with the same action mode; Wu et al. (2022) have reported organophosphates, carbamates and neonicotinoids all have the same primary mode of action as nicotinic acetylcholine receptor modulators. In the present study,

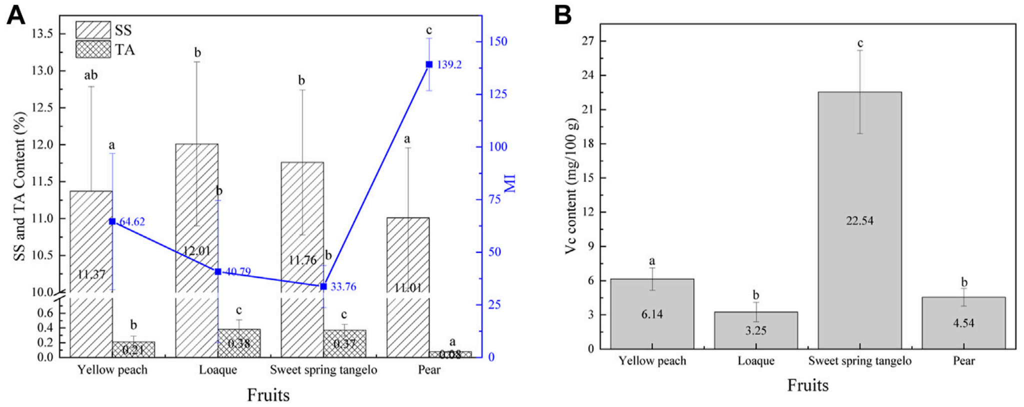

FIGURE 4
The quality of the four characteristic fruits in Zhejiang Province, China. Note: **(A)** Soluble solids (SS), titratable acid (TA) content and SS/TA ratio (MI); **(B)** vitamin C (Vc) content. Different lowercase letters represented a significant difference at $p < 0.05$ level.

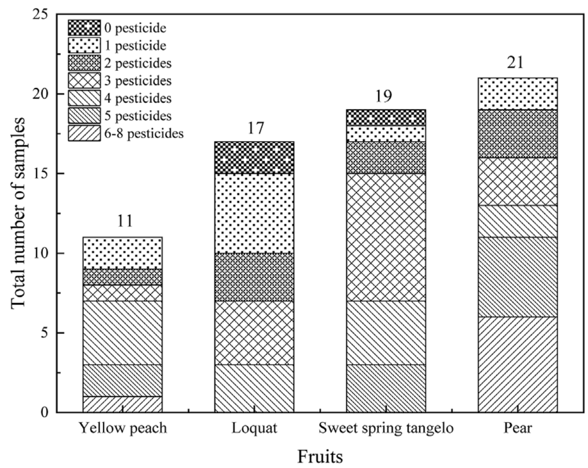

FIGURE 5
Detection of pesticide residues in the four fruit types.

the exposure due to all the detected pesticides has been taken into account. Therefore, although the calculated HQ_a and HQ_c values show that the exposure risk after consumption can be ignored, the accumulation in organisms may have harmful effects, which need further investigation. According to the risk assessment results, HI value of children is generally higher than that of adults (HI < 1 in both age groups). In our results, the pesticide residues in the four fruit samples were consistent with those reported in recent studies which indicated a food commodity is considered safe to consumers when the HI < 1 (Galani et al., 2020; Sharma et al., 2022; Tripathy et al., 2022). It can be acknowledged that the cumulative intake of multiple pesticides from the consumption of the four fruit types may not pose a marked health risk, and these fruits are considered safe for consumers.

Generally, pesticides can be degraded in the environment by hydrolysis or photolysis. Besides, studies have shown that phytoremediation is a potential method to reduce the risk of these pesticides, involving many components of plants, including plant antioxidant machinery, phytochromes, glycoproteins and the interaction of various metabolic systems (Mahmood et al., 2014). Salicylic acid (SA) is a common plant hormone and an effective signal molecule, it plays an important role in the degradation of pesticides. Zhang et al. (2018) combined research on wheat, corn and rape has proved that SA has a broad spectrum for accelerated degradation of pesticides; Li et al. (2020) investigated isoproturon degradation which was affected by SA, Profiling genomic loci of isoproturon-exposed rice identified many genes associated with isoproturon degradation and transport enzymes, confirming that SA is necessary for isoproturon degradation in rice plants. Cytochrome P450s (CYPs) are a versatile group of enzymes exists in plants, animals and other living organisms, controlling various physiological processes *via* biosynthetic and detoxification pathways. Most of the plants' CYPs are present in the endoplasmic reticulum, providing resistance to antibiotics, insecticide, herbicide, and drugs. Reports are suggesting that CYP members can break down PAHs and PCDDs into more minor toxic compounds (Sakaki et al., 2002; Shinkyo et al., 2003; Shinkyo et al., 2006).

The control of pesticide residue limits is the basis of product quality and determines consumer preference and market popularity. Early studies showed that citrus fruits are one of the main sources of vitamin C in the human diet (Nagy, 1980). Ramful et al. (2011) reported that the content of vitamin C in the pulp extracts of 21 common citrus fruits in Mauritius reached 677 ± 22 μg/mL. It cannot be ignored that the quality of the four fruit types was not sufficiently stable. Figure 4 shows that the contents of SS, TA and vitamin c in the same kind of fruit exhibited considerable differences. Wu et al. (2021) found that the application of P fertilizer improved fruit quality in citrus, as supported by the decreasing TA and increasing SS contents and the ratio of SS and TA. Lin et al. (2021) observed that light environment affected V_{cmax} (maximum carboxylation rate under Rubisco restriction), Jmax (maximum electron transfer rate under light saturation), V_{tpu} (rate of triose phosphate utilization) and CE (carboxylation efficiency) differently between the two canopy shapes. Compared with conventional condensed round and large canopy, hardness and SS content of open-central canopy were significantly increased, and the TA content of apples was sharply decreased. Among the four photosynthetic parameters, Jmax and V_{cmax} were the two most sensitive to the change in light environment. The reason may be that Jmax and V_{tpu} are limiting factors in the process of photosynthetic carbon assimilation. Therefore, scientific planting technology is the key to ensure the quality of fruit. Individual and small-scale production of farmers in China may be one of the main reasons for the differences in the quality of fruits in the same region. Most farmers do not have scientific planting technology because they do not receive enough education. Zhou et al. (2015) introduced three types of agricultural production in China, i.e., farmer cooperatives, agricultural companies and family farms. With the expansion of the agricultural scale, production and management are gradually standardized (Jin and Zhou, 2011). Fortunately, the planting of yellow peach (Miaoxi), loquat (Lanxi), sweet spring tangelo (Qingyuan) and pear (Haining) has gradually shifted from local small-scale farmers to commercial planting, mainly due to the obvious price advantage, and high-quality fruits have high sales potential in the market (Chalak et al., 2014).

Ensuring food safety and improving product quality are two key factors for the development of fruit industry, and the application of new technologies is essential. Nanotechnology has a great promise in modern agriculture, where novel nanomaterials are used to increase productivity and quality of produce and reduce environmental pollution (Rana et al., 2021). Nano-pesticides have the properties of eco-friendly, target-specific and controlled release, thus improving the utilization of pesticides and significantly reducing the level of pesticide residues and environmental pollution. Nano-fertilizer can improve crop yield and nutrition by slowly and target-specifically release into plants. Davarpanah et al. (2016) reported that the application of sodium and boron nano-fertilizer on pomegranate can significantly improve the product quality, including 4.4%–7.6% increases in SS, 9.5%–29.1% decreases in TA.

5 Conclusion

In this study, the residue levels and potential health risks of pesticides in four characteristic fruits certified by geographical indications from Zhejiang Province in China were investigated. Among the analyzed samples, 25 pesticide residues were detected in 68 samples corresponding to the four different types of fruits, and the detection rate of pesticides reached 95.59%. Among these, prochloraz in a pear sample exceeded the MRLs values for this pesticide. Fortunately, compared with ADI or ARfD, the chronic or acute intake of the analyzed pesticide residues in adults and children appeared to be very low. Therefore, no long- or short-term consumer risk is expected. In summary, the exposure assessment showed that the levels of pesticides in the four fruit types were safe for human consumption. In addition, the quality of the four fruit types was analyzed and found to not be sufficiently stable. In brief, these results presented important data on the current contamination levels of pesticides and quality evaluation in characteristic fruits of Zhejiang Province, China. Our research results provide new ideas for the development of local fruit industry. Therefore, we suggest that individual farmers strengthen standardized planting and management technology by joining family farms and farmer cooperatives, as well as solve problems such as small-scale production challenges and pesticide residue problems by purchasing inputs, undergoing technical training and supervising members' product production, and ensuring the stability and safety of product quality through the unified distribution of fertilizers and pesticides.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by CS, YL, KB, WZ, and GY. The first draft of the manuscript was written by YL and CS. Formal analysis was carried by KB, WZ, and GY. All authors commented on previous versions of the manuscript. All authors read and approved the final version of the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2023.1124094/full#supplementary-material

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