Food Control 22 (2011) 1114–1120

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Evaluation of pesticide residues in fruits and vegetables from Xiamen, China

Chen Chen [a], Yongzhong Qian [a,*], Qiong Chen [b], Chuanjiang Tao [c], Chuanyong Li [b], Yun Li [a]

[a] Key Laboratory of Agro-Product Quality and Safety, Institute of Quality Standards Testing Technology for Agro-Products, Chinese Academy of Agricultural Sciences, Beijing 100081, PR China
[b] The Supervision, Inspection and Testing Center of Agricultural Products Quality and Security, Ministry of Agriculture, Fujian 361000, PR China
[c] The Institute for the Control of Agrochemicals, Ministry of Agriculture, Beijing 100125, PR China

ARTICLE INFO

Article history:
Received 12 October 2010
Received in revised form
14 January 2011
Accepted 18 January 2011

Keywords:
Monitoring
Pesticide residues
Gas chromatography–Mass spectrometry
Fruits and vegetables
Health risk
Estimated daily intake

ABSTRACT

In the present study an effort has been made to evaluate the residues of selected insecticides (organophosphorous and pyrethroid) and fungicides (triazoles and chloronitriles) in fruits and vegetables collected from Xiamen, China, during the October 2006 to March 2009 monitoring campaign. Gas chromatography with electron capture detector (GC-ECD) was used to determine the concentrations of 22 pesticide residues among those recommended for pest treatment. Of 1135 samples (37.7%) that contained pesticide residues, pakchoi cabbage, legumes, and leaf mustard were the commodities in which pesticide residues were most frequently detected, with 17.2%, 18.9% and 17.2% of the samples exceeding the maximum residue limits (MRLs), respectively. Concerning the most frequently detected pesticide residues, cypermethrin was found in 18.7% of the samples analyzed. Data obtained were then used for estimating the potential health risks associated with the exposures to these pesticides. The estimated daily intakes (EDIs) range from 0.1% of the ADI for cyfluthrin to 2.61% of the ADI for omethoate and 0.1% of the ADI for omethoate. The most critical commodity is legumes, contributing 2.61% to the hazard index (HI). The results show that despite a high occurrence of pesticide residues in fruits and vegetables from this region, it could not be considered a serious public health problem. Nevertheless, an investigation into continuous monitoring and tighter regulation of pesticide residues in fruits and vegetables is recommended.

1. Introduction

Pesticides are widely used to ensure high crop yields. They are used during production and post-harvest treatment of agricultural commodities (FAO/WHO, 2004). However, increased use of chemical pesticides has resulted in contamination of the environment and also caused many associated long-term effects on human health (Bhanti & Taneja, 2007; Calvert, Sanderson, Barnett, Blondell, & Melher, 2001). The presence of pesticide residues in food commodities has always been a matter of serious concern. The problem is especially serious when these commodities are consumed fresh (Solecki et al., 2005). Pesticides have been associated with a wide spectrum of human health hazards, ranging from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm, and endocrine disruption (Berrada et al., 2010).

Insecticides (including organophosphorous and pyrethroid) and fungicides (including triazoles and chloronitriles) are commonly used in developing countries (like China) for pest control and disease vector eradication. Due to the poor pesticide handling practices and use of more toxic pesticides by farmers as well as inadequate management and regulation of these chemicals in developing countries (Waichman, Eve, & Nina, 2007), the occurrence of pesticide poisonings in the developing countries is far greater than that of in the developed (Bhanti, Shukla, & Taneja, 2004). Control programs for pesticide residues in the developing countries are often limited due to lack of resources and rigorous legislation is not in place. Some farmers do not wait long enough for the residues to wash off after spraying before harvesting because of their high demand for farm produce and low perception of the toxic effects of pesticide residues in food (Amoah, Drechsel, Abaidoo, & Ntow, 2006). Thus increased use of pesticides in agriculture has resulted in the occurrence of residues in food commodities (Darko & Akoto, 2008). A risk assessment is necessary to ascertain the health effects due to intakes of pesticide residues on food.

Pesticide residue monitoring is the only tool to control the quantity of pesticides on food. For the past few decades regulatory authorities in many countries have been setting up monitoring systems for the agricultural products and the environment. The surveillance focuses on the proper use of pesticides in terms of

* Corresponding author. Tel.: +86 10 82106298; fax: +86 10 82106551.
E-mail address: qyzcaas@yahoo.cn (Y. Qian).

0956-7135/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodcont.2011.01.007

authorization and registration (application rates and pre-harvested intervals), and on compliance with maximum residue limits (MRLs). Pesticide residue monitoring is also recognized as a significant aspect of initiatives to reduce potential hazards to human health (Blasco, Font, Mañes, & Picó, 2005; Dogheim, El-Marsafy, Salama, Gadalla, & Nabil, 2002; Fernández-Alba, Valverde, Aguera, & Contreras, 2001). MRLs encourage food safety by restricting the concentration of a residue permitted on a commodity, and by limiting the type of commodity on which it is allowed (Blasco, Font, & Picó, 2006; European Communities, 2005; FAO/UNEP/WHO, 1991; FDA, 2005). The establishment of MRLs is based on good agricultural practices (GAP) data on food derived from commodities. MRLs are not toxicological limits, but they must be toxicologically acceptable. Exceeded MRLs are strong indicators of violations of GAP (Nasreddine & Parent-Massin, 2002). These regulatory monitoring programs are mainly conducted by official laboratories. Presence of pesticide residues were found in a number of agricultural commodities at diverse geographical locations (EFSA, 2010; European Commission, 2001; FAO/UNEP/WHO, 1991; FDA, 2005; JMPR, 1999; PRC, 2009; The Netherlands Food Inspection Service, 2002).

Fruits and vegetables have been given a lot of attention in monitoring programs since most of them are eaten raw, it is expected that they contain higher pesticide residue levels compared to other food groups of plant origin. According to the Pesticide Residues Committee in the UK, consumers are encouraged to eat at least five portions of fruits and vegetables daily. Xiamen is an important fruits and vegetables exporting area in south China. Therefore, assessing the risk of pesticide residues in these commodities intended for human consumption is necessary. The aim of the present study is to analyze the presence of 22 pesticides commonly used on fruits and vegetables and to check their compliance with existing regulations. The results of the monitoring program in combination with food consumption data were taken into consideration to evaluate whether the estimated daily intake (EDI) of pesticides through the fruits and vegetables consumed by the local inhabitants is a cause of toxicological concern according to the recommended dose by the FAO/WHO. The results can be used when designing future control programs for this region and taking preventive actions to minimize human health risks.

2. Materials and methods

2.1. Sample collection and reagents

A total of 3009 samples of fruits and vegetables were collected from October 2006 to March 2009. The samples were collected during the appropriate season at randomly selected wholesalers or large supermarkets from each of the 5 districts of Xiamen city. The sampling was performed by authorized personnel from the food control authorities in the districts involved. Samples were taken among commodities with known possibilities for high frequencies of pesticide residues from the previous years or commodities with high consumption rate (WHO/GEMS/FOODS, 2006a). The fresh fruit samples analyzed in this study included apple, grape, orange, peach, and pear while the fresh vegetable samples included cabbage, Chinese cabbage, spinach, legumes, radish, cucumber, leaf mustard, capsicum, eggplant, broccoli, pakchoi cabbage, lettuce, celery, cauliflower and tomato.

The sampling was done according to guideline in China (SAC, 2008) on sampling for official control of pesticide residues. Samples were taken at various places distributed through the lot (weight of lot is about 50 kg). The sample size was at least one kg for small- and medium-sized fresh products and included ten units such as apples. The minimum weight for large sample sizes was 2 kg (for example broccoli and cabbage), where the unit was generally more than 250 g (Codex Alimentarius, 2000). Samples were immediately wrapped in aluminum foil, placed in an ice-chest kept at 4 °C and sent to the laboratory until the extraction was done.

Pesticide-grade acetonitrile, methanol, ethyl acetate, and hydrous sodium sulfate were obtained from Merck (Darmstadt, Germany). Pesticide standards of purity 99.0–99.9% were purchased from the Institute of Food Safety, the Ministry of Health of China in sealed vials. Glassware used was free from residue contamination. The individual stock standard solutions of each pesticide were prepared by dissolving 100 mg of each compound in 100 ml methanol. A mixed standard working solutions at various concentrations were daily prepared by appropriate dilution of aliquots of the stock solution in methanol and stored at 4 °C in a refrigerator.

2.2. Analytical procedure

Gas chromatography is the technique most widely used in pesticide analysis because of its high resolution capacity and the availability of selective detectors (Fernández, Pico, & Manes, 2001). In laboratory practice it serves as a screening method for over 300 pesticides. Gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM) was chosen because of its capability for sensitive and specific detection (Sannino, Mambriani, Bandini, & Bolzoni, 1996). GC–MS has been used in confirmation studies of pesticide residues in fruits and vegetables (Colume, Cardenas, Gallego, & Valcarcel, 2001; Fernández-Alba, Valverde, Aguera, & Contreras, 1994; Gelsomino, Petrovicova, Tiburtini, Magnani, & Felici, 1997). Confirmatory analysis was needed due to the large probability of false positive results obtained by GC-ECD (Gelsomino et al., 1997).

A portion of sample (200 g) was chopped and homogenized for 3 min at high speed. Twenty grams of the homogenized sample was mixed with 100 ml ethyl acetate and 75 g anhydrous sodium sulfate, and the mixture was blended using a stainless steel-armed blender for 5 min. The resulting mixture was filtered through 20 g anhydrous sodium sulfate. The solid residue was washed with 50 ml ethyl acetate and the organic extract was concentrated to less than 10 ml on a vacuum rotary evaporator using a water bath at 45 °C and 250 mbar. Then it was passed to a conical tube (15 ml) and evaporated to dryness under a stream of nitrogen gas. Finally, the extract was reconstituted to 10 ml with ethyl acetate and 2 ml were analyzed by GC.

Samples, thus obtained, were injected (1 μl) and analyzed for the presence of pesticides by gas chromatography (Agilent HP 6890 N) with selective electron capture detector (ECD) that allowed the detection of contaminants even at trace level concentrations.

Compounds were separated on a DB-1701 capillary column of 30 m, 0.25 mm I.D. and 0.25 μm film thickness. Super-purified nitrogen was used as the carrier gas. Injector temperature was set at 250 °C. Oven temperature was initially set at 90 °C and held for 2 min, then programmed to 250 °C at 8 °C min^{-1} and then held for 12 min. Detector temperature was set at 240 °C. The peak area was compared to that of the calibration standards to determine the residue quantitatively. Any detected residues were confirmed using mass spectrometry to prevent any misinterpretation of results. Detection limits (DL) of the method for each of the pesticides were 0.01 mg kg^{-1}, which were found by determining the lowest concentrations of the residues in each of the matrices that could be reproducibly measured at the operating conditions of the GC using a signal-to-noise ratio of 3. The spectra were obtained at an ionizing energy of 70 eV in the selected ion-monitoring (SIM) mode.

To test the quality of the method during each batch, 10 g samples in which no pesticides had been detected previously were spiked by the addition of 0.1 ml acetonitrile solution of pesticides at

10.0 mg kg^{-1} of each compound. The samples were prepared for analysis according to the procedure described above. Each batch consisted of 30 unit extracts. Mean recoveries of the extraction procedure for all samples ranged from 80 to 120%.

2.3. Calculation of the average content of pesticides

The equation used to calculate the average content of a pesticide in a particular commodity was (Poulsen, Andersen, Petersen, & Hartkopp, 2005):

$$C_{p,f} = \frac{C_{avg,pos,p,f} \times N_{pos,p,f}}{N_{p,f}} \quad (1)$$

where $C_{p,f}$ is the average content (mg kg^{-1}) of pesticide p in commodity f; $C_{avg,pos,p,f}$ is the average content (mg kg^{-1}) of pesticide p in commodity f with detected residues; $n_{pos,p,f}$ is the number of samples with detected residues; and $N_{p,f}$ is the number of commodities analyzed for the pesticide.

In some cases the average content can be calculated with compensation for undetected residues below the detection limit:

$$C_{p,f} = \frac{C_{avg,pos,p,f} \times n_{pos,p,f} + 0.5 \times DL \times \left(N_{p,f} - n_{pos,p,f}\right)}{N_{p,f}} \quad (2)$$

2.4. Calculation of pesticide residue intakes

Health risk estimations were done based on an integration of pesticide residue analysis data (obtained from the present study for Xiamen city) and food consumption assumptions, which aim at representing the actual residue levels in food consumed by the local population, with a body weight of 60 kg. Food consumption data was derived from WHO/Global Environment Monitoring System–Food Contamination Monitoring and Assessment Program average consumption cluster G diets (WHO/GEMS/FOODS, 2006a). The estimated daily intake (EDI) of pesticide residues for each combination of pesticide and commodity was calculated as follows:

Table 1
Frequency of samples with and without detected pesticide residues, and samples containing residues above MRL for fruits and vegetables collected from Xiamen, China.

Commodity	No. of samples analyzed	No. of samples without detectable residues (%)	No. of samples ≤ MRL (%)	No. of samples > MRL (%)
Apple	41	30 (73.2%)	11 (26.8%)	0 (0%)
Broccoli	46	29 (63.0%)	10 (21.7%)	7 (15.2%)
Cabbage	261	197 (75.5%)	33 (12.6%)	31 (11.9%)
Capsicum	189	122 (64.6%)	50 (26.5%)	17 (9.0%)
Cauliflower	171	142 (83.0%)	16 (9.4%)	13 (7.6%)
Celery	174	95 (54.6%)	42 (24.1%)	37 (21.3%)
Chinese cabbage	281	185 (65.8%)	65 (23.1%)	31 (11.0%)
Cucumber	258	204 (79.1%)	44 (17.1%)	10 (3.9%)
Eggplant	194	122 (62.9%)	55 (28.4%)	17 (8.8%)
Grape	30	21 (70.0%)	5 (16.7%)	4 (13.3%)
Leaf mustard	99	45 (45.5%)	37 (37.4%)	17 (17.2%)
Legumes	354	148 (41.8%)	139 (39.3%)	67 (18.9%)
Lettuce	147	95 (64.6%)	41 (27.9%)	11 (7.5%)
Orange	13	13 (100.0%)	0 (0%)	0 (0%)
Pakchoi cabbage	309	129 (41.7%)	127 (41.1%)	53 (17.2%)
Peach	28	25 (89.3%)	2 (7.1%)	1 (3.6%)
Pear	23	17 (73.9%)	6 (26.1%)	0 (0%)
Radish	105	80 (76.2%)	15 (14.3%)	10 (9.5%)
Spinach	55	37 (67.3%)	15 (27.3%)	3 (5.5%)
Tomato	231	138 (59.7%)	69 (29.9%)	24 (10.4%)
Total	3009	1874 (62.3%)	782 (26.0%)	353 (11.7%)

Table 2
Pesticides detected in fruits and vegetables from Xiamen, China.

Pesticides	Mean value (mg kg^{-1})	Range (min–max)	No. of detectable samples	No. of samples > MRL
Acephate	0.013	<DL[a]–4.082	45 (1.5%)	6 (0.2%)
Bifenthrin	0.001	<DL–0.138	10 (0.3%)	0 (0.0%)
Chlorothalonil	0.003	<DL–1.190	84 (2.8%)	0 (0.0%)
Chlorpyrifos	0.013	<DL–2.545	219 (7.3%)	47 (1.6%)
Cyfluthrin	0.003	<DL–0.767	124 (4.1%)	0 (0.0%)
Cyhalothrin	0.004	<DL–0.363	62 (2.1%)	2 (0.1%)
Cypermethrin	0.056	<DL–13.92	563 (18.7%)	23 (0.8%)
Deltamethrin	0.001	<DL–0.215	7 (0.2%)	0 (0.0%)
Dichlorvos	0.003	<DL–1.515	49 (1.6%)	4 (0.1%)
Dimethoate	0.003	<DL–4.210	25 (0.8%)	1 (0.0%)
Fenitrothion	0.002	<DL–0.651	4 (0.1%)	1 (0.0%)
Fenpropathrin	0.003	<DL–0.697	85 (2.8%)	2 (0.1%)
Fenvalerate	0.004	<DL–2.361	58 (1.9%)	2 (0.1%)
Isocarbophos	0.005	<DL–0.984	9 (0.3%)	0 (0.0%)
Methamidophos	0.034	<DL–9.885	205 (6.8%)	166 (5.5%)
Omethoate	0.022	<DL–16.132	76 (2.5%)	76 (2.5%)
Phorate	0.000	<DL–0.405	7 (0.2%)	0 (0.0%)
Parathion-methyl	0.001	<DL–0.250	25 (0.8%)	0 (0.0%)
Parathion	0.002	<DL–1.395	23 (0.8%)	23 (0.8%)
Permethrin	0.000	<DL–0.012	1 (0.0%)	0 (0.0%)
Triadimefon	0.002	<DL–0.900	96 (3.2%)	0 (0.0%)
Triazophos	0.005	<DL–0.792	6 (0.2%)	0 (0.0%)

[a] Detection limit.

$$EDI_{p,f} = C_{p,f} \times K_f \quad (3)$$

where $EDI_{p,f}$ is the estimated daily intake (μg kg^{-1} bw day^{-1}) for each combination of pesticide p and commodity f; $C_{p,f}$ is the average content of that pesticide (mg kg^{-1}) in a particular commodity; and K_f is the average consumption rate of that commodity (g^{-1} bw day^{-1}). The individual $EDI_{p,f}$ can be summed for commodities, pesticides and for combinations of pesticides and commodities. The long-term risk assessments of the intakes compared to the pesticide toxicological data were performed by calculating the hazard quotient (HQ), by dividing the estimated daily intake with the relevant acceptable daily intake (ADI) (EFSA, 2007).

$$HQ = \frac{EDI}{ADI} \quad (4)$$

The HQ was calculated both for pesticides and commodities. The HQs are summed up to give a hazard index (HI) (EFSA, 2007):

$$HI = \sum_{n=1}^{i} HQ_n \quad (5)$$

The consumer is considered to be adequately protected if the HI of a pesticide residue does not exceed unity. If HI exceeds a value of

Table 3
Number of samples with multiple pesticide residues for each commodity.

Commodity	No. of residues in one sample				Commodity	No. of residues in one sample			
	1	2	3	4		1	2	3	4
Apple	10	1	–	–	Grape	6	2	–	1
Broccoli	12	4	–	–	Leaf mustard	31	14	6	3
Cabbage	46	15	2	1	Lettuce	30	13	9	–
Capsicum	45	13	8	1	Orange	–	–	–	–
Cauliflower	21	3	5	–	Pakchoi cabbage	94	58	23	5
Celery	47	21	8	3	Peach	3	–	–	–
Chinese cabbage	60	23	10	3	Pear	3	1	1	1
Cucumber	45	9	–	–	Radish	16	4	5	–
Eggplant	58	11	3	–	Spinach	12	5	1	–
Legumes	95	66	27	18	Tomato	60	20	8	5

Table 4
Mean levels of pesticide residues in all commodities.

Commodity/Pesticide	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
Acephate	0.0008	0	0.022	0.035	0.028	0.0001	0.003	0.0036	0.0027	0.029	0.0002	0.0009	0	0.029	0.0013	0	0	0	0	0
Bifenthrin	0	0	0.0002	0	0.0007	0	0	0.0003	0.006	0.0003	0.0005	0	0	0.0023	0	0	0	0	0	0
Chlorothalonil	0.0001	0.0017	0.0009	0.002	0.014	0.0011	0	0.0019	0.0003	0.01	0.0017	0.0001	0	0.0009	0.0059	0.0012	0	0	0.0001	0
Chlorpyrifos	0.0175	0.0077	0.02	0.007	0.0038	0.0027	0.018	0.0019	0.031	0.0052	0.012	0.0004	0.061	0.032	0.009	0.0011	0.0007	0	0.0038	0.0017
Cyhalothrin	0.0061	0.042	0.0034	0	0.0019	0	0.0001	0.0006	0.024	0.0022	0.0005	0.0003	0	0.017	0	0	0	0	0.0033	0
Cyfluthrin	0.0005	0.0003	0.0052	0.0004	0.0016	0.0025	0.0009	0.0003	0.0049	0.002	0.001	0.0004	0.0019	0.015	0.0025	0	0	0	0.0003	0.0006
Cypermethrin	0.074	0.156	0.055	0.017	0.025	0.023	0.0018	0.005	0.148	0.057	0.027	0.012	0.0018	0.22	0.049	0.0041	0.0002	0	0.0078	0.0057
Deltamethrin	0	0.0007	0	0	0.0028	0	0	0.0004	0.007	0	0	0	0	0	0.007	0.0015	0	0	0	0.0001
Dichlorvos	0.0022	0.0007	0.0034	0.00173	0.012	0.013	0.0005	0	0.0016	0.0034	0.0015	0.001	0.0059	0.0022	0.0001	0	0	0	0	0.0156
Dimethoate	0.0019	0	0.00025	0.0049	0	0.0026	0	0.0007	0	0.0051	0.001	0.0002	0.0009	0	0.033	0	0	0	0	0
Fenpropathrin	0.0041	0.001	0.0058	0.002	0.0025	0.0024	0.0001	0.0002	0.0025	0.0065	0.0034	0.0043	0.0004	0.006	0.004	0.001	0	0	0.0001	0
Fenitrothion	0	0	0	0	0	0	0	0	0.056	0	0	0.0021	0	0	0	0	0	0	0	0
Fenvalerate	0.0004	0.0006	0.0144	0	0.0008	0	0.0008	0.0001	0.0004	0	0.0019	0.0008	0	0.0016	0.019	0.0005	0	0	0.0017	0.0078
Isocarbophos	0.0008	0	0.03	0	0.0003	0	0	0.0003	0.03	0	0	0	0	0	0	0	0	0	0	0
Methamidophos	0.0051	0.048	0.09	0.027	0.03	0	0.008	0.0055	0.05	0.076	0.06	0.029	0.008	0.0145	0.054	0	0	0	0	0.032
Omethoate	0.005	0	0.009	0.006	0.001	0.313	0.036	0.0005	0	0.0009	0.0015	0.0012	0.27	0.0011	0.047	0	0.002	0	0	0.0042
Parathion	0.0004	0	0.0038	0	0.0002	0	0	0	0.008	0	0.0002	0.0014	0.003	0.008	0.002	0	0	0	0	0
Parathion-methyl	0.0011	0	0.0017	0.0005	0.0002	0.0002	0	0	0	0	0.0006	0.0002	0.0008	0.0009	0.001	0	0	0	0	0
Permethrin	0	0	0	0	0	0	0	0	0.0015	0	0	0	0	0	0	0	0	0	0	0
Phorate	0	0	0	0	0	0.0002	0	0	0	0	0	0	0	0	0.005	0	0	0	0	0
Triadimefon	0.0034	0.0003	0.0019	0.0007	0.0016	0.002	0.0006	0.0007	0.005	0.0011	0.0006	0.0007	0.0038	0.0085	0.005	0.0001	0	0	0.0001	0
Triazophos	0	0	0.033	0	0	0	0	0	0	0	0	0	0	0.0035	0	0	0	0	0	0

A: Chinese cabbage, B: Spinach, C: Legumes, D: Cabbage, E: Tomato, F: Radish, G: Cauliflower, H: Cucumber, I: Leaf mustard, J: Lettuce, K: Eggplant, M: Broccoli, N: Pakchoi cabbage, O: Celery, P: Apple, Q: Peach, R: Orange, S: Pear, T: Grape.

Table 5
Estimated daily intake (EDI) and risk assessment for each commodity.

Commodity	EDI [a], μg kg^{-1} bw day^{-1}	HQ (%)	Commodity	EDI, μg kg^{-1} bw day^{-1}	HQ (%)
Legumes	9.80E-02	2.61	Lettuce	8.00E-03	0.11
Radish	3.33E-02	1.49	Chinese cabbage	7.00E-03	0.07
Broccoli	1.91E-02	0.78	Grape	3.20E-03	0.07
Cabbage	4.10E-02	0.62	Cucumber	2.90E-03	0.04
Tomato	4.95E-02	0.59	Apple	3.30E-03	0.02
Spinach	4.06E-02	0.46	Pear	1.60E-03	0.01
Eggplant	1.84E-02	0.33	Peach	3.00E-04	0.01
Leaf mustard	2.15E-02	0.30	Celery	4.00E-04	0.01
Capsicum	1.65E-02	0.29	Orange	0	0
Pakchoi cabbage	2.06E-02	0.17	Total EDI	0.389 μg kg^{-1} bw day^{-1}	
Cauliflower	3.70E-03	0.12	Hazard index (HI)	8.12%	

[a] EDI of each commodity was calculated as the sum of the EDI for all pesticides detected in that commodity.

1, this could indicate an unacceptable health risk. This method gives an indication of which commodities that contribute most to the hazard. Together with the HQ for the individual pesticides, an indication is thereby given as to which pesticides and commodities it would be the most appropriate to reduce the intake of pesticide residues (EFSA, 2007; Poulsen et al., 2005).

3. Results and discussion

3.1. Evaluation by commodity

Table 1 gives an overview of the data obtained after the analysis of 3009 samples. With regard to all twenty commodities investigated, in 1874 (62.3%) no pesticide residues were detected. 782 (26.0%) analyzed samples contained pesticide residues at or below MRLs laid down by the Standardization Administration of China (SAC, 2005). 353 samples (11.7%) contained pesticide residues above MRLs in terms of commodity groups, MRL values were exceeded most often in pakchoi cabbages, in which 17.2% of the samples above MRLs. All samples of oranges were residue-free. The occurrence of pesticide residues in fruits and vegetables and the total number of commodities containing residues above MRLs are shown in Table 1.

3.2. Evaluation by pesticide

In this monitoring program, pesticide residues exceeding the MRLs were found for 12 different pesticides. Residues of methamidophos were found most often exceeding the Chinese MRLs (5.5% of the samples); the majority of these samples were legumes.

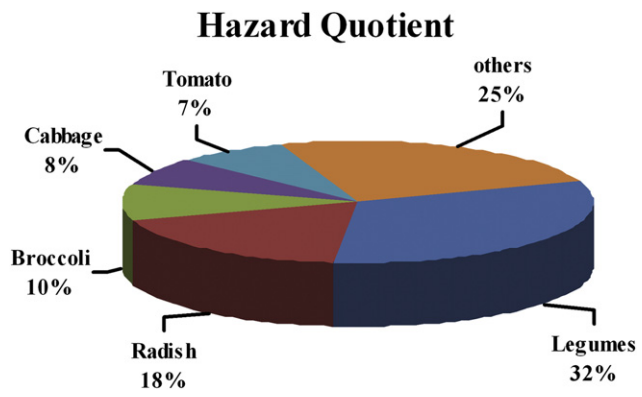

Fig. 1. The commodities that contribute most to the hazard index (HI).

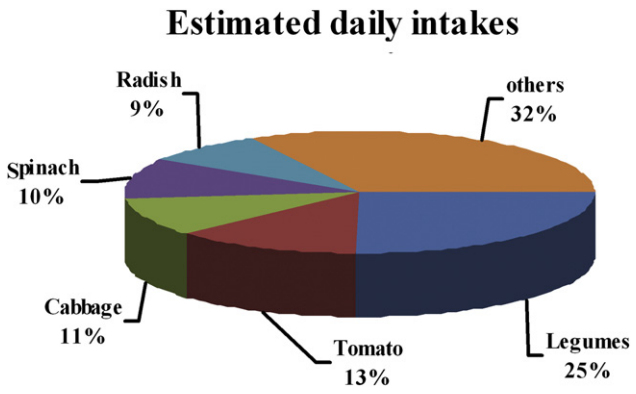

Fig. 2. The commodities that contribute most to the total pesticide residue intake (mg kg^{-1} bw day^{-1}).

Exceedance of the MRLs for omethoate and chlorpyrifos was found in 2.5% and 1.6%, respectively, of samples (distributed among several commodities). The mean levels and ranges of 22 pesticide residues in fruits and vegetables are presented in Table 2. Residues were found most frequently of cypermethrin, followed by chlorpyrifos, methamidophos, cyfluthrin, triadimefon, fenpropathrin, chlorothalonil, omethoate, cyhalothrin, fenvalerate, dichlorvos, acephate, parathion-methyl, dimethoate, parathion, bifenthrin, isocarbophos, phorate, deltamethrin, triazophos, fenitrothion, and permethrin.

Cypermethrin was found most frequently in 18.7% of the samples analyzed in the concentration range of lower than the detection limit (DL) to 13.92 mg kg^{-1}, most were from pakchoi cabbage. Chlorpyrifos had measurable residues in 7.3% of the samples mainly in Chinese cabbage, at concentrations from <DL to 2.545 mg kg^{-1}. Methamidophos, cyfluthrin, triadimefon, fenpropathrin, chlorothalonil, omethoate, cyhalothrin, fenvalerate, and dichlorvos were each found in 4.1–1.6% of samples. For the remaining 10 pesticides, the frequency of samples with detected residues corresponded to less than 1.5%. Fenitrothion was detected in four of the samples, and permethrin was only detected in one of the samples.

Since the use of methamidophos is no longer authorized in China, it is recommended to check the possible misuse of the product containing methamidophos at national level. The use of omethoate has not been authorized in China since 2007, while the use of dimethoate is authorized. Nevertheless, residues of omethoate in food commodities may occur as omethoate is a plant metabolite of dimethoate. Chlorpyrifos is a non-systemic insecticide used to control different pests in soil or on foliage in fruits and other crops and is likely commonly used in many countries. The rates of exceedance for the remaining pesticides were all below 1%.

A more detailed overview of mean levels of pesticide residues in all commodities is illustrated in Table 4.

The proportion of samples in which pesticide residues were detected in this study was higher than the proportion of similar samples with pesticide residues in the most recent monitoring programs conducted in Europe (EFSA, 2010; PRC, 2009). The number of samples exceeding the MRLs in this study (11.7%) is also higher than that of in recent European monitoring programs.

There are more than 300 registered pesticides in China, but only one-third have MRLs. The pesticides included in the analytical scope were prioritized in relation to high frequency of application and high toxicity. A positive residue finding or residues exceeding MRLs in previous monitoring programs is also a criterion for including the pesticide. It should also be pointed out that most of the pesticides registered in fruits and vegetables in China could not be measured in this study due to budget constraints. However, most of the pesticides identified as those that are commonly in use were included.

3.3. The co-occurrence of pesticide residues

The co-occurrence of pesticide residues is listed in detail in Table 3. Residues of two or more pesticides were found in 440 (14.6%) analyzed fruits and vegetables samples. A total of 283 (9.4%) samples of the commodities studied contained two residues of pesticides and 116 (3.9%) samples were contaminated with three pesticide residues, and 41 (1.4%) samples contained more than four pesticide residues.

3.4. Intake and risk assessment based on commodities

The contributions of each commodity to the total estimated daily intakes (EDI) as well as the HQs have been calculated, as are shown in Table 5. The HQ ranged from 0.01% for pear, peach, and celery, to 2.61% for legumes. Since no pesticide residues were detected in oranges, the contribution of this particular commodity to the total intake was calculated as zero. The results are sorted by HQ. In Fig. 1, the 5 commodities that contribute most to the HI are shown together with the contribution from the rest of the commodities called 'others'. In Fig. 2, the same is shown for the EDI. As it can be seen, in these figures it is not entirely the same commodities that contribute most to the HI and to the EDI, as only legumes, radishes, cabbages and tomatoes are mentioned in both cases. In any case, legumes contribute much more than any other commodity to both intake and HI. The HQs of these commodities are much lower than one and, therefore, they are unlikely to reach exposures above acceptable levels.

Table 6
Estimated daily intake (EDI) of a pesticide from all commodities and risk assessment.

Pesticide	ADI (Source), μg kg^{-1} bw day^{-1}	EDI, μg kg^{-1} bw day^{-1}	HQ (%)	Pesticide	ADI (Source), μg kg^{-1} bw day^{-1}	EDI, μg kg^{-1} bw day^{-1}	HQ (%)
Omethoate	2 (JMPR, 1996)	5.23E-02	2.61	Parathion-methyl	3 (JMPR, 1995)	1.16E-03	0.04
Methamidophos	4 (JMPR, 2002)	8.78E-02	2.20	Fenvalerate	20 (JMPR, 1986)	6.58E-03	0.03
Triazophos	1 (JMPR, 2002)	1.10E-02	1.10	Chlorothalonil	30 (JMPR, 1994)	8.37E-03	0.03
Cypermethrin	20 (JECFA, 2006)	9.96E-02	0.50	Fenpropathrin	30 (JMPR, 1993)	7.36E-03	0.02
Isocarbophos	3 (Australia, 1995)	1.17E-02	0.39	Deltamethrin	10 (JMPR, 2000)	2.19E-03	0.02
Dichlorvos	4 (JMPR, 1993)	9.89E-03	0.25	Triadimefon	30 (JMPR, 2004)	3.46E-03	0.01
Chlorpyrifos	10 (JMPR, 2004)	2.43E-02	0.24	Cyfluthrin	40 (JMPR, 2006)	4.52E-03	0.01
Cyhalothrin	5 (JECFA, 2004)	1.18E-02	0.24	Bifenthrin	20 (JMPR, 1992)	9.34E-04	0.00
Dimethoate	2 (JMPR, 2003)	2.97E-03	0.15	Phorate	0.7 (JMPR, 2004)	2.67E-05	0.00
Acephate	30 (JMPR, 2005)	3.59E-02	0.12	Permethrin	50 (JMPR, 2002)	8.50E-05	0.00
Fenitrothion	5 (JMPR, 2000)	3.88E-03	0.08	Total EDI	0.389 μg kg^{-1} bw day^{-1}		
Parathion	4 (JMPR, 1995)	2.91E-03	0.07	Hazard index (HI)	8.12%		

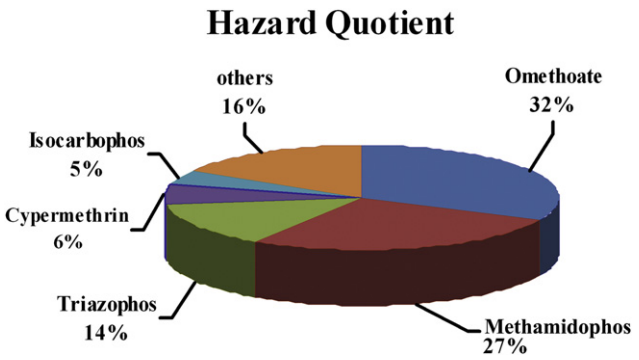

Fig. 3. The pesticides that contribute most to the hazard index (HI).

3.5. Intake and risk assessment based on pesticides

The list of the ADI values used for the assessment of the chronic exposure is reported in Table 6. The contribution of each pesticide in the monitoring program to the total EDI as well as the HI has been calculated, as shown in Table 6. The results are sorted by HQ. The estimated exposures range from 0.1% of the ADI for cyfluthrin to 2.61% of the ADI for omethoate. For bifenthrin, phorate, and permethrin, in which no positive findings were reported among all the samples, therefore the contribution of these three pesticides to the total intake was calculated as zero. As can be seen from Table 6, there is a big difference in ordering the pesticides according to HQ and EDI due to the differences in their ADI values. In Fig. 3, the 5 pesticides that contributed most to the HI are shown together with the contribution from the rest of the commodities called 'others', and in Fig. 4 the same is shown for EDI. Methamidophos, cypermethrin and omethoate are the pesticides among the 5 most important contributors in both instances. The HI value shows that all the intakes of pesticide residues remains clearly below the safe limit.

It should be emphasized that dietary pesticide intakes estimated in this study considered only exposures from fruits and vegetables and did not include other food products such as grains, dairy, fish, and meats. As such, estimates are not considered as total dietary exposure to the pesticides, nor do we consider drinking water, residential, or occupational exposures. Therefore, it is an underestimation of the total exposure of pesticides studied. It should also be noted that not all registered pesticides were measured in this study. On the other hand, processing factors were ignored, whereas fruits and vegetables are often peeled, cooked or boiled before consumption, resulting in an overestimation of the actual exposure

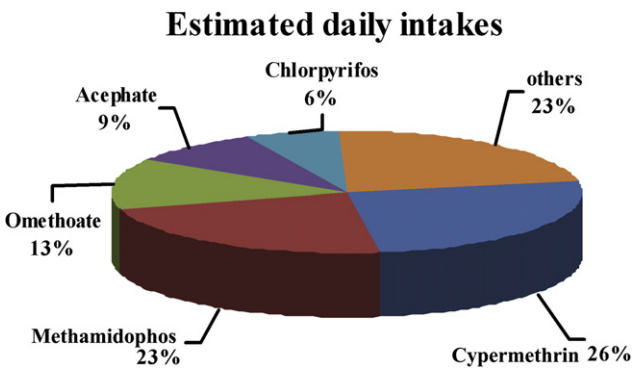

Fig. 4. The pesticides that contribute most to the total pesticide residue intake (mg kg^{-1} bw day^{-1}).

Table 7
Effect of limiting the correction factor on total intake for all pesticide–commodity combination groups.

	EDI, μg kg^{-1} bw day^{-1}	Hazard index (HI), %
No correction for undetected residues	0.389	8.12
Correction for undetected residues (50% DL)	0.674	18.14
Correction for undetected residues (50% DL), limiting the correction factor to 25	0.533	11.65

to pesticide residues. Additionally, the effect of pesticides on more vulnerable groups such as children and pregnant women could all affect these calculations.

Although the dietary intakes estimated from all pesticide levels detected in fruits and vegetables do not represent a health risk to local consumers, the intake estimated from the highest pesticide residues level is uncomfortably near or exceeds the short-term health standards. The highest detected cypermethrin level (13.92 mg/kg in a sample of pakchoi cabbage) resulted in an intake which is at 400% of the ARfD value of 40 μg kg^{-1} bw day^{-1} when using WHO/GEMS high consumption diets (WHO/GEMS/FOODS, 2006b).

3.6. Intake corrections

In many circumstances no detectable amount of pesticide residues is found but this does not necessarily mean that the content is true zero. The content may just be too low for detection with the currently available methods. Therefore a calculation has been performed where all the undetected residues were treated at zero and another where they have been set at one-half of the detection limit. In some cases, it was found that a very low incidence of positive samples has an excessive impact on the result from the model, when the pesticide content in samples without detected residues is estimated to be one-half of the detection limit (Poulsen et al., 2005). For this reason, there is a need to modify the calculation in order to minimize an over-correction for undetected residues.

The correction factor can be defined as the intake with correction divided by intake without correction. Although arguments for using a higher or a lower cut-off level could be found, a maximum correction factor of 25 has been chosen as a best estimate, eliminating an over-correction of the calculated residue content in samples without detected residue levels (Poulsen et al., 2005). Overcompensation could be the case for some pesticide/commodity combinations in the present study when using an unmodified 50% DL-correction (e.g., dichlorvos was found in 1 of 174 samples of celery), the low frequency of detection results in an intake of 0.0085 μg kg^{-1} bw day^{-1}. Without a correction for residue levels in samples, the intake calculates to 0.0002 μg kg^{-1} bw day^{-1}. The correction factor is 50.

The majority of the pesticide/commodity combinations with detected residues had correction factors below 25. From Table 7, it can be seen that limiting the correction factor to 25 for all combinations of pesticide/commodity will reduce the calculated intake by 0.141 μg kg^{-1} bw day^{-1} to 0.533 μg kg^{-1} bw day^{-1}.

4. Conclusions

The present study shows that despite the high occurrence rate of pesticide residues in fruits and vegetables from Xiamen city from 2006 to 2009, the contamination level could not be considered a serious public health problem. To prevent exposure to pesticides, it is necessary to reduce and control the use of pesticides in these commodities by enforcement activities. It also calls for improved

residue control at production, tighter regulation of pesticide spraying and also tighter regulation in the sale of pesticides as well as for education of farmers and the implementation of integrated pest management methods. Nevertheless, monitoring programs are increasingly important and essential to ensure minimal pesticide residue levels in food.

Acknowledgements

The study was supported by the National Department Public Benefit Research Foundation of China (Grant Number 200903054).

References

Amoah, P., Drechsel, P., Abaidoo, R. C., & Ntow, W. J. (2006). Pesticide and pathogen contamination of vegetables in Ghana's urban markets. *Archives of Environmental Contamination and Toxicology, 50*, 1–6.

Berrada, H., Fernández, M., Ruiz, M. J., Moltó, J. C., Mañes, J., & Font, G. (2010). Surveillance of pesticide residues in fruits from Valencia during twenty months (2004/05). *Food Control, 21*, 36–44.

Bhanti, M., Shukla, G., & Taneja, A. (2004). Contamination levels of organochlorine pesticides and farmers' knowledge, perception, practices in rural India: a case study. *Bulletin of Environmental Contamination and Toxicology, 73*, 787–793.

Bhanti, M., & Taneja, A. (2007). Contamination of vegetables of different seasons with organophosphorous pesticides and related health risk assessment in northern India. *Chemosphere, 69*, 63–68.

Blasco, C., Font, G., Mañes, J., & Picó, Y. (2005). Screening and evaluation of fruit samples for four pesticide residues. *Journal of AOAC International, 88*, 847–853.

Blasco, C., Font, G., & Picó, Y. (2006). Evaluation of 10 pesticide residues in oranges and tangerines from Valencia (Spain). *Food Control, 17*, 841–846.

Calvert, G. M., Sanderson, W. T., Barnett, M., Blondell, J. M., & Melher, L. (2001). Surveillance of pesticide-related illness and injury in humans. In R. Krieger, J. Doull, D. Ecobichon, E. Hodgson, L. Reiter, & J. Ross (Eds.), *Handbook of pesticide toxicology* (2nd ed.). (pp. 603–641) New York, NY: Academic Press.

Codex Alimentarius. (2000)*Food Standards Programme. Pesticide residues in food. Methods of analysis and sampling, Vol. 2A(1)*. World Health Organization.

Colume, A., Cardenas, S., Gallego, M., & Valcarcel, M. (2001). Multiresidue screening of pesticides in fruits using an automatic solid-phase extraction system. *Journal of Agricultural and Food Chemistry, 49*, 1109–1116.

Darko, G., & Akoto, O. (2008). Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana. *Food and Chemical Toxicology, 46*, 3703–3706.

Dogheim, S. M., El-Marsafy, A. M., Salama, E. Y., Gadalla, S. A., & Nabil, Y. M. (2002). Monitoring of pesticide residues in Egyptian fruits and vegetables during 1997. *Food Additives and Contaminants, 19*, 1015–1027.

European Commission. (2001). *Monitoring of pesticides residues in products of plant origin in the European Union, Norway and Iceland. Report 1999*.

European Communities. (2005). *The European union on-line*. Official Documents. <http://europa.eu.int> (accessed April 2010).

European Food Safety Authority (EFSA). (2007). *Cumulative risk assessment of pesticides to human health: The way forward*.

European Food Safety Authority (EFSA). (2010). 2008 annual report on pesticide residues according to article 32 of regulation (EC) no 396/2005. *EFSA Journal, 8*, 1646. <http://www.efsa.europa.eu> (accessed April 2010).

FAO/UNEP/WHO. (1991). *Food Contamination Monitoring Program, summary of 1986–1988 monitoring data*. Geneva (Switzerland): World Health Organization.

FAO/WHO, 2004. <http://www.codexalimentarius.net> (accessed May 2010).

Fernández, M., Pico, Y., & Manes, J. (2001). Pesticide residues in oranges from Valencia (Spain). *Food Additives and Contaminants, 18*, 615–624.

Fernández-Alba, A. R., Valverde, A., Aguera, A., & Contreras, M. (1994). Gas chromatographic determination of organochlorine and pyrethroid pesticides of horticulture concern. *Journal of Chromatography A, 686*, 263–274.

Food and Drug Administration of United States (USFDA). (2005). *Pesticide program residues monitoring 1993–2003*. <http://vm.cfsan.fda.gov/~dms/pesrpts.html> (accessed April 2010).

Gelsomino, A., Petrovicova, B., Tiburtini, S., Magnani, E., & Felici, M. (1997). Multiresidue analysis of pesticide in fruits and vegetables by gel permeation chromatography followed by gas chromatography with electron-capture and mass spectrometric detection. *Journal of Chromatography A, 782*, 105–122.

JMPR. (1999). *Pesticides residues in food: Report of the 1999 joint FAO/WHO meeting of experts*. Geneva (Switzerland): World Health Organization.

Nasreddine, L., & Parent-Massin, D. (2002). Food contamination by metals and pesticides in the European Union. Should we worry? *Toxicology Letters, 127*, 29–41.

Pesticide Residues Committee (PRC). (2009). *Chemicals Regulation Directorate. Annual report of the Pesticide Residues Committee*. <http://www.pesticides.gov.uk/uploadedfiles/Web_Assets/PRC/PRC_Annual_Report_2008.pdf> (accessed March 2010).

Poulsen, M. E., Andersen, J. H., Petersen, A., & Hartkopp, H. (2005). *Food monitoring, 1998–2003. Part 2: Pesticides*. Søborg, Denmark: Danish Institute for Food and Veterinary Research. <http://www.foedevarestyrelsen.dk/forside.htm> (accessed February 2010).

SAC. (2005). *Maximum residue limits for pesticides in food. GB 2763-2005*. Beijing (China): The Standardization Administration of China.

SAC. (2008). *Fresh fruits and vegetables-sampling. GB/T 8855-2008*. Beijing (China): The Standardization Administration of China.

Sannino, A., Mambriani, P., Bandini, M., & Bolzoni, L. (1996). Multiresidue method for determination of organochlorine insecticides and polychlorinated biphenylcongeners in fatty processed foods. *Journal of AOAC International, 79*, 1434–1446.

Solecki, R., Davies, L., Dellarco, V., Dewhurst, I., Raaij, M. V., & Tritscher, A. (2005). Guidance on setting of acute reference dose (ARfD) for pesticides. *Food and Chemical Toxicology, 43*, 1569–1593.

The Netherlands Food Inspection Service. (2002). *Report of pesticide residue monitoring results of Netherlands for 2001. Concerning Directive 90/642/ECC, 86/362/EEC and recommendation 2001/42/EU*. Amsterdam: Inspectorate of Health Protection, Commodities and Veterinary Public Health Publications.

Waichman, A. A., Eve, E., & Nina, N. C. S. (2007). Do farmers understand the information displayed on pesticide product labels? A key question to reduce pesticides exposure and risk of poisoning in the Brazilian Amazon. *Crop Protection, 26*, 576–583.

WHO/GEMS/FOODS (WHO/Global Environment Monitoring System-Food Contamination Monitoring and Assessment Program). (2006a). *Consumption cluster diets*. <http://www.who.int/foodsafety/chem/gems/en/> (accessed August 2009).

WHO/GEMS/FOODS. (2006b). *Highest reported 97.5th percentile consumption figures (eaters only) for various commodities by the general population and children ages 6 and under*. <http://www.who.int/foodsafety/chem/gems/en/> (accessed September 2009).