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Research article

Pesticide residue and dietary intake risk of vegetables grown in Shanghai under modern urban agriculture in 2018–2021

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A B S T R A C T

Shanghai as an international metropolis is representative of modern urban agriculture in China, so it is of great significance to analyse the pesticide residue in vegetables grown in Shanghai. This study investigated the residue of 68 commonly used pesticides (divided into insecticides, fungicides, herbicides and plant growth regulators) in 7028 vegetable samples in Shanghai from 2018 to 2021, and estimated the dietary intake risk of these pesticides. These samples were divided into 6 categories. A total of 29.21% of vegetable samples had pesticide residues, and 0.47% of samples exceeded the maximum residue limits (MRLs) set by the national food safety standard of China. Leafy vegetables had the highest detection rate of pesticide residues (32.9%), multiple detection rate (12.2%), pesticide residue concentration (35.7 mg/kg), and the number of samples exceeding the MRL (30). There were 36 out of 68 pesticides detected in vegetables, and the top 3 were dimethomorph, propamocarb and acetamiprid. The target hazard quotient (THQ) and hazard index (HI) of these noticeablepesticides were all less than 1, illustrating that there may be no obvious health hazard for residents exposed to the pesticide levels. This study can promote the green development of the pesticide industry and provide important reference data for the monitoring of pesticide residues and their hazards under modern urban agriculture.

1. Introduction

With the development of modern agriculture, pesticides are widely used in the production of agricultural products. According to their different efficacies, pesticides can be mainly divided into insecticides, fungicides, herbicides and plant growth regulators, which play a key role in increasing product yield [1–3]. As shown by the statistics of China Crop Protection Industry Association (CCPIA), due to incorrect and discontinued of pesticide application, crop production will be reduced by 35%–40%, and the loss of vegetables and fruits can reach 40%–60%. However, with the development of the pesticide industry and its wide application in agricultural production, the illegal production and unreasonable use of high-toxicity and high-residue pesticides have led to the frequent occurrence of excessive pesticide residues [4,5].

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Vegetables are rich in vitamins, dietary fibre and other nutrients, and their antioxidant activity is conducive to clearing free radicals in the body and preventing various diseases and ageing caused by oxidation [6]. Pesticide residues in vegetables are influenced by transport within the organism and external environmental factors, and they can also further bioaccumulate in the fatty tissues of consumers via dietary exposure through the food chain [7]. These pesticides also accumulate in crops and soil to produce complex intermediates and metabolites [8]. These are collectively referred to as 'emerging pollutants', which cause serious harm to human health and the environment and have attracted increasing attention [9–12]. Some reports suggest that pesticide intake may contribute to headaches, allergies, depression, respiratory diseases even teratogenicity, cancer and foetal death [13–15].

As an international metropolis, Shanghai is constantly boosting the development of urban modern agriculture to meet consumers' demand for high-quality agricultural products. Compared with traditional agriculture, urban modern agriculture has the characteristics of integration, standardization, and restriction of fertilizers and pesticides, with an emphasis on environmental friendliness [5, 16]. However, a large number of current studies still focus on the residues and hazards of pesticides under traditional agriculture, and the excavation of pesticide residue levels under modern urban agriculture is not deep enough.

Therefore, this study first carried out high-throughput detection and comprehensive analysis of pesticide residues in vegetables produced locally in Shanghai from 2018 to 2021, including the categories of vegetables with pesticide residues and the types and concentrations of high-frequency residual pesticides. Furthermore, the dietary intake risk of vegetables grown in Shanghai was estimated through the target hazard quotient (THQ) and the hazard index (HI). By comparing the pesticide residues in vegetables with other countries, we can determine the risk level of pesticide residues in vegetables grown in Shanghai on a global scale. This study shows the necessity for the green development of the pesticide industry and provides data support for the monitoring of pesticide residues and their hazards in modern urban agriculture in China and around the world.

2. Materials and methods

2.1. Sample collection

The vegetable samples were from Shanghai, which is at the mouth of the Yangtze River and has a subtropical monsoon climate. In this study, a total of 7028 samples of local vegetables were randomly collected from Shanghai in 2018–2021, as shown in Fig. 1. These vegetables were mainly divided into 6 categories: leafy vegetables, solanaceous fruits, melons, brassicas, beans, and bulbs. The sampling was conducted following NY/T 789–2004 [17]. It was the agricultural industry standard of the People's Republic of China, named guideline on sampling for pesticide residue analysis. The collected samples were immediately transported to the laboratory for refrigeration. The edible parts of the vegetables were homogenized with a pulverizer within 24 h and stored at −20 °C for detection and analysis of pesticide residues.

2.2. Materials and reagents

Pesticide reference standards (≥95.0% purity) were purchased from the First Standard (Tianjin, China) and Dr. Ehrenstorfer (Augsburg, Germany). Mixed standard stock solutions of various concentrations were prepared in proper solvents and stored at −18 °C for 3 months. Standard working pesticide solutions were prepared from the stock solutions and stored at 4 °C for 1 month. The purchased standard reference substances were 68 common-used pesticides (Table S1, Supplementary file). High-performance liquid chromatography (HPLC)-grade acetonitrile and formic acid were obtained from Merck GmbH (Darmstadt, Germany) and ANPEL Laboratory Technologies (Shanghai, China), respectively. ProElut QuEChERS sample extraction kit (4 g $MgSO_4$, 1 g NaCl, 1 g trisodium citrate dihydrate, 0.5 g disodium hydrogen citrate) and purification kit (150 mg primary and secondary amine exchange material sorbents, 45 mg Carbon, 900 mg $MgSO_4$) were purchased from DiKMA (Beijing, China). Ultra-pure water was prepared by Milli-Q® IQ Element water purification and dispensing unit (Merck, USA).

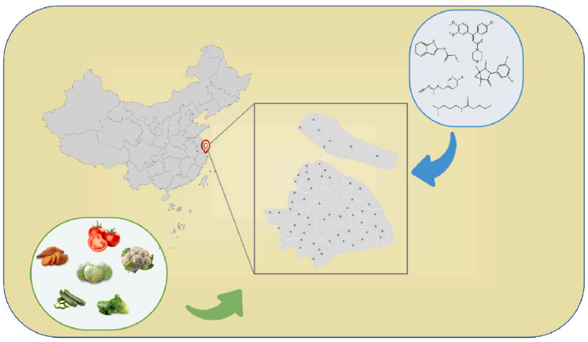

Fig. 1. The strategy of sampling.

2.3. Sample preparation

The homogenized vegetable samples were pretreated for instrumental analysis through an optimized QuEChERS method [18]. 10 g of the homogenized samples were weighed in 50 mL polypropylene centrifuge tubes, and then 20 mL of acetonitrile and a salt pack from the ProElut QuEChERS sample extraction kit were added. After the mixture was ultrasonicated for 30 min and centrifuged at 8000 rpm for 5 min, 10.0 mL of the supernatant was transferred to 15 mL purification tubes of purification kit for the clean-up step. The tube was vortex-mixed for 1 min and centrifuged for 5 min at 3000 rpm. The supernatant was filtered through 0.45 μm membranes for gas chromatography-mass spectrometry (GC-MS) analysis and mixed with ultra-pure water (1:1,V/V) for liquid chromatography-mass spectrometry (LC-MS) analysis. The pesticides tested in this study were 68 commonly used pesticides.

2.4. Instrumental analysis

2.4.1. GC-MS/MS

GC-MS analysis were carried out on a gas chromatography-mass spectrometer QP 2010 Plus (Shimadzu, Japan) with the separation of a DB-5MS capillary column(0.25 μm, 30 m × 0.25 mm). The injector temperature was 280 °C and injection volume was 1.0 μL. Oven temperature was programmed as follows: it held at 40 °C for 1 min, and ramped to 120 °C at a rate of 40 °C/min, and increased to 280 °C at a rate of 5 °C/min, and increased to 300 °C at a rate of 12 °C/min, then held for 7 min. Helium was set as carrier gas with flow rate 0.75 mL/min. The ion source of MS was operated in the electron ionization mode (EI, 70 eV). Qualitative and quantitative analyses were based on internal standards and standard curves.

2.4.2. LC-MS/MS

LC-MS analysis were carried out on an ultra-high performance liquid chromatography system equipped with a Xevo TQ-S mass spectrometry (Waters, USA). The mobile phase consisted of 0.1% formic acid in ultrapure water (A) and acetonitrile (B) was in the following gradients: 0–4 min, 10% B; 4–15 min, 50% B; 15–23 min, 60% B; 23–30 min, 80% B; 30–35 min, 95% B; 35–50 min, 10% B. The flow rate was 0.2 mL/min and the injection volume of the sample was 20 μL. The positive electrospray ionization mode (ESI^+) with multiple reaction monitoring (MRM) was carried out in MS analysis. Qualitative and quantitative analysis based on internal standards and standard curves.

2.4.3. Quality assurance and quality control

Six-point standard calibration curve combined with internal standard to reduce matrix effect and ensure the accuracy of detection results. In this study, the recoveries of pesticides in vegetables were all in range of 80%–120%, and the correlation coefficients of standard curves (R^2) are not less than 0.99. Pesticide concentrations exceeding the limits of quantification (LOQs) were recorded. Vegetables which pesticide concentrations above the maximum residue limits (MRL) formulated by the national food safety standard of China (GB2763) were requantified with matrix-matching standard solution.

2.5. Health risk assessment

The dietary intake risk assessment of vegetables containing pesticide residues mainly involves in estimated daily intake (EDI), the target hazard quotient (THQ) and the hazard index (HI) [19]. These risk assessments depend on pesticide residue concentration and daily consumption, using the following equations can be investigated:

$$EDI = \frac{C \times W}{Bw} \tag{1}$$

$$THQ = \frac{EDI}{ADI} \tag{2}$$

$$HI = \sum_{n=1}^{i} THQ_n \tag{3}$$

Equation (1) reflected the level of exposure of each individual compound, where C (ng/kg) represented the concentration of each pesticide residue in all vegetable samples; LOQ was set as the pesticide concentration for pesticides whose residue level was below LOQ in order to estimate the highest risk; W (g/d) was the average daily intake of vegetables per person, according to the maximum vegetable intake recommended by the Chinese balance dietary pagoda, which can be set as 500 g/d. The average body weight of Chinese adults was set as 60 kg [20].

Equation (2) expressed the health risk of each individual pesticide in vegetables [21,22]. The acceptable daily intake (ADI) was derived from GB 2763. If THQ <1, the exposed population was unlikely to experience obvious health risks. Conversely, THQ >1 suggested an obvious health risk for the exposed population.

Equation (3) estimated the risk of cumulative exposure to the mixtures of pesticide residues by summation of the THQ for an individual pesticide residue [23]. HI < 1 implied that the exposed population was unlikely to experience obvious cumulative risk, while HI > 1 was prone to exist cumulative exposure risk of pesticides.

3. Results and discussion

3.1. Overall residue level of pesticides in vegetables

Vegetables were collected from various production areas in Shanghai, a central city on the east coast of China, as shown in Fig. 1. These vegetables can be divided into 6 categories: leafy vegetables, solanaceous fruits, melons, brassicas, beans, and bulbs. The residues of 68 commonly used pesticides, such as dimethomorph, acetamiprid, propamocarb, and carbendazim, in these samples were detected by analytical instruments.

The results are shown in Table 1, the vegetables grown in Shanghai were mainly leafy vegetables, followed by solanaceous fruits, melons and brassicas. The planting amounts of beans and bulbs were not large, and bulbs were the lowest. Among these categories of vegetables, leafy vegetables had the highest detection rate of pesticide residues, reaching 32.9%, followed by solanaceous fruits, melons and beans, with 26.5%, 21.7% and 20.8% respectively. The lowest detection rates of brassicas and bulbs were 13.4% and 12.4%, respectively. Multiple pesticide residues (at least three types) were positively correlated with the detection rate of pesticide residues. The multiple detection rate of leafy vegetables was the highest, reaching 12.2%, followed by solanaceous fruits, melons and beans, at 6.6%, 5.4% and 5.4%, respectively; brassica and bulb were the lowest at 2.8% and 2.1%, respectively. In addition, bulbs, leafy vegetables and brassicas had pesticides exceeding the MRLs, and the exceeding rates were 1.38%, 0.62% and 0.20%, respectively. The result was in an agreement with the study of Yu, Liu, Liu, Wang, & Wang, (2016) that leafy vegetables have a higher risk of pesticide residues and require further analysis.

A mixture of multiple pesticides is often applied to control plant diseases and insect pests in vegetable crops many times. As a result, the presence of multiple pesticide residues in vegetables was common (Fig. 2). Among them, multiple residues were the most common for leafy vegetables, and even a single sample of leafy vegetables contained up to 9 pesticides simultaneously. As the main vegetables grown in Shanghai, it is important to enhance the targeted supervision of leafy vegetables and improve the efficiency of pesticides.

It is also worth noting that although bulbs and brassicas possessed the lowest D.R and M.D.R, they had cases exceeding the MRLs, which may be caused by the excessive dosage of the drug. It is necessary to pay attention to the issue of the growers' agrochemical regulation for these vegetables.

3.2. Residue levels of different pesticides in vegetables

To investigate the specific types of pesticides detected at high frequency in vegetables, the detected pesticides were subdivided into fungicides, insecticides, plant growth regulators and herbicides. As shown in Table 2, 36 of the 68 pesticides were detected, accounting for 52.94% of the analysed samples. Among these pesticides, the detection rates of dimethomorph, propamocarb and acetamiprid had the highest detection rates, reaching 7.93%, 5.76% and 5.71% respectively. The pesticides detected at high frequency were mainly insecticides and fungicides, with only one plant growth regulator (paclobutrazol) and one herbicide detected (pendimethalin). There were differences in the types of pesticides detected at high frequency in specific vegetables. Specifically, the top three pesticides in beans were cyromazine, acetamiprid and imidacloprid; the top three pesticides in bulbs were carbendazim, propamocarb and dimethomorph; and the top three pesticides in solanaceous fruits were propamocarb, procymid one and acetamiprid. Interestingly, the high-frequency pesticides in bulbs were all fungicides while in beans, they were all insecticides. This result indicated that the prevention and control of diseases and insect pests in different types of vegetables should have different emphases and targets.

In this study, there were 9 pesticides exceeding MRLs in vegetables: acetamiprid, cypermethrin, chlorpyrifos, procymidone, phoxim, imidacloprid, dimethomorph, thiamethoxam and bifenthrin. These pesticides were all insecticides except procymidone and dimethomorph, which indicated that there was a higher risk of excessive residues in the use of insecticides. It was possible that the poor effect of insecticides in vegetables led to repeated spraying or increased application dosage. As a prohibited pesticide in vegetables, chlorpyrifos has continued to exceed the MRLs in some vegetable samples in the last two years, and its monitoring should also be strengthened. In addition, the lack of MRL limit requirements for some vegetables hindered the analysis of the rejection ratio of these vegetables, so enriching the MRL of various vegetables in GB 2763 in China is an important development direction for future pesticide safety evaluation.

Table 1
Detection and exceeding levels of pesticides in different categories of vegetables.

Vegetable species	Number of vegetable samples	D.R(%)	M.D.R(%)	>MRL(%)
Leafy vegetables	4862	32.9 (1598)	12.2 (595)	0.62 (30)
Solanaceous fruits	845	26.5 (224)	6.6 (56)	0
Melons	515	21.7 (112)	5.4 (28)	0
Brassicas	493	13.4 (66)	2.8 (14)	0.20(1)
Beans	168	20.8 (35)[a]	5.4 (9)	0
Bulbs	145	12.4 (18)	2.1 (3)	1.38 (2)
Total	7028	29.21 (2053)	10.03 (705)	0.47 (33)

D.R: detection rate = number of samples containg pesticide residues/total of samples.
M.D.R: multiple detection rate = number of samples containg pesticide residues (≥3)/total of samples.
MRL: Maximum residue limit for pesticides in China (according to GB 2763).
[a] The number of related vegetable samples is in parentheses.

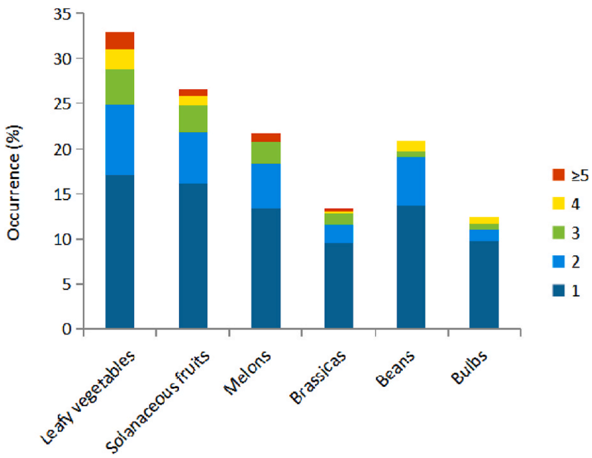

Fig. 2. Detection frequency of multiple pesticide residues in different categories of vegetables. Dark slate blue indicates the detection rate of 1 pesticide in a single sample, steel blue indicates the detection rate of 2 pesticides in a single sample. Green, yellow and red describe the detection rate of 3, 4 and $\geq$ 5 pesticides in a single sample, respectively.

The usage scale of different pesticides in vegetables was explored by analysing the residue map of various pesticides in vegetables. As shown in Fig. 3, leafy vegetables had the most types of residual pesticides, with 36 pesticides detected, which was also consistent with having the highest multiple detection rate. 20, 15 and 14 pesticides were detected in solanaceous fruits, brassica and melons, respectively. Bulbs had the least, with only 11 pesticides. Dimethomorph, propamocarb, acetamiprid, carbendazim, imidacloprid and procymidone were all detected in various vegetables, indicating that these pesticides play a broad role in the prevention and control of vegetable pests and diseases. In addition, the detection rates of cyromazine and paclobutrazol in beans were also high. Cyromazine is an insecticide with low toxicity and strong selectivity to kill dipteran insects [24,25]. Paclobutrazol is a low toxicity, plant growth regulator that can improve crop yield and stress resistance [26]. This result indicated that the growth of legume crops should pay more attention to its pests, lodging and other phenomena.

3.3. Daily intake and potential health risk of pesticides in vegetables

The 10 pesticides with the highest detection rate and exceeding the MRL are listed in Table 3. The residue concentrations of each pesticide were analysed to assess dietary exposure and health risks. In this study, dimethomorph and propamocarb had the highest detected concentrations in leafy vegetables reaching 35.7 mg/kg and 33.6 mg/kg, respectively. They are both fungicides, so it is necessary to boost the killing effectiveness of fungi in leafy vegetables, especially for the *Oomycetes* class, *Botrytis* spp. and *Sclerotinia* spp. In terms of vegetable categories, the detected doses of pesticides in beans and bulbs were relatively low, while leafy vegetables were generally higher. It is supposed that leafy vegetables had more rampant pests and diseases, and pesticides were sprayed more frequently. The overlapping and wrapping structure of leaves with larger surface areas is also prone to residues of pesticides [3,27,28].

By calculating the EDI of various pesticides in vegetables, it was found that none of them exceeded the ADI value, ranging from 0.016 μg/kg/d to 0.489 μg/kg/d. The pesticide with the highest EDI value was propamocarb (0.489 μg/kg/d), followed by dimethomorph (0.420 μg/kg/d), which were only 0.12% and 0.21% of the ADI, respectively. The health hazards of all pesticides were evaluated by calculating THQ. The THQs of all pesticides were far less than 1, indicating that there may be no obvious health hazard for residents exposed to a single pesticide level. Considering the co-occurrence of pesticide residue in vegetables, thr cumulative dietary risk of pesticides detected at high frequencies was assessed through the HI method. The HI of these pesticides was 0.0865 ($<$1), which indicated that the cumulative dietary risk of these pesticides in vegetables was acceptable. Among them, the top 5 contributors to HI were phoxim, chlorpyrifos, pyridaben, carbendazim and procymidone, as the key components inducing the potential health risk of adverse effects for inhabitants. Furthermore, dietary intake risk for some special groups, such as elderly individuals, pregnant women and children, deserves prospective policy defence because they are more susceptible to pesticides than adults [29]. Overall, compared with Beijing, which developed greenhouse vegetables under modern urban agriculture, Shanghai presented similar kinds and concentrations of pesticides detected. They may possess a similar process of urban agriculture modernization [17].

In this study, we also compared the pesticide level and detection rate of these high frequencies with those reported in other countries. The concentration and detection rate of vegetables in Shanghai were significantly lower than the data reported in other countries (Table 4). In relevant foreign reports, the main focus of pesticides were acetamiprid, imidacloprid, cypermethrin, chlorpyrifos and other insecticides, which may be related to the differences in climate environment and vegetable species.

4. Conclusion

In this study, high-throughput determination and risk assessment of 68 pesticides were investigated in 7028 vegetable samples from 6 categories in Shanghai between 2018 and 2021. The results showed that pesticide residues were detected in 29.21% of the

Table 2
Residue levels of different pesticides in vegetables.

Vegetable Species	Leafy vegetables		Solanaceous fruits		Melons		Brassicas		Beans		Bulbs		Total	
Pesticides	D.R(%)	>MRL(%)	D.R(%)	>MRL(%)	D.R(%)	>MRL(%)	D.R(%)	>MRL(%)	D.R(%)	>MRL(%)	D.R(%)	>MRL(%)	D.R(%)	>MRL(%)
Dimethomorph(F)	10.02	0	3.55	0	2.52	0	4.46	0	0.60	0	2.76	0.69	7.93	0.01
Propamocarb(F)	5.59	0	6.86	0	8.93	0	4.06	0	2.38	0	3.45	0	5.76	0.00
Acetamiprid(I)	6.68	0.33	4.62	0	3.11	0	2.43	0	4.76	0	0.69	0	5.71	0.23
Thiamethoxam(I)	4.87	0.02	3.55	0	4.27	0	1.42	0	0.60	0	–	–	4.23	0.01
Carbendazim(F)	4.79	0	2.72	0	2.91	0	1.62	0	2.38	0	4.14	0	4.11	0
Chlorantraniliprole(I)	4.01	0	0.59	0	0.19	0	1.22	0	1.79	0	–	–	2.99	0
Pyridaben(I)	3.87	0	0.59	0	–	–	1.01	0	–	–	1.38	0	2.85	0
Imidacloprid(I)	3.19	0.02	3.08	0	0.97	0	0.81	0	2.98	0	0.69	0	2.79	0.01
Azoxystrobin(F)	2.90	0	1.66	0	0.78	0	0.41	0	1.19	0	–	–	2.32	0
Procymidone(F)	1.69	0.02	6.86	0	2.72	0	–	–	0.60	0	0.69	0.69	2.22	0.03
Cyromazine(I)	1.34	0	0.95	0	2.14	0	–	–	5.36	0	–	–	1.32	0
Chlorfenapyr(I)	1.36	0	0.12	0	–	–	0.81	0	–	–	–	–	1.01	0
Emamectin(I)	1.36	0	0.12	0	–	–	0.41	0	0.60	0	–	–	1.00	0
Pyrimethanil(F)	0.97	0	1.54	0	1.36	0	–	–	–	–	0.69	0	0.97	0
Metalaxyl(I)	0.82	0	–	–	2.52	0	0.20	0	–	–	0.69	0	0.78	0
Cypermethrin(I)	0.99	0.10	–	–	–	–	0.20	0	–	–	–	–	0.70	0.07
Iprodione(F)	0.33	0	2.60	0	0.19	0	–	–	–	–	–	–	0.55	0
Difenoconazole(F)	0.66	0	–	–	–	–	0.41	0	–	–	–	–	0.48	0
Pyraclostrobin(F)	0.43	0	0.47	0	–	–	–	–	–	–	0.69	0	0.37	0
Paclobutrazol(F,P)	0.27	0	–	–	1.55	0	–	–	1.79	0	–	–	0.34	0
Cyhalothrin(I)	0.43	0	0.24	0	–	–	–	–	–	–	–	–	0.33	0
Abamectin(I)	0.41	0	–	–	–	–	–	–	–	–	–	–	0.28	0
Bifenthrin(I)	0.23	0	0.59	0	–	–	0.41	0.20	–	–	–	–	0.26	0.01
Phoxim(I)	0.16	0.04	–	–	–	–	–	–	0.60	0	–	–	0.13	0.03
Chlorpyrifos(I)	0.12	0.08	–	–	–	–	–	–	–	–	–	–	0.09	0.06
Ethofenprox(I)	0.08	0	–	–	–	–	–	–	–	–	–	–	0.06	0
Chlorothalonil(F)	0.06	0	0.12	0	–	–	–	–	–	–	–	–	0.06	0
Diflubenzuron(I)	0.04	0	0.12	0	–	–	–	–	–	–	–	–	0.04	0
Fenpropathrin(I)	0.06	0	–	–	–	–	–	–	–	–	–	–	0.04	0
Tebufenozide(I)	0.06	0	–	–	–	–	–	–	–	–	–	–	0.04	0
Pendimethalin(H)	0.04	0	–	–	–	–	–	–	–	–	0.69	0	0.04	0
Diflubenzuron(I)	0.04	0	–	–	–	–	–	–	–	–	–	–	0.03	0
Fenvalerate(I)	0.04	0	–	–	–	–	–	–	–	–	–	–	0.03	0
Triazolone(F)	0.04	0	–	–	–	–	–	–	–	–	–	–	0.03	0
Flucythrinate(I)	0.02	0	–	–	–	–	–	–	–	–	–	–	0.01	0
Prochloraz(F)	0.02	0	–	–	–	–	–	–	–	–	–	–	0.01	0

-: No detected. F: fungicide. I: insecticide. P: plant growth regulator. H: herbicide.
D.R: detection rate = number of samples containg pesticide residues/total of samples.
MRL: Maximum residue limit for pesticides in China (according to GB 2763).

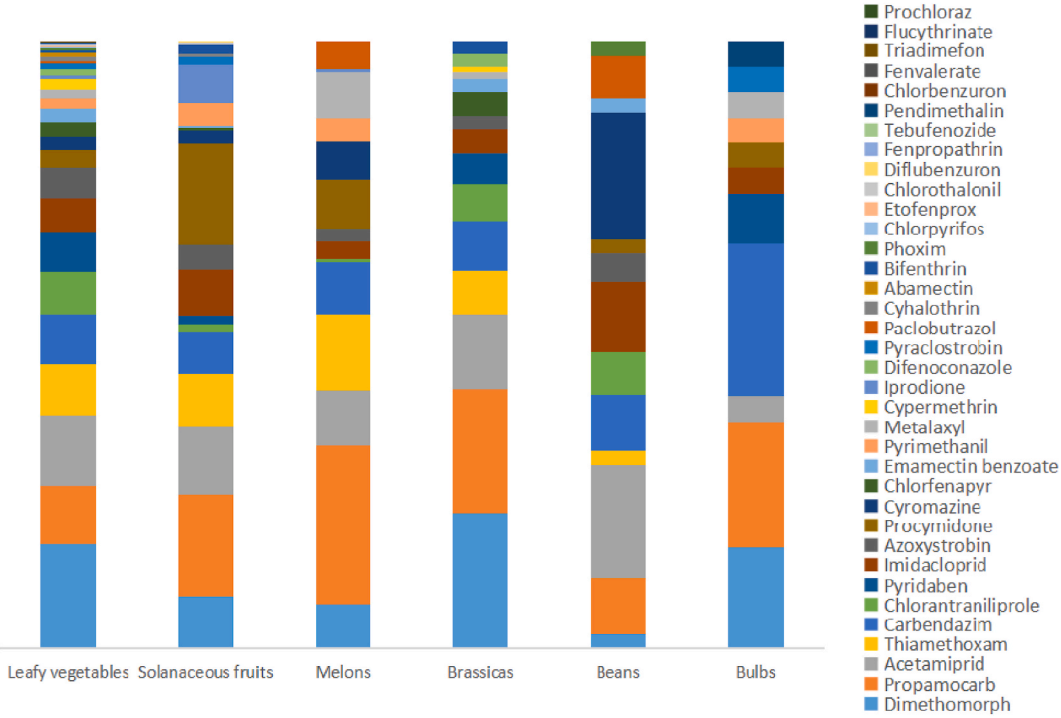

Fig. 3. Residue map of various pesticides in vegetables.

Table 3
Estimated daily intake and potential health risk of pesticides through the consumption of vegetable.

Vegetable Species		Leafy vegetables	Solanaceous fruits	Melons	Brassicas	Beans	Bulbs	Total	
Pesticides	ADI	C.R	C.R	C.R	C.R	C.R	C.R	EDI	THQ
Dimethomorph	200	1.7–35700	4.1–7800	6.5–630	6.8–2780	28	18–1320	0.4200	0.0021
Acetamiprid	70	3.5–3610	12–1220	2.3–220	7.6–770	15–93	14	0.1417	0.0020
Propamocarb	400	4.5–33600	1.02–8280	9.4–1220	13–12700	30–39	7.3–92	0.4886	0.0012
Carbendazim	30	2.8–15400	8.1–4410	5–67	2.8–360	15–1080	3.3–920	0.2824	0.0028
Thiamethoxam	80	9.1–2740	8.8–280	11–460	23–110	14	–	0.1046	0.0013
Chlorantraniliprole	2000	9–5770	10–400	20	33–1820	17–27	–	0.1475	0.0001
Pyridaben	10	12–4930	12–4500	–	24–560	–	24–29	0.0701	0.0070
Imidacloprid	60	7.1–1640	8.3–700	12–58	12–320	11–18	12	0.0696	0.0012
Azoxystrobin	200	12–14740	16–700	24–160	66–260	260	–	0.1618	0.0008
Procymidone	100	32–20000	11–2080	25–220	–	30	5970	0.2357	0.0024
Cypermethrin	20	21–1290	44–1940	–	110	–	–	0.0470	0.0023
Bifenthrin	10	27–1370	73–360	–	150–2450	–	–	0.0163	0.0016
Phoxim	4	21–3740	35	–	–	26	–	0.1795	0.0449
Chlopyrifos	10	77–130	470	–	–		–	0.1676	0.0168
HI									0.0865

ADI: Acceptable daily intake (μg/kg/d, according to GB 27631, China).
C.R: Detected concentration range, μg/kg.
EDI: Estimated daily intake, μg/kg/d.
THQ: Target hazard quotient.
HI: Hazard index.

vegetables, and 0.47% of vegetable samples containing pesticides above the MRL. Among the 6 categories of vegetables, leafy vegetables had the highest detection rate of pesticide residues (32.9%), multiple detection rate (12.2%), pesticide residue concentration (35.7 mg/kg), and number exceeding the MRLs (30). Therefore, as leafy vegetables are the main vegetables grown in Shanghai, the supervision of pesticides in leafy vegetables should be strengthened. Although the detection rates of pesticide residues in bulbs and brassicas were the lowest, there were still pesticide residues above MRLs containing excessive hazards.

36 out of 68 pesticides were detected in vegetables, among which dimethomorph, propamocarb, acetamiprid, carbendazim, imidacloprid and procymid were detected in all categories of vegetables. As a whole, dimethomorph, propamocarb and acetamiprid were the top 3 pesticides with the highest detection rates. The types of pesticides with high-frequency detection rates varied by specific

Table 4
Pesticides residues in vegetables reported in the literature.

Pesticides	Regions	Vegetables	Concentrations(ug/kg)	D.R (%)	Reference	Corresponding concentration in Shanghai (ug/kg)
Cypermethrin	kuwait	Tomato	20-240[a]	Na	[30]	Nd
		Eggplant	Nd-130[a]			Nd
Imidacloprid		Tomato	Nd-510[a]			17–68
		Bell pepper	Nd-10			Nd
		Eggplant	Nd-90			15–49
		Cucumber	50-1200[a]			12–58
		Zucchini	Nd-80			Nd
Acetamiprid		Bell pepper	Nd-50			Nd
		Cabbage	Nd-100			Nd
Imidacloprid	southern Punjab, Pakistan	Okra	Ave490[a]	30.6	[31]	Nd
		Eggplant	Ave810[a]	28.1		15–49
		Pumpkins	Ave450[a]	8.3		Nd
Chlorpyrifos	western Algeria	Tomato	78–107	5	[32]	Nd
Chlorpyrifos	Bangladesh	Tomato	40-700[a]	13.25	[33]	Nd
		Cauliflower	62-80[a]	9.09		Nd
Cypermethrin	Bangladesh	Cauliflower	20–52	9.09		Nd
Acetamiprid	European Union	Sweet peppers	Ave620	22.1	[34]	Nd
Acetamiprid	chile	Tomato	15-490[a]	21.3	[35]	12–19
Imidacloprid		Tomato	2.5–45	3.3		17–68
Dimetomorph	colombia	Tomato	10	7.5	[36]	2.5–500
Imidacloprid		Tomato	280–485	13.5		17–68
Dimethomorph	Beijing china	Pakchoi	50.0–87.2	9.4	[17]	2.6–2960
		Chinese cabbage	1.0–2.13	1.1		35–130
Acetamiprid		Chinese cabbage	0.5–5.23	1.1		Nd
		Tomato	2.41–85.1	24.5		12–190
Cypermethrin		Pakchoi	12.0–370.0	25		35–500
		Chinese cabbage	4.0–473.0	22.3		Nd
		Tomato	7.0–31.0	10.2		Nd
		Chinese chive	6.0–191.0	11.3		Nd
Chlorpyrifos		Pakchoi	32.0–150.0	6.3		82
		Chinese cabbage	13.1–480.0[a]	7.4		Nd
Imidacloprid		Pakchoi	21.0–480.0	21.9		8.6–170
		Chinese cabbage	13.1–51.7	8.5		14–140
Pyridaben		Pakchoi	130.0–3400.2	18.8		10–4500
		Tomato	0.5–2.3	2		Nd
Thiamethoxam		Chinese cabbage	8.81–48.0	5.3		13–16
		cucumber	8.46–17.4	5.6		17–460
		Tomato	10.2–35.5	8.2		16–63

D.R: detection rate = number of samples containg pesticide residues/total of samples.
NA: not available. Nd: pesticide residue not detected.
[a] Pesticide residue above the MRL. Ave: average concentration.

categories of vegetables. Improving the selectivity and targeting of pesticide application according to categories of vegetables is of great significance, for instance, beans are prone having insecticide or plant growth regulator residues. The residue levels of 9 pesticides were higher than the MRLs: acetamiprid, cypermethrin, chlorpyrifos, procymidone, phoxim, imidacloprid, dimethomorph, thiamethoxam and biphenthrin, among which insecticides dominated. The THQs of these hot-spot pesticides were all less than 1, indicating that there may be no obvious health hazard for residents exposed to a single pesticide. The cumulative dietary risk of these pesticides in vegetables was also acceptable with an HI of 0.0865. The concentration and detection rate of vegetables grown in Shanghai were significantly lower than the data reported in other countries, which still have high-toxicity forbidden pesticide residues. Shanghai with modern urban agriculture, had a similar pesticide framework as Beijing, where greenhouse vegetables were developed under modern urban agriculture. To some extent, these results reflected the pesticide residue level of vegetables in coastal cities of eastern China. In this article, a very enormous database of pesticide residue results was constructed with a rich sample size (7028) and pesticide parameters (68). It will promote the green development of the pesticide industry and provide important reference data for the monitoring of pesticide residues and their hazards in modern urban agriculture. Based on leafy vegetables with a high frequency of pesticide residues, we will further analyse the impact of the co-occurrences or "cocktail effect" interaction in our subsequent risk assessment study.

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Data availability statement

The raw data contains confidential parts and is therefore not deposited into a publicly available repository. If there are any concerns about the data, please contact with the authors.

CRediT authorship contribution statement

Jinrong Tong: Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Dongsheng Feng:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Xia Wang:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Min Wang:** Writing – review & editing, Validation, Investigation, Conceptualization. **Meilian Chen:** Writing – review & editing, Validation, Investigation, Conceptualization. **Yanfen Chen:** Writing – review & editing, Validation, Investigation, Conceptualization. **Yingqing Ma:** Writing – review & editing, Validation, Investigation, Conceptualization. **Bo Mei:** Validation, Methodology, Investigation. **Rouhan Chen:** Validation, Methodology, Investigation. **Mengfeng Gao:** Validation, Methodology, Investigation. **Siwen Shen:** Validation, Methodology, Investigation. **Hongkang Wang:** Validation, Methodology, Investigation. **Weiyi Zhang:** Writing – review & editing, Supervision, 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.

Appendix B. Supplementary data

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References

[1] M.S. AL-Ahmadi, Pesticides, anthropogenic activities, and the health of our environment safety, in: M. Larramendy, S. Soloneski (Eds.), Pesticides-Use and Misuse and Their Impact in the Environment, 2019, https://doi.org/10.5772/intechopen.84161.
[2] S.H. Tseng, C.C. Liu, Y.J. Lin, H.C. Chen, S.C. Su, H.K. Chou, et al., Analysis of 81 pesticides and metabolite residues in fruits and vegetables by diatomaceous earth volumn extraction and LC/MS/MS determination, J. Food Drug Anal. 17 (5) (2009) 319–332, https://doi.org/10.38212/2224-6614.2586.
[3] R. Yu, Q. Liu, J.S. Liu, Q.C. Wang, Y. Wang, Concentrations of organophosphorus pesticides in fresh vegetables and related human health risk assessment in Changchun, Northeast China, Food Control 60 (2016) 353–360, https://doi.org/10.1016/j.foodcont.2015.08.013, 2016.
[4] Y.Y. Fang, Z.Q. Nie, Y.M. Yang, Q.Q. Die, F. Liu, J. He, et al., Human health risk assessment of pesticide residues in market-sold vegetables and fish in a northern metropolis of China, Environ. Sci. Pollut. Res. Int. 22 (8) (2015) 6135–6143, https://doi.org/10.1007/s11356-014-3822-7.
[5] J.M. Montiel-Leon, S.V. Duy, G. Munoz, M.A. Verner, M.Y. Hendawi, H. Moya, et al., Occurrence of pesticides in fruits and vegetables from organic and conventional agriculture by QuEChERS extraction liquid chromatography tandem mass spectrometry, Food Control 104 (2019) 74–82, https://doi.org/10.1016/j.foodcont.2019.04.027.
[6] S. Mebdoua, M. Lazali, S.M. Ounane, S. Tellah, F. Nabi, G. Ounane, Evaluation of pesticide residues in fruits and vegetables from Algeria, Food Addit. Contam. Part B, Surveillance 10 (2) (2017) 91–98, https://doi.org/10.1080/19393210.2016.1278047.
[7] Z.J. Li, Spatiotemporal pattern models for bioaccumulation of pesticides in common herbaceous and woody plants, J. Environ. Manag. 276 (15) (2020) 111334, https://doi.org/10.1016/j.jenvman.2020.111334.
[8] G.F. Chen, Y.X. Qiao, X.B. Zhang, F. Liu, H. Liao, R.Y. Zhang, et al., Identification and characterization of herbicide penoxsulam transformation products in aqueous media by UPLC-QTOF-MS, Bull. Environ. Contam. Toxicol. 102 (6) (2019) 854–860, https://doi.org/10.1007/s00128-019-02612-2.
[9] C.J. Li, H.M. Zhu, C.Y. Li, H. Qian, W.R. Yao, Y.H. Guo, The present situation of pesticide residues in China and their removal and transformation during food processing, Food Chem. 354 (2021) 129552, https://doi.org/10.1016/j.foodchem.2021.129552.
[10] R. Jayaraj, P. Megha, P. Sreedev, Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment, Interdiscipl. Toxicol. 9 (3–4) (2016) 90–100, https://doi.org/10.1515/intox-2016-0012.
[11] R.C. Gilden, K. Huffling, B. Sattler, Pesticides and health risks, J. Obstet. Gynecol. Neonatal Nurs. 39 (2010) 103–110.
[12] J. Fenik, M. Tankiewicz, M. Biziuk, Properties and determination of pesticidesin fruits and vegetables, Trac. Trends Anal. Chem. 30 (6) (2011) 814–826, https://doi.org/10.1016/j.trac.2011.02.008.
[13] M.F. Bouchard, J. Chevrier, K.G. Harley, K. Kogut, M. Vedar, N. Calderon, et al., Prenatal exposure to organophosphate pesticides and IQ in 7-year-old children, Environ. Health Perspect. 119 (8) (2011) 1189e1195, https://doi.org/10.1289/ehp.1003185.
[14] E.E. Ntzani, G. Ntritsos, M. Chondrogiorgi, E. Evangelou, I. Tzoulaki, Literature review on epidemiological studies linking exposure to pesticides and health effects, EFSA Supporting Publications 10 (10) (2013).
[15] P. Sadighara, T. Mahmudiono, N. Marufi, N. Yazdanfar, Y. Fakhri, A. Rikabadi, A. Khaneghah, Residues of carcinogenic pesticides in food: a systematic review, Rev. Environ. Health (2023), https://doi.org/10.1515/reveh-2022-0253.
[16] F. Orsini, R. Kahane, R. Nono-Womdim, G. Gianquinto, Urban agriculture in the developing world: a review, Agron. Sustain. Dev. 33 (4) (2013) 695–720, https://doi.org/10.1007/s13593-013-0143-z.

[17] H. Ping, B.H. Wang, L. Cheng, C. Li, Y. Li, X.J. Ha, et al., Potential health risk of pesticide residues in greenhouse vegetables under modern urban agriculture: a case study in Beijing, China, J. Food Compos. Anal. 105 (2022) 104222, https://doi.org/10.1016/j.jfca.2021.104222, 2022.
[18] M. Biziuk, J. Stocka, Multiresidue methods for determination of currently used pesticides in fruits and vegetables using QuEChERS technique, Int. J. Environ. Sustain Dev. 6 (1) (2015) 18, https://doi.org/10.7763/IJESD.2015.V6.554.
[19] H. Li, Q. Chang, R. Bai, X. Lv, T. Cao, S. Shen, et al., Simultaneous determination and risk assessment of highly toxic pesticides in the market-sold vegetables and fruits in China: a 4-year investigational study, Ecotoxicol. Environ. Saf. 221 (2021) 112428, https://doi.org/10.1016/j.ecoenv.2021.112428.
[20] P. Zhuang, M.B. McBride, H. Xia, N. Li, Z. Li, Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China, Sci. Total Environ. 407 (5) (2009) 1551–1561, https://doi.org/10.1016/j.scitotenv.2008.10.061.
[21] G. Darko, O. Akoto, Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana, Food Chem. Toxicol. 46 (12) (2008) 3703–3706, https://doi.org/10.1016/j.fct.2008.09.049.
[22] T.K. Reffstrup, J.C. Larsen, O. Meyer, Risk assessment of mixtures of pesticides. Current approaches and future strategies, Regul. Toxicol. Pharmacol. : RTP (Regul. Toxicol. Pharmacol.) 56 (2) (2010) 174–192, https://doi.org/10.1016/j.yrtph.2009.09.013.
[23] O. Golge, F. Hepsag, B. Kabak, Health risk assessment of selected pesticide residues in green pepper and cucumber, Food Chem. Toxicol. 121 (2018) 51–64, https://doi.org/10.1016/j.fct.2018.08.027.
[24] H. Khan, W. Akram, Cyromazine resistance in a field strain of house flies, Musca domestica L.: resistance risk assessment and bio-chemical mechanism, Chemosphere 167 (2017) 308–313, https://doi.org/10.1016/j.chemosphere.2016.10.018.
[25] A.P. Van de Wouw, P. Batterham, P.J. Daborn, The insect growth regulator insecticide cyromazine causes earlier emergence in Drosophila melanogaster, Arch. Insect Biochem. Physiol. 63 (3) (2006) 101–109, https://doi.org/10.1002/arch.20146.
[26] S.J. Hua, Y.F. Zhang, H.S. Yu, B.G. Lin, H.D. Ding, D.Q. Zhang, et al., Paclobutrazol application effects on plant height, seed yield and carbohydrate metabolism in Canola, Int. J. Agric. Biol. 16 (2014).
[27] W.H. Li, L.Y. Tai, J.X. Liu, Z.K. Gai, G.T. Ding, Monitoring of pesticide residues levels in fresh vegetable form Hebei Province, North China, Environ. Monit. Assess. 186 (10) (2014) 6341–6349, https://doi.org/10.1007/s10661-014-3858-7.
[28] R. Sapbamrer, S. Hongsibsong, Organophosphorus pesticide residues in vegetables from farms, markets, and a supermarket around Kwan Phayao Lake of Northern Thailand, Arch. Environ. Contam. Toxicol. 67 (1) (2014) 60–67, https://doi.org/10.1007/s00244-014-0014-x.
[29] B. Eskenazi, K. Kogut, K. Huen, K.G. Harley, M. Bouchard, A. Bradman, et al., Organophosphate pesticide exposure, PON1, and neurodevelopment in school-age children from the CHAMACOS study, Environ. Res. 134 (2014) 149–157, https://doi.org/10.1016/j.envres.2014.07.001.
[30] M. Jallow, D.G. Awadh, M.S. Albaho, V.Y. Devi, N. Ahmad, Monitoring of pesticide residues in commonly used fruits and vegetables in Kuwait, Int. J. Environ. Res. Publ. Health 14 (8) (2017) 833, https://doi.org/10.3390/ijerph14080833.
[31] S.A. Baig, N.A. Akhter, M. Ashfaq, M.R. Asi, U. Ashfaq, Imidacloprid residues in vegetables, soil and water in the southern Punjab, Pakistan, International Journal of Agricultural Technology 8 (3) (2012) 903–916. http://www.ijat-aatsea.com.
[32] Z.L. Gaouar, B. Chefirat, R. Saadi, S. Djelad, H. Rezk-Kallah, Pesticide residues in tomato crops in Western Algeria, Food Addit. Contam. Part B, Surveillance 14 (4) (2021) 281–286, https://doi.org/10.1080/19393210.2021.1953156.
[34] P. Kuchheuser, M. Birringer, Pesticide residues in food in the European union: analysis of notifications in the European rapid alert system for food and feed from 2002 to 2020, Food Control 133 (2022) 108575, https://doi.org/10.1016/j.foodcont.2021.108575.
[33] M. Chowdhury, A. Fakhruddin, M.N. Islam, M. Moniruzzaman, M.K. Alam, Detection of the residues of nineteen pesticides in fresh vegetable samples using gas chromatography-mass spectrometry, Food Control 34 (2) (2013) 457–465.
[35] S. Elgueta, M. Valenzuela, M. Fuentes, P.E. Ulloa, C. Ramos, A. Correa, S. Molinett, Analysis of multi-pesticide residues and dietary risk assessment in fresh tomatoes (Lycopersicum esculentum) from local supermarkets of the metropolitan region, Chile, Toxics 9 (10) (2021) 249, https://doi.org/10.3390/toxics9100249.
[36] C.R. Bojacá, L.A. Arias, D.A. Ahumada, H.A. Casilimas, E. Schrevens, Evaluation of pesticide residues in open field and greenhouse tomatoes from Colombia, Food Control 30 (2) (2013) 400–403, https://doi.org/10.1016/j.foodcont.2012.08.015.