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Degradation of Chlorpyrifos and Fipronil in Rice from Farm to Fork and Risk Assessment

ZHANG Cun-zheng[1], ZHANG Xin-ming[4], TIAN Zi-hua[2], HE Dan-jun[3] and LIU Xian-jin[1]

[1] *Institute of Food Safety, Jiangsu Academy of Agricultural Sciences/Key Laboratory of Food Safety Monitoring and Management, Ministry of Agriculture/Key Lab of Food Quality and Safety of Jiangsu Province – State Key Laboratory Breeding Base, Nanjing 210014, P.R. China*

[2] *Nanjing Centre of Inspection and Testing for Agricultural Products, Ministry of Agriculture, Nanjing 210036, P.R.China*

[3] *Nanjing Exit-Entry Inspection and Quarantine Bureau, Nanjing 210003, P.R.China*

[4] *Taicang Centre of Inspection and Testing for Agricultural Products, Taicang 215412, P.R.China*

Abstract

Degradation of pesticide residues (chlorpyrifos and fipronil) in rice from farm to fork and risk assessment for human health were studied to reveal the magnitude of risks faced by different populations of interest, so that appropriate measures can be taken to control the risks, and to refine and update the human health risk assessment data while helping to determine the maximum residue level (MRL) value and harvest interval. Different dosages and treatments were used in field trials for the harvest residue test. Residue levels of postharvest-applied chlorpyrifos and fipronil during storage, exposure to sunlight, washing and boiling processes (boiled rice) were investigated for brown rice. The dietary exposure evaluation model (DEEM) was employed to estimate acute and chronic risks faced by different populations of interest. Percent of reference dose (POR) and margin of exposure (MOE) were calculated. A positive correlation between pesticide residues and the dosage and application frequency of pesticide was found in the field trials. Risk quotients indicate that multiple applications and double dosages of chlorpyrifos increase the risks to the entire population and prolong exposures to toxic concentrations. The concentration of pesticide residues decreased as a function of time, after sunlight exposure, storage, washing, and boiling processes. 91.6 and 96.16% degradations were achieved at the end of the experimental period for fipronil and chlorpyrifos, respectively. The boiling process played an important role in the degradation of these pesticides. The result of risk assessment to human health showed that harvest residues of chlorpyrifos in rice and acute dietary risks of chlopyrifos were of concern. The acute dietary (food only) risk estimated for chlorpyrifos as percent of acute population adjusted dose (aPAD) was frequently over 100%. The risk faced by boys under the age of 14 was higher than that for girls of the same age. For the subpopulation above age 14, the risk reversed. The chronic dietary risk from food alone showed that dietary exposures with fipronil were below the level of concern for the entire population, including children. The risk faced by rural residents was more serious than that for urbanite residents with the most sensitive populations being children and male residents who faced higher acute dietary risk than the other subpopulation groups. The harvest interval was found to be the critical measure to mitigate risk for all populations for safe rice eating. All risk levels decreased to acceptable levels when the harvest interval was extended to 14 d. To address these risks, a number of measures including reduced application rates (should not be doubled at single application), increased retreatment intervals (longer than 7 d) and extended interval of harvest (at least 14 d) will be needed. The MRL for fipronil in rice is recommended to be 0.01 mg kg^{-1} in accordance with Codex (ref).

Key words: rice, risk assessment, pesticide residue, chlorpyrifos, fipronil

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Correspondence ZHANG Cun-zheng, Associate Professor, Tel: +86-25-84390401, Fax: +86-25-84390401, E-mail: zhcz2007@gmail.com

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INTRODUCTION

Rice is the staple food for Chinese people and China is the largest world rice producing and consuming nation. Chinese planting area accounts for about 23% of that of world and output accounts for more than 30%, ranking the first in the world (Zhang 2007). Concerns over rice safety have increased due to the tons of agrichemicals, such as chlopyrifos and fipronil, which are widely used in China as efficient pest control agents. Chlopyrifos has been limited in use by Environmental Protection Agency (EPA) since December 31, 2001 (Adgate *et al*. 2001). Although fipronil has been listed as an environmental hormone suspect by the World Wildlife Fund (WWF), there is no maximum residue level (MRL) for rice in China to date (Chanda and Pope 1996). Risk assessment can provide basic information for agrichemical control while helping to establish MRL limits (Purchase 2000). Several risk assessment models have been reported by Fryer *et al*. (2006), Ferriery *et al*. (2002) and Tennant (1999). Qian *et al*. (2008) reported that the harvest residue of pesticides was much related to the treatment times and dosages of agrichemicals employed at the mid- and late-period of the rice crop. Residue levels of postharvest-applied dichlorvos (DDVP), chlorpyrifos-methyl, malathion, fenitrothion, and bromide during storage and boiling processes (boiled rice and rice noodles) were investigated for unhulled and brown rice by Nakamura *et al*. (1993), which showed that organophosphorus pesticides could be mostly removed by washing with water followed by boiling. Cabras *et al*. (2000) studied the fate of quinoxyfen residues in grapes, wine and their processing products. No effect on alcoholic or malolactic fermentation was observed and the yeasts partially degraded the pesticides. Bacteria did not have any degradative effect on the pesticide and also sun-drying and oven-drying had different degradative effects. Kawahara *et al*. (2007) reported on dietary exposure to organophosphorus pesticides by young children in Tokyo, Japan, and found that chlopyrifos was frequently (11%) presented in their weekly diet. Gao *et al*. (2006) gave a review of the Joint FAO/WHO (Food and Agriculture Organization of the United Nations/World Health Organization) Meeting on Pesticide Residues (JMPR) pesticide residue acute dietary exposure assessment, and suggested that acute dietary risk assessment for high or moderately toxic pesticides should be a component of agrichemical registration process in China. Residues and risk assessment of organochlorine pesticides in oysters of Jinjiang, Guangdong Province, China, were reported by Gan *et al*. (2007), and oyster consumption limits were recommended using acceptable exposure risk indexes (ERI) and carcinogenic risk indexes (CRI). So far, there has been no risk assessment for pesticide residues in rice reported in China. Our study was designed to (1) profile the basic degradation pathways of pesticides in rice from farm to fork after used in paddy situations, (2) provide risk assessment information to estimate the magnitude of risks faced by Chinese people when they consume rice, and (3) help to determine MRL values and refine harvest interval and pesticide application information. Chlorpyrifos and fipronil were chosen as representative pesticides for a case study in Jiangsu Province, China. Both theoretical (MRL) and actual (simulated) levels of pesticide concentration in rice were used in the risk assessment process.

MATERIALS AND METHODS

Materials

Chemicals and reagents Chlorpyrifos and fipronil standards were obtained from the Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA), China, and purity was certified by the supplier to be greater than 99%. Stock solutions of 1 mg mL^{-1} were prepared in acetone and stored at -4°C. Acetone, n-hexane, acetonitrile, ethyl acetate, dichloromethane, and anhydrous sodium sulfate were all analytical grade and obtained from China National Medicines Corporation Ltd.

Instruments and analytical conditions GC (Agilent 6890, USA) equipped with flame photometric detector (FPD) and electron capture detector (μECD); nitrogen evaporator (Organomation-24, USA); cultivation box (Labcoaco515H, USA); centrifuge (Eppendorf5417R, Germany); electronic balance (Ohaus Analytical Plus, USA); blender (IKA T18, Germany); rice cooker; and other glass apparatus. Two capillary columns were used to provide qualitative data. One column was DB-17 (0.1 mm film thickness, 30 m length, 0.53 mm *i.d.*, J&W Scientific, USA) for chlorpyrifos determination by FPD; detector temperature was 200°C, inlet temperature was 220°C, initial oven temperature was 150°C for 2 min, then ramped to 250°C at 8°C min^{-1} and held for 12 min. The second column was HP-5 (0.25 µm film thickness, 30 m length, 0.25 mm *i.d.*, J&W Scientific, USA) for fipronil determination by ECD; inlet temperature was 250°C, initial oven temperature was 120°C for 1 min; the temperature was then increased 20°C min^{-1} to 260°C and held for 8 min. Ultra-pure quality nitrogen was used as carrier gas and injections were carried out in splitless mode using 1 µL injection volumes.

Methods

Field trials Field trials were designed according to the Guideline on Pesticide Residue Trials (NY/T788-2004). The recommend dosage (R.D.) of 750 g (a.i.) ha^{-1} for chlorpyrifos and 30 g (a.i.) ha^{-1} for fipronil and double recommend dosages (D.D.) were employed in paddy conditions of mid- and late-rice planting periods with 2 or 3 treatments of 7 d retreatment intervals. The trial fields were near Nanjing, Jiangsu Province, China, at different locations which were previously investigated to be free of these 2 pesticides. The rice crop planted was Yangmai 6. Sampling was carried out at 7 and 14 d before harvest.

Simulation experiment of pesticides on food processing Rice was mixed with chlorpyrifos and fipronil solutions (0.1 mg mL^{-1}, 0.1 mg mL^{-1}) to approximate the concentration level of field trial samples. After air drying for 2 h without light exposure, the initial concentrations of both pesticides were determined. Sunlight exposure was carried out for 3 d and then samples were stored at 50°C for 2 h (2 mon storage simulation process) according to the methods reported by Liu *et al*. (2002) and Zhang (1998). After that, samples were washed with tap water 3 times (every 5 min), and the extra weight of water added to samples was calculated. Final samples were steamed for 20 min and the pesticide concentrations were determined after each treatment. The dissipation amount for each treatment was calculated and all experiments were performed in triplicate.

Sample extraction 10 g homogenized rice grain samples were extracted with 60 mL acetone and then sonicated for 15 min. After centrifugation, the supernatant was partitioned thrice with 60 mL dichloromethane. The dichloromethane phase was further dried by passing through a 2-cm layer of anhydrous sodium sulphate. The organic solvent was eliminated by nitrogen evaporation and the extract was redissolved in 1 mL acetone for chlopyrifos analysis. For fipronil, 10 g homogenized rice samples were extracted with 60 mL acetonitrile, sonicated for 15 min, and then filtered through a Buchner funnel. The solvent was evaporated and the extract was redissolved in 1 mL 5% toluene/ethyl acetate (v/v). Cleanup was carried out using a neutral alumina column with 0.2 g carbon added to the top. The column was conditioned with 10 mL methanol and 10 mL toluene followed by washing with 50 mL of 5% toluene/ethyl acetate (v/v) . The organic solvent was evaporated and the extract was redissolved in 1 mL ethyl acetate for fipronil analysis (Zhou *et al*. 2001).

Data sources for risk assessment (1) MRLs. The MRLs for chlorpyrifos and fipronil from different countries and organizations are listed in Table 1. The values cited have been marked for theoretical risk assessment, which assumed that all foods (rice only) were treated and contained tolerance level residues. Data from the field trials, calculated using the degradation information from the simulation experiment (through sunlight exposure, storage, washing, and boiling), were used for the actual risk assessment.

(2) Characterization of the populations and consumption information. The body weights of males and females by age were investigated by the General Administration of Sport of China (2005) as listed in Table 2. Rice consumption data were compiled from Health Status of the Chinese People (2004), Chinese Dietary Reference Intakes (2000) (Chinese Nutrition Society 2000), articles published by Yuan *et al*. (2007) and Zhai *et al*. (2005) were consulted, and an investigation involving 500 residents in Nanjing where uncertainty and variability of dietary rice intake was processed according

Table 1 MRLs (mg kg^{-1}) used in the acute and chronic dietary exposure analyses

Agrichemical	China GB 2763-2005	Japan-positive list	Codex	Eu.	USA (EPA)
Chlorpyrifos	0.1 √	0.1	0.5	0.05	–
Fipronil	–	0.01	0.01	0.01	0.04 √

–, there are no established or proposed MRLs for this item; √, this value is used in our case.

Table 2 Characteization of the population and dietary intake of rice

Subpopulation	Age	Body weight (kg)		Dietary intake of rice (g d^{-1})			
				Male		Female	
		Male	Female	Urbanite	Countryside	Urbanite	Countryside
3-6 yr old	3	16.0	15.4	60	78	55	70
	4	17.7	16.9	64	83	57	73
	5	19.7	18.8	70	92	62	79
	6	21.6	20.5	72	94	63	80
	Average	18.8	17.9	66.6	86.6	59.3	75.4
7-13 yr old	7	24.5	23.0	85	101	70	87
	8	27.5	25.7	96	111	78	96
	9	30.4	28.7	102	118	88	102
	10	33.9	32.5	108	128	96	110
	11	37.5	36.9	120	136	108	121
	12	41.7	40.6	128	146	116	130
	13	46.7	44.7	140	158	124	142
	Average	34.6	33.2	111.3	128.3	97.1	112.6
14-17 yr old	14	51.6	47.4	156	175	140	160
	15	55.3	49.4	178	190	170	186
	16	58.0	50.5	205	225	180	205
	17	59.6	51.2	220	250	200	225
	Average	56.1	49.6	189.8	210.0	172.5	194.0
18-adult	18	60.3	51.5	218.0	246.0	196.0	221.0

to the report of Bennett *et al*. (1999). Standard people (18-yr old) were chosen to represent the adult population as shown in Table 2.

(3) Toxicological properties of chlorpyrifos and fipronil. Data source was from Pesticide Database, Pesticide Information Center, USEPA. The population adjusted dose (PAD) was adopted in our case to protect the sensitive subpopulation (USEPA 1997a). The data are presented in Table 3.

Dietary exposure model Dietary ingestion is a significant pathway of human exposure to pesticides. The dietary exposure model is used to evaluate the types (routes and media), magnitude or doses of exposure.

Table 3 Summary of toxicological dose and endpoints of pesticides used in risk assessment

Exposure scenario	Dose used in risk assessment [1)]	Chlorpyrifos	Fipronil
Acute dietary	NOAEL (mg kg^{-1} d)	0.5	2.5
	UF; FQPA SF	100; 10	100; 1
	aRfD (mg kg^{-1} d)	0.005	0.025
	aPAD (mg kg^{-1} d)	0.0005*	0.025
	LOAEL (mg kg^{-1} d)	1.5	7.0
Chronic dietary	NOAEL (mg kg^{-1} d)	0.03	0.019
	UF; FQPA SF	100; 10	100; 1
	cRfD (mg kg^{-1} d)	0.0003	0.0002
	cPAD (mg kg^{-1} d)	0.00003*	0.0002
	LOAEL (mg kg^{-1} d)	0.1	0.059

[1)] NOAEL, no observed adverse effect Level; UF, uncertainty factor; SF, safety factor; PAD, population adjusted dose (includes UF and FQPA safety factor); LOAEL, lowest observed adverse effect level; FQPA SF, food quality protection act safety factor; RfD, reference dose; a, acute; c, chronic.

*, FQPA safety factor was used for population subgroup, such as infants, children and females 13-50 yr old; otherwise for general population.

Where known, time and duration of actual or anticipated exposures and, when appropriate, the number of persons likely to be exposed should be included to predict pesticide residue intake. In our case, food (rice) was set to be the only way by which people were exposed to the target chemicals. Margin of exposure (MOE) and percent of reference dose (POR) were used to estimate the probable incidence of adverse health effects under conditions of food only exposure, including a description of the uncertainties involved (USEPA 1999).

Dietary exposure equations In our case, food (rice) was set to be the only route and media for pesticide residue exposure.

Dietary exposure = Mean × Residue × 10^{-6} (Barraj *et al*. 2000) (1)

Where, dietary exposure, mg kg^{-1} bw^{-1} d^{-1}; mean, rice intake per day of per bodyweight of population, mg kg^{-1} bw^{-1} d^{-1}; residue, concentration of pesticide in rice, mg kg^{-1}.

Risk assessment MOE and POR were adopted to estimate the acute and chronic risks faced by the different populations of interest for which the pesticide of NOEL (no observed adverse effect level, mg kg^{-1} bw^{-1}) $\neq 0$ and Rfd $\neq 0$ are levels of concern for risk assessment as listed in Table 4 (Purchase 2000; Castorina *et al*. 2003). When the results of MOE and POR do not agree, the result of MOE will be the concerned level of risk characterization. In our case, because the Food Quality

Table 4 Level of concern for risk assessment (POR & MOE)

Risk characterization	LOC for MOE [1)]	Percent RfD (or PAD)
Concerned	MOE≤100	POR≥100
Acceptable	MOE>100	POR<100

[1)] LOC, level of concern.

Protection Act safety factor (FQPA, value > 1) was used in the PAD, the result of percent of PAD is more sensitive than POR in order to protect the special population. Generally, a dietary risk estimate that is less than 100% of the acute or chronic PAD does not exceed the risk concerns of EPA. Sometimes 1 000% was used, but in our case, the level of concern was still set to 100% and the serious result was taken into account when the MOE and POR presented different results. The MOE and POR equations are as follows:

$$MOE = NOEL/\text{Dietary exposure} \quad (2)$$

$$POR = \text{Dietary exposure}/RfD \times 100\% \quad (3)$$

RESULTS

Analytical method

Sensitivity was expressed by limit of quantification (LOQ): LOQ of chlorpyrifos was 0.005 mg kg^{-1}; LOQ of fipronil was 0.001 mg kg^{-1}. The accuracy and precision of the measurements were described by recovery and relative standard deviation at different concentrations (0.01, 0.1 and 1.0 mg kg^{-1}). The recovery of chlorpyrifos obtained was in the range of 90.0-102.0%, and recovery of fipronil was 94.0-100%, as shown in Table 5. The relative standard deviations for repeatability were less than 4.5%.

Reduction by food processing

The concentration of chlorpyrifos and fipronil in brown rice decreased as a function of time in each step of food processing (Fig.1). The removal rates of pesticides by the end of the experimental periods were as follows: chlorpyrifos, 96.16%; fipronil, 91.6%. The result showed that the boiling process played an important role in pesticide reduction.

(1) Reduction of pesticides during sunlight exposure. The reduction in concentration of chlorpyrifos and fipronil during sunlight exposure is shown in Table 6. After 8 h sun exposure each day, the degradation was calculated and after 3 d of exposure was 19.6 and 15.2% for chlorpyrifos and fipronil, respectively.

(2) Reduction of pesticides during storage. 47.6% of initial chlorpyrifos and 38.4% of initial fipronil degraded after 60 d of storage (Table 7).

(3) Reduction of pesticides by washing. Polished rice (200 g) was washed with 500 mL of water 3 times by shaking every 5 min, then air-dried for 1 h, and milled for residue analysis. The percentages of

Table 5 The spiked recoveries and precision of determination for fipronil and chlorpyrifos residues

Sample	Spike level (mg kg^{-1})	Mean value (mg kg^{-1})	Recovery (%)	RSD (%)
Fipronil	0.01	0.009	94.32	4.28
	0.1	0.096	95.84	3.14
	1.0	0.999	99.87	1.36
Chlorpyrifos	0.01	0.009	90.12	3.41
	0.1	0.102	101.50	3.85
	1.0	0.996	99.58	2.07

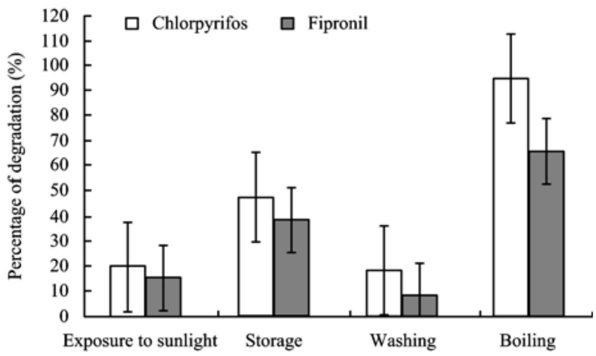

Fig. 1 Reductions of postharvest-applied chlorpyrifos and fipronil by food (rice) processing.

Table 6 Reduction of postharvest-applied chlorpyrifos and fipronil in rice during sunlight exposure

Insolation treatment (d)	Degradation (%)	
	Chlorpyrifos	Fipronil
1	6.4	5.6
2	9.5	8.5
3	19.6	15.2

Table 7 Reduction of postharvest-applied chlorpyrifos and fipronil in rice during storage

Storage treatment (d)[1)]	Degradation (%)	
	Chlorpyrifos	Fipronil
10	14.6	8.2
30	31.9	16.7
60	47.6	38.4

[1)] These are simulation days and storage was at 50°C.

chlorpyrifos and fipronil removed by washing with water were 18.2 and 8.2%, respectively.

(4) Reduction of pesticides by steaming. Polished rice was boileded 20 min. The percentages of chlorpyrifos and fipronil removed by steaming were 94.7 and 65.7%, respectively.

Harvest residue of different treatment

Harvest residues of chlorpyrifos and fipronil with different field treatments. Pesticides were applied during the rice developmental period (around heading) with 2 and 3 times the recommend dosage and double the recommend dosage at 7 d retreat intervals. The results showed that for the recommend dosage, the fipronil residues exceeded the MRL (0.04 mg kg^{-1}) at the harvest interval of 7 d but were not detected when the harvest interval was extended to 14 d. For double the recommend dosage, only the 2 application treatments were less than the MRL. The harvest residue for all treatments of chlorpyrifos exceeded the MRL (0.1 mg kg^{-1}). Also, the pesticide concentrations after food processing were calculated to predict the actual intake concentrations and are shown in Table 8.

Risk assessment

Theoretical risk assessment (based on MRL and theoretical maximum daily intake) Rice was evaluated in this analysis by using the established tolerances in/on the raw agricultural commodity as cited in Table 1 for the acute and chronic dietary analysis. For fipronil, the acute and chronic dietary risk from food alone is not of concern, as shown in Table 9. For chlorpyrifos, the chronic di-

Table 8 Pesticides residues in harvested rice

Dosage (g ha^{-1}) [1)]	Times treated	Preharvest interval (d)	Harvest residual (±SD) (mg kg^{-1})			
			Fipronil		Chlorpyrifos	
			Harvest	After food processing (96.16% degraded)	Harvest	After food processing (91.6% degraded)
R.D	2	7	0.11±0.02*	0.0042	1.23±0.14*	0.1033*
		14	aND	ND	0.57±0.07*	0.0479
	3	7	0.19*	0.0073	1.54±0.21*	0.1294*
		14	ND	ND	0.68±0.08*	0.0571
D.D	2	7	0.32±0.06*	0.0123*	1.89±0.15*	0.1588*
		14	0.006±0.0001	0.0002	0.75±0.09*	0.063
	3	7	0.39±0.04*	0.015*	2.04±0.14*	0.1714*
		14	0.024±0.003*	0.0009	0.86±0.07*	0.0722

[1)] R.D, recommend dosage; D.D, double recommended dosage.
ND, not detected (<0.001 mg kg^{-1}); *, exceed the MRL value. The same as below.

Table 9 Summary of acute and chronic dietary exposure and risk for chlorpyrifos and fipronil based on MRL values

Subpopulation	Chemicals	Risk assessment	POR (%)				MOE (%)			
			Male		Female		Male		Female	
			Urbanite	Countryside	Urbanite	Countryside	Urbanite	Countryside	Urbanite	Countryside
3-6 yr old	Chlorpyrifos	Acute dietary	71.02	92.33	66.21	84.26	1 407.96	1 083.05	1 510.42	1 186.76
		Chronic dietary	1 183.74	1 538.87	1 103.44	1 404.38	84.48	64.98	90.63	71.21
	Fipronil	Acute dietary	0.57	0.74	0.53	0.67	17 599.53	13 538.10	18 880.28	14 834.50
		Chronic dietary	71.02	92.33	66.21	84.26	133.76	102.89	143.49	112.74
7-13 yr old	Chlorpyrifos	Acute dietary	64.33	74.18	58.60	67.92	1 554.56	1 348.06	1 706.62	1 472.27
		Chronic dietary	1 072.12	1 236.35	976.59*	1 132.04	93.27	80.88	102.40*	88.34
	Fipronil	Acute dietary	0.51	0.59	0.47	0.54	19 431.96	16 850.72	21 332.72	1 8403.43
		Chronic dietary	64.33	74.18	58.60	67.92	147.68	128.07	162.13	139.87
14-17 yr old	Chlorpyrifos	Acute dietary	67.62	74.83	69.52	78.19	1 478.92	1 336.31	1 438.41	1 278.99
		Chronic dietary	1 126.95	1 247.22	1 158.69	1 303.11	88.74	80.18	86.30	76.74
	Fipronil	Acute dietary	0.54	0.60	0.56	0.63	18 486.50	16 703.87	17 980.07	15 987.44
		Chronic dietary	67.62	74.83	69.52	78.19	140.50	126.95	136.65	121.50
18-adult	Chlorpyrifos	Acute dietary	72.31	81.59	76.12	85.83	1 383.03	1 225.61	1 313.78	1 165.16
		Chronic dietary	1 205.09	1 359.87	1 268.61	1 430.42	82.98	73.54	78.83	69.91
	Fipronil	Acute dietary	0.58	0.65	0.61	0.69	17 287.84	15 320.12	16 422.19	14 564.48
		Chronic dietary	72.31	81.59	76.12	85.83	131.39	116.43	124.81	110.69

*, different result.

etary risk is of concern, but potential acute dietary risks still also exist. Acute dietary risk assessment indicated that the percentage of the acute PAD occupied for countryside children 3-6 yr old (the population subgroup of concern for acute toxicity effects) ranged from 84 to 92%. The results of POR and MOE matched well except for the subgroup of females aged 7-13. The results of MOE showed that this subpopulation faced marginal (MOE = 102.4), but the POR was 976.6 because FQPA (10) was used, where the risk level was amplified by 10 times. Otherwise it would be 97.66, a marginal exposure risk level. Since this also matches the result of MOE, in order to protect this subpopulation, the result of POR is taken into account in our case. The result faced by different subpopulations showed that boys at the age of 14 faced more serious health risks than girls of the same age. At ages above 14, female faced more serious health risks than males. The risks faced by countryside residents were more serious than residents in urban areas.

In our case, the MRL of fipronil, 0.04 mg kg^{-1} (EPA, 180.517) was used for the risk assessment. If a MRL of 0.01 mg kg^{-1} had been used, the risk level would have been lower. Because of concern about the toxicity of fipronil to fish, bees and aquatic invertebrate species, a MRL of 0.01 mg kg^{-1} is suggested in China. Since food (rice) alone was set to be the single way of exposure, the result of POR was used for the actual risk assessment, which also matched the result of MOE (data not shown).

Actual risk assessment (based on field trial residue data and degradation in the boiling process) Field trial data and buoiling process degradation percent were used in accrual risk assessment with the results shown in Tables 10 (for chlorpyrifos) and 11 (for fipronil). For chlorpyrifos, the chronic dietary risk from food alone is

Table 10 Dietary risk assessment of chlorpyrifos in rice based on field trial data (Table 8) and degradation by food processing

Subpopulation	Treatment [1)]	Risk assessment	Preharvest interval (7 d)				Preharvest interval (14 d)			
			Male (POR)		Female (POR)		Male (POR)		Female (POR)	
			Urbanite	Countryside	Urbanite	Countryside	Urbanite	Countryside	Urbanite	Countryside
3-6 yr old	R.D.-2	Acute dietary	73.19	95.17	68.44	87.03	33.94	44.13	31.74	40.35
		Chronic dietary	1 219.82	1 586.13	1 140.72	1 450.43	565.63	735.49	528.95	672.56
	R.D.-3	Acute dietary	91.68	119.21*	85.74	109.01*	40.46	52.60	37.83	48.10
		Chronic dietary	1 528.02	1 986.89	1 428.94	1 816.90	674.27	876.75	630.55	801.74
	D.D.-2	Acute dietary	112.51*	146.30*	105.22*	133.78*	44.64	58.04	41.74	53.07
		Chronic dietary	1 875.19	2 438.31	1 753.60	2 229.71	743.94	967.34	695.70	884.58
	D.D.-3	Acute dietary	121.44*	157.91*	113.56*	144.40*	51.15	66.52	47.84	60.83
		Chronic dietary	2 023.98	2 631.78	1 892.74	2 406.62	852.57	1 108.60	797.29	1 013.76
7-13 yr old	R.D.-2	Acute dietary	66.46	76.61	60.42	70.07	30.82	35.52	28.02	32.49
		Chronic dietary	1 107.64	1 276.82	1 007.07	1 167.83	513.61	592.06	466.98	541.52
	R.D.-3	Acute dietary	83.25	95.97	75.69	87.77	36.74	42.35	33.40	38.73
		Chronic dietary	1 387.50	1 599.42	1 261.52	1 462.90	612.26	705.77	556.67	645.53
	D.D.-2	Acute dietary	102.16*	117.77*	92.89	107.72*	40.53	46.72	36.85	42.73
		Chronic dietary	1 702.74	1 962.82	1 548.14	1 795.27	675.52	778.70	614.19	712.23
	D.D.-3	Acute dietary	110.27*	127.11*	100.26*	116.26*	46.45	53.54	42.23	48.97
		Chronic dietary	1 837.84	2 118.56	1 670.98	1 937.71	774.17	892.41	703.88	816.24
14-17 yr old	R.D.-2	Acute dietary	69.90	77.34	71.85	80.81	32.41	35.86	33.32	37.47
		Chronic dietary	1 164.96	1 288.95	1 197.53	1 346.79	540.19	597.68	555.29	624.50
	R.D.-3	Acute dietary	87.56	96.88	90.01	101.22*	38.64	42.75	39.72	44.67
		Chronic dietary	1 459.31	1 614.62	1 500.10	1 687.07	643.94	712.48	661.95	744.45
	D.D.-2	Acute dietary	107.45*	118.89*	110.46*	124.22*	42.63	47.17	43.82	49.28
		Chronic dietary	1 790.86	1 981.46	1 840.93	2 070.38	710.48	786.10	730.34	821.37
	D.D.-3	Acute dietary	115.98*	128.32*	119.22*	134.08*	48.85	54.05	50.22	56.48
		Chronic dietary	1 932.96	2 138.68	1 987.00	2 234.65	814.23	900.89	837.00	941.32
18-adult	R.D.-2	Acute dietary	74.69	84.28	78.63	88.66	34.63	39.08	36.46	41.11
		Chronic dietary	1 244.85	1 404.74	1 310.47	1 477.62	577.24	651.38	607.66	685.17
	R.D.-3	Acute dietary	93.56	105.58*	98.49	111.06*	41.29	46.59	43.46	49.01
		Chronic dietary	1 559.38	1 759.67	1 641.58	1 850.96	688.10	776.48	724.38	816.77
	D.D.-2	Acute dietary	114.82*	129.57*	120.87*	136.29*	45.55	51.40	47.95	54.07
		Chronic dietary	1 913.68	2 159.47	2 014.55	2 271.51	759.20	856.72	799.22	901.17
	D.D.-3	Acute dietary	123.93*	139.85*	130.46*	147.10*	52.20	58.91	54.96	61.97
		Chronic dietary	2 065.52	2 330.81	2 174.39	2 451.74	870.07	981.82	915.94	1 032.76

[1)] Pesticide was applied when target insects emerged, treatment rates were 2 and 3 times. The retreatment was employed after 7 d intervals each time. Samples were collected after 7 and 14 d preharvest intervals. The same as below.

*, concerned.

Table 11 Dietary risk assessment of fipronil in rice based on field trial data (Table 8) and degradation by food processing

Subpopulation	Treatment	Risk assessment	Preharvest interval 7 d				Preharvest interval 14 d			
			Male (POR)		Female (POR)		Male (POR)		Female (POR)	
			Urbanite	Countryside	Urbanite	Countryside	Urbanite	Countryside	Urbanite	Countryside
3-6 yr old	R.D.-2	Acute dietary	0.06	0.08	0.06	0.07	–	–	–	–
		Chronic dietary	7.44	9.67	6.96	8.85	–	–	–	–
	R.D.-3	Acute dietary	0.10	0.13	0.10	0.12	–	–	–	–
		Chronic dietary	12.93	16.81	12.09	15.37	–	–	–	–
	D.D.-2	Acute dietary	0.17	0.23	0.16	0.21	0.00	0.00	0.00	0.00
		Chronic dietary	21.79	28.33	20.37	25.91	0.35	0.46	0.33	0.42
	D.D.-3	Acute dietary	0.21	0.28	0.20	0.25	0.01	0.02	0.01	0.02
		Chronic dietary	26.57	34.55	24.85	31.59	1.59	2.07	1.49	1.90
7-13 yr old	R.D.-2	Acute dietary	0.05	0.06	0.05	0.06	–	–	–	–
		Chronic dietary	6.76	7.79	6.14	7.12	–	–	–	–
	R.D.-3	Acute dietary	0.09	0.11	0.09	0.10	–	–	–	–
		Chronic dietary	11.74	13.53	10.68	12.38	–	–	–	–
	D.D.-2	Acute dietary	0.16	0.18	0.14	0.17	0.00	0.00	0.00	0.00
		Chronic dietary	19.78	22.80	17.99	20.86	0.32	0.37	0.29	0.34
	D.D.-3	Acute dietary	0.19	0.22	0.18	0.20	0.01	0.01	0.01	0.01
		Chronic dietary	24.13	27.81	21.94	25.44	1.45	1.67	1.32	1.53
14-17 yr old	R.D.-2	Acute dietary	0.06	0.06	0.06	0.07	–	–	–	–
		Chronic dietary	7.10	7.86	7.30	8.21	–	–	–	–
	R.D.-3	Acute dietary	0.10	0.11	0.10	0.07	–	–	–	–
		Chronic dietary	12.35	13.66	12.69	8.21	–	–	–	–
	D.D.-2	Acute dietary	0.17	0.18	0.17	0.19	0.00	0.00	0.00	0.00
		Chronic dietary	20.81	23.02	21.39	24.05	0.34	0.37	0.35	0.39
	D.D.-3	Acute dietary	0.20	0.22	0.21	0.23	0.01	0.01	0.01	0.01
		Chronic dietary	25.37	28.07	26.08	29.33	1.52	1.68	1.57	1.76
18-adult	R.D.-2	Acute dietary	0.06	0.07	0.06	0.07	–	–	–	–
		Chronic dietary	7.59	8.57	7.99	9.01	–	–	–	–
	R.D.-3	Acute dietary	0.11	0.12	0.11	0.13	–	–	–	–
		Chronic dietary	13.20	14.89	13.89	15.66	–	–	–	–
	D.D.-2	Acute dietary	0.18	0.20	0.19	0.21	0.00	0.00	0.00	0.00
		Chronic dietary	22.23	25.09	23.41	26.39	0.36	0.41	0.38	0.43
	D.D.-3	Acute dietary	0.22	0.24	0.23	0.26	0.01	0.01	0.01	0.02
		Chronic dietary	27.11	30.60	28.54	32.18	1.63	1.84	1.71	1.93

–, no residue was detected.

of concern. Acute dietary risk based on all double and recommend dosages with 3 treated times and 7 d preharvest intervals is also of concern. For fipronil, the acute and chronic dietary risks are negligible based on low percentage of the acute and chronic PAD occupied for all populations. The assessment indicated that the percentage of acute and chronic PAD for males under 14-yr old was higher than for females of the same age, which means boys under 14-yr old faced higher risks than girls of the same age. For females 14-adult, the risks were higher than for males of the same age and countryside residents faced higher risk than urbanite residents. A similar trend was also observed by Castorina *et al*. (2003). Children and males in the countryside were the most sensitive population from the acute risk assessment of chlorpyrifos. The assessment results also showed that dosage and treatment times affected the risk and that the preharvest interval was found to be the critical measure to mitigate risk. When the preharvest interval was extended to 14 d, all risks (except the chronic dietary assessment) decreased to an acceptable level.

DISCUSSION

The field trials were carried out at the mid- and late-rice crop development periods. Positive correlation between pesticide residues and the dosage and application frequency of pesticide was found. The harvest residue of chlorpyrifos with 2 or 3 treatments all exceed the MRL, which is consistent with the result reported by Qian *et al*. (2008). Extending the preharvest interval was found to reduce the residue levels at harvest. Residues of chlorpyrifos and fipronil in rice grain were reduced by food processing. The residues were almost completely removed by boiling. In real life, there may be multi-route and multi-media exposure to pesticide residues, such as inhalation, oral, skin contact, or occupational exposure, etc. The actual diet exposure to pesticides is more varied and complex. Also, boiling methods and food preparation may lead to reducing concentrations of pesticide residues. The amount of different food items eaten by members of a population can vary greatly between different individuals and between the same individual over time. Successful dietary exposure models, therefore, have to be able to understand and incorporate this variety and complexity in human consumption patterns. Chlorpyrifos and fipronil are wildly used in Chinese agriculture and can be found in various agricultural products. People's exposure to these pesticides may be greater than estimated. Residues are assumed to be at the MRL in our theoretical risk assessments, which therefore, produces conservative estimates. The justification in our case is understandable as the large uncertainty attached to the single aspects of pesticide exposure and the potential health risk for the whole population means that the worst-case scenarios and conservative estimates were thought to be the best way to proceed. There are many factors that influence the choice of the estimate method used, including the time and resources available, the degree of accuracy needed, the quality and quantity of data and the level of concern over the potential hazard. As observed in this study and previous reports, the frequent detection of chlorpyrifos in the diet is a characteristic trend in China. This trend could be due to the considerably higher usage of chlorpyrifos in China compared to the USA, where the usage of chlorpyrifos is limited to terrestrial and greenhouse non-food crops. Reduction of postharvest applied chropyrofos and fipronil in rice during boiling processes was studied to simulate the practical exposure to the pesticide residues, and to predict the actual concentration of exposure to these pesticides.

For future studies, more detailed parameters for the estimate model and environment risk assessment should be included. Meanwhile for the registrant, environment impact, target pest, crop identification, and chemical application period should be addressed clearly in China. Lack of pesticide residue and diet databases, and even risk assessment software may delay food safety control in China. In US risk assessment, food consumption rates are based on the 1987-1988 US Department of Agriculture study entitled, "Nationwide Food Consumption Survey" and Exposure Factors Handbook (USEPA 1997b, 2005). The individual average consumption rate of food by age group (0-14 yr old children, and adults aged 20 and over) were weighted, and used to adjusted the loss by boiling and the preparation process (USEPA 1997b). The coefficient of variation is mainly used for fitting data derived from surveys. Each age group of the U.S. population is presented as a log-normal distribution, which is based on the assumption that the average value represents the average level and variation of the inhalation and dietary intake rate with the uncertainty related to the residents and non-occupational exposure (Bennett 1999). Multi-routes and multi-pathway exposure models, database establishment, software development, and aggregated and accumulated risk assessment models should be taken into account for registering agrichemicals in China.

CONCLUSION

Reduction of chlorpyrifos and fipronil from farm to fork and risk assessment to human health were studied in Jiangsu case. Different dosages and preharvest intervals resulted in different magnitude of residue. The concentration of pesticide residues decreased as a function of time after the boiling processes. The boiling process played an important role in pesticide degradation. Risk assessment to human health showed that harvest residues of chlorpyrifos in rice and acute dietary risks of chlopyrifos are of concern. Different subpopulation faced different risks, but in our case, the most sensitive population subgroups were children and male residents in countryside. Reidentification of the appropriate harvest interval was found to be the critical measure to mitigate risk to all populations for safe rice eating. Risk assessment should be adopted for agrichemical registration in China. Concerning the toxicity of fipronil to fish, bees and aquatic invertebrate species, a MRL for fipronil of 0.01 mg kg^{-1} is suggested which would be in accord with Codex.

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References

Adgate J L, Barr D B, Clayton C A, Eberly L E, Freeman N C G, Lioy P J, Needham L L, Pellizzari E D, Kukowski A, Quackenboss J J, *et al*. 2001. Measurement of children's exposure to pesticides: analysis of urinary metabolite levels in a probability-based sample. *Environmental Health Perspectives*, **109**, 583-590.

Barraj L M, Petersen B J, Daniel A S. 2000. *Background Document for the Sessions: Dietary Exposure Evaluation Model (DEEM™) and DEEM™ Decopositing Procedure and Software*. Novigen Sciences, Inc., Washington D.C. **3**, 1-62.

Bennett D H, Kastenberg W E, McKone T E. 1999. A multimedia, multiple pathway risk assessment of atrazine: the impact of age differentiated exposure including joint uncertainty and variability. *Reliability Engineering and Systems Safety*, **63**, 185-198.

Cabras P, Angioni A, Garau V L, Pirisi F M, Cabitza F, Pala M, Farris G A. 2000. Fate of quinoxyfen residues in grapes, wine, and their processing products. *Journal of Agricultural and Food Chemistry*, **48**, 6128-6131.

Castorina R, Bradman A, Mckone T E, Barr D B, Harnly M E, Eskenazi B. 2003. Cumulative organophosphate pesticide exposure and risk assessment among pregnant woman living in an agricultural community: A case study from the CHAMACOS Cohort. *Environmental Health Perspectives*, **111**, 1640-1648.

Chanda S M, Pope C N. 1996. Neurochemical and neurobehavioral effects of repeated gestational exposure to chlorpyrifos in maternal and developing rats. *Pharmacology Biochemistry Behavior*, **53**, 771-776.

Chinese Nutrition Society. 2000. *Chinese Dietary Reference Intakes, DRIs*. China Light Industry Press, Beijing. (in Chinese)

Ferriery H, Nieuwenhuijseny M, Boobis A, Elliott P. 2002. Current knowledge and recent developments in consumer exposure assessment of pesticides: A UK perspective. *Food Additives and Contaminants* (Part A), **19**, 837-852.

Fryer M, Collins C D, Ferrier H, Colvile R N, Nieuwenhuijsen M J. 2006. Human exposure modelling for chemical risk assessment: A review of current approaches and research and policy implications. *Environmental Science & Policy*, **9**, 261-274.

Gan J L, Lin Q, Jia X P, Liu J J. 2007. Residue and risk assessment of organochlor in pesticides in Jinjiang oyster (*Crassostrea rivularis*) from the coast of Guangdong, China. *Journal of Agro-Environment Science*, **26**, 2323-2328. (in Chinese)

Gao R J, Wang W, Chen L Z, Zhang W J. 2006. JMPR pesticide residue acute dietary exposure assessment method. *Chinese Agricultural Science Bulletin*, **22**, 101-105. (in Chinese)

General Adminstration of Sport of China. 2005. The second monitoring report of the citizen's physiques in China. [2008-12-20]. http://www.sport.gov.cn/n16/n1077/n1467/n1587/616932.html (in Chinese)

Kawahara J, Yoshinaga J, Yanagisawa Y. 2007. Dietary exposure to organophosphorus pesticides for young children in Tokyo and neighboring area. *Science of the Total Environment*, **378**, 263-268.

Liu G C, Wu L S, Zhang J H, Li Y. 2002. Four pesticides partitioning features in turf grass and comparison between two simulation models. *Acta Scientiae Circumstantiae*, **22**, 261-266. (in Chinese)

Nakamura Y, Sekiguchi Y, Hasegawa S, Tsumura Y, Tonogai Y, Ito Y. 1993. Reductions in postharvest-applied dichlorvos, chlorpyrifos-methyl, malathion, fenitrothion, and bromide in rice during storage and boiling processes. *Journal of Agricultural and Food Chemistry*, **41**, 1910-1915.

Purchase I F H. 2000. Risk assessment principles and consequences. *Pure and Applied Chemistry*, **72**, 1051-1056.

Qian Y H, Wang Z Q, Zhang X L, Lu Z Q. 2008. Studies on the dynamics of pesticide residues and application frequency at the middle-late stage of rice. *Scientia Agricultura Sinica*, **41**, 2678-2685. (in Chinese)

Tennant D R. 1999. Estimating acute dietary intakes of chemicals. *Regulatory Toxicology and Pharmacology*, **30**, 99-102.

USEPA. 1997a. *Environmental Protection Agency's Office of Pesticide Programs//Memorandum*. Office of Pesticide Programs Reference Dose Tracking Report, Washington D.C.

USEPA. 1997b. *Exposure Factor Handbook*. EPA/600/P-95/002Fc, US Environmental Protection Agency, National Center for Environmental Assessment, Office of Research and Development, Washington D.C.

USEPA. 2005. *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities*. EPA530-R-05-006, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington D.C.

USEPA. 1999. *The Role of the Use-Related Information in Pesticide Risk Assessment and Risk Management.* Draft document (64 FR 37977). Environmental Protection Agency, Washington D.C.

Yuan B J, Pan X Q, Dai Y, Shi Z M. 2007. Study on transition of dietary pattern in Jiangsu province. *Acta Nutrimenta Sinica*, **29**, 569-572. (in Chinese)

Zhai F Y, He Y N, Ma G S, Li Y P, Wang Z H, Hu Y S, Zhao L Y, Cui Z H, Li G, Yang X G. 2005. Study on the current status and trend of food consumption among Chinese population. *Chinese Journal of Epidemiology*, **26**, 485-488. (in Chinese)

Zhang J E. 2007. The issues and countermeasures for safe production of rice in China. *North Rice*, **4**, 1-7. (in Chinese)

Zhang Q G, Xu L. 1998. Studies on optimizing algorithm for fitting the parameters of pesticide degradation model. *Journal of Biomathematics*, **13**, 84-87. (in Chinese)

Zhou P, Lu Y T, Wu Y L. 2001. Residue dynamics of fipronil in rice and fields. *Agro-Environmental Protection*, **20**, 360-365. (in Chinese)

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