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Distribution of chlorpyrifos in rice paddy environment and its potential dietary risk

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ABSTRACT

Chlorpyrifos is one of the most extensively used insecticides in China. The distribution and residues of chlorpyrifos in a paddy environment were characterized under field and laboratory conditions. The half-lives of chlorpyrifos in the two conditions were 0.9–3.8 days (field) and 2.8–10.3 days (laboratory), respectively. The initial distribution of chlorpyrifos followed the increasing order of water < straw < soil, and soil was characterized as the major absorber. The ultimate residues in rice grain were below the maximum residue limit (MRL) with a harvest interval of 14 days. The chronic exposure for chlorpyrifos was rather low compared to the acceptable daily intake (ADI = 0.01 mg/kg bw) due to rice consumption. The chronic exposure risk from chlorpyrifos in rice grain was 5.90% and 1.30% ADI from field and laboratory results respectively. Concerning the acute dietary exposure, intake estimated for the highest chlorpyrifos level did not exceed the acute reference dose (ARfD = 0.1 mg/kg bw). The estimated short-term intakes (ESTIs) were 0.78% and 0.25% of the ARfD for chlorpyrifos. The results showed that the use of chlorpyrifos in rice paddies was fairly safe for consumption of rice grain by consumers.

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Introduction

Rice, one of the most important agricultural crops in the world, is the main nutrition source for more than half of the human population globally owing to its balance of nutrients, vitamins, minerals, and complex carbohydrates (Koesukwiwat et al., 2014). As one of the world's largest producers and an important exporter of rice, China exported 4.8 million tons of rice in 2013 according to the China Department of Foreign Trade Statistics (DFT, 2013). In order to achieve high-quantity food production, a wide range of pesticides were used, which has become a major concern for consumers. Monitoring of pesticide dissipation and distribution is thus considered to be an important issue for food safety control in agricultural products.

Since the withdrawal of several highly-toxic organophosphorus insecticides, chlorpyrifos (O,O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) has been recommended as an alternative insecticide and broadly applied in rice cultivation (Lu et al., 2014). However, household use of chlorpyrifos was limited by the Environmental Protection Agency in 31 December 2001 due to the issue of children's health (Adgate et al., 2001). Furthermore, chlorpyrifos was found to be associated with neurodevelopmental deficits, autoimmune disorders, and chromosomal damage (Ostwal et al., 2013; Rauh et al., 2011). Public concerns for chlorpyrifos safety have been raised (Affam and Chaudhuri, 2013; Yuan et al., 2014). The degradation of chlorpyrifos has been studied in various fruits and vegetables. For instance, it was reported

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that chlorpyrifos residues in tomato remained nearly constant with little degradation detected, and followed the order cuticle > pulp (Wang et al., 2013). In a more recent study, chlorpyrifos residue at harvest time was found to mainly remain in the bottom part of bamboo shoots, and its half-life in non-covered cultivation soil was 48.1 days (Liu et al., 2014b).

So far, few studies have investigated the persistence of chlorpyrifos in the paddy environment. It was reported that the half-lives (DT_{50}) of chlorpyrifos in rice plants, water and soil in Nanjing and Guangxi based on measurements in 2009–2010 were 3.86–4.28 days, 0.52–0.58 days and 1.21–1.35 days, respectively (Zhang et al., 2012). Additionally, the local climate conditions were not alike for different cities, which always resulted in differences in the environmental fate and persistence of pesticides. Wang et al. (2013) found that the DT_{50} values of chlorpyrifos in a paddy soil in Nanjing (Southeast of China) were shorter compared to those in Guangxi (southwest of China). The distribution of chlorpyrifos in the paddy environment has been still poorly understood and insufficiently investigated. In addition to field trials, experiments conducted under laboratory conditions are necessary for further understanding the persistence of chlorpyrifos in rice paddies.

In the present study, the dissipation of chlorpyrifos in a paddy environment was investigated in a laboratory (flooded soil and liquid conditions) in combination with field trials conducted in a typical paddy cultivation region (Zhejiang, South of China). In addition, the accumulation and distribution of pesticide residues in different parts of paddy plants (straw and root) were also explored. To properly assess the potential risk posed by human exposure to this pesticide, evaluation of the chronic and acute dietary risk of chlorpyrifos using the ultimate residues was further conducted. The aim of the present work was to determine the residual characteristics of chlorpyrifos in the paddy environment, in order to further promote the proper and safe use of this pesticide and protect the consumers from potential health problems.

1. Materials and methods

1.1. Materials and reagents

Analytical standard chlorpyrifos (99.0%) was supplied from the Institute for the Control of Agrochemicals, Ministry of Agriculture, China. Chlorpyrifos emulsion in water (EW) (30%) was purchased from Zhejiang Xinnong Chemical Co. Ltd. (Zhejiang, China). Acetone, n-hexane, acetonitrile, ethyl acetate and anhydrous sodium sulfate were all analytical grade and obtained from China Huadong Medicines Corporation Ltd. Purified water was prepared by a Cascada AN (Pall Corporation, New York, NY, USA) water purification system.

1.2. Experimental design

1.2.1. Field experiment

The field experiment was carried out at Machege, a village located in Zhuji, Zhejiang Province, China. Soil organic matter content and pH were 1.94% and 6.9, respectively. Chlorpyrifos 30% emulsion in water (EW) was sprayed once (at the tillering stage of the growth period) and twice (at the jointing stage of the growth period) with 10 days interval at 690 g a.i.hm^2 (1.5-fold of the recommended dose). Representative samples were taken about 0 (2 hr), 1, 3, 5, 7 and 10 days after application. To examine the effect of chlorpyrifos frequency on the residue accumulation, two or three applications were used. At the end of the cultivating period, rice was collected for examination of the ultimate residues of chlorpyrifos in husked grains.

1.2.2. Laboratory experiment

The dissipation of chlorpyrifos was investigated in rice microcosms where flooded soil conditions and liquid (nutrient solution) cultivation were simulated, respectively. The soil used in experiments was collected from the 0–10 cm layer of the rice field. Rice microcosms consisted of plastic pots ($26 \times 19 \times 20$ cm^3) where 2.7 kg of soil was added. The soil in the pots was then flooded with 2 L of deionized water to form a water layer (approximately 5 cm). By contrast, nutrient solution (2 L) was added into hydroponic pots directly. One liter of nutrient solution included (in mg): 114 NH_4NO_3, 89 K_2SO_4, 406 $MgSO_4{\cdot}7H_2O$, 147 $CaCl_2{\cdot}2H_2O$, 50 $NaH_2PO_4{\cdot}2H_2O$, 1.8011 $MnCl_4{\cdot}H_2O$, 0.0920 $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.0442 $ZnSO_4{\cdot}7H_2O$, 1.124 H_3BO_3, 0.0390 $CuSO_4{\cdot}5H_2O$, 27.85 $FeSO_4{\cdot}7H_2O$, and 37.25 Na_2EDTA (Xu et al., 2004). After seedlings were transplanted and equilibrated for a week, chlorpyrifos was applied at 1.5-fold of the recommended dose onto flooded microcosms. Representative samples were taken at 1, 3, 5, 7, 10 and 14 days after application. To examine the effect of chlorpyrifos frequency on the residue accumulation, two or three applications were used. At the end of the cultivating period, rice was collected for examination of the ultimate residues of chlorpyrifos in husked grains.

1.3. Pesticide extraction

1.3.1. Soil and rice plants

A sample (20.0 g) was placed in an Erlenmeyer flask along with 10 mL distilled water and 50 mL acetonitrile, then was subjected to shaking-extraction for 60 min. The filtrate was extracted thrice with 50 mL ethyl acetate. The ethyl acetate phase was further dried by passing through a 2-cm layer of anhydrous sodium sulfate. The organic solvent was evaporated and the extract was redissolved in 5 mL ethyl acetate. Prior to analysis, the ethyl acetate analyte was filtered through a 0.22 μm filter (Millipore, Boston, MA, USA).

1.3.2. Water

Water samples (100 mL) were filtered through a Buchner funnel into a 250 mL separatory funnel and 10 g of NaCl was added. After shaking for 30 sec, the sample was extracted thrice with 50 mL ethyl acetate. The subsequent steps were identical to those adopted for soil samples.

1.3.3. Rice tissue

The comminuted rice tissue (husk and rice) sample (10 g) was placed in a 50 mL polypropylene centrifuge tube with 10 mL distilled water, then extracted with 30 mL of acetonitrile by homogenization with a high speed blender (Ultra-Turrax T18, IKA, Staufen, Germany) for 3 min. After the addition of 3 g $MgSO_4$ and 2 g NaCl, each mixture was shaken vigorously for

1 min and centrifuged for 5 min at 4000 r/min. An aliquot of the organic phase (20 mL) was evaporated and the extract was redissolved in 5 mL ethyl acetate. Prior to analysis, the ethyl acetate analyte was filtered through a 0.22 μm PTFE filter (Millipore, Boston, MA, USA).

1.4. Chromatographic analysis

GC analysis was performed with a SHIMADZU (Shimadzu, Kyoto, Japan) GC-2010 gas chromatograph equipped with an ECD and a HP-5 column (30 m × 0.32 mm and film thickness 0.25 μm). Extraction recoveries for chlorpyrifos in soil, straw, water and rice tissue were 85.3%–106.8%, 98.3%–110.3%, 102.7%–110.8%, and 94.4%–105.3%, respectively and the limits of quantification (LOQ) were 0.010, 0.010, 0.005 and 0.010 mg/kg respectively.

1.5. Risk assessment

Exposure was calculated by multiplying residue concentrations by the average daily per capita consumption estimated for cereal grains & flours on the basis of the GEMS/Food Consumption cluster diets. The estimated intake was expressed as a percentage of the ADI (Acceptable Daily Intake) and ARfD (Acute References Doses) for a 60 kg person.

The Estimated Daily Intake (EDI) of pesticide residues was calculated as grain consumption multiplied by residue (FAO/WHO, 2009). Long-term risk assessment of intakes was performed by calculating the chronic risk quotient (RQ_c) by dividing the estimated daily intake by the relevant acceptable daily intake (Lozowicka et al., 2014):

$$RQ_c = EDI/ADI \times 100\% \quad (1)$$

where, EDI (mg/kg bw) is the Estimated Daily Intake; ADI (mg/kg bw) is the Acceptable Daily Intake.

The Estimate of Short-Term Intake (ESTI) was expressed as grain consumption multiplied by the highest residue. The estimate of pesticide intake in the diet was then compared to the ARfD. The acute risk quotient (RQ_a) was calculated as follows:

$$RQ_a = ESTI/ARfD \times 100\% \quad (2)$$

where, ESTI (mg/kg bw) is the Estimate of Short-Term Intake; ARfD (mg/kg bw) is the Acute Reference Dose.

2. Results and discussion

2.1. Degradation of chlorpyrifos under field conditions

Chlorpyrifos was applied at the tillering and jointing stages of rice growth. The residual level of chlorpyrifos in the paddy environment was accordingly determined (Table 1). The initial deposits (2 hr, day 0) at the tillering stage were 6.25 mg/kg in paddy water and 0.28 mg/kg in paddy soil, respectively. The initial deposit in soil at the jointing stage was 0.99 mg/kg. The higher initial deposit at the jointing stage may be related to the increasing application frequency of pesticide. The highest residue of chlorpyrifos in the soil was detected at 1 day after application, with the concentration of 0.79 mg/kg. A sharp decrease of chlorpyrifos residues occurred from 2 hr to 1 day in paddy water at the tillering stage. This was possibly due to the adsorption equilibrium between water and soil established over 2 hr in this paddy ecosystem. Field studies in paddy soil from Chaohu showed that chlorpyrifos possessed high adsorption affinity, at K_d of 38.99 L/kg (Liang et al., 2011), which might indicate the acceleration of adsorption and sorption in paddy soil. The initial concentrations of chlorpyrifos ranged from 17.81 to 20.12 mg/kg in the straw. Degradation rates of chlorpyrifos in straw were higher than 50% at 3 days after application. At the end of the field experiment (10 days), the degradation rates of chlorpyrifos in straw, water and soil were all above 95%. The dissipation of chlorpyrifos was well described by the first-order kinetic ($C_t = C_0e^{-kt}$) model. The dissipation of chlorpyrifos proceeded rapidly in both stages. In paddy water, chlorpyrifos was dissipated rapidly, with DT_{50} values of 0.9 days. This is in agreement with the previous work, in which the dissipation of chlorpyrifos was found to have a DT_{50} value of less than a day in paddy water (Zhang et al., 2012). However, the DT_{50} values of chlorpyrifos in rice plants (3.6–3.8 days) were higher compared to field values in pepper plants (0.9 days) (Lu et al., 2014). This may be attributed to the different species with various growing conditions, for instance, one of the most important factors influencing the dissipation behavior of pesticides in plants is photodegradation. Hence, a greater effective foliar area in the pepper plant leading to larger exposure to ultraviolet light may be responsible for the lower DT_{50} values of chlorpyrifos in contrast to that in the rice plants (Lu et al., 2014).

2.2. Distribution of chlorpyrifos under field conditions

Distribution of pesticide in the environment is measured by the absolute pesticide quantity. The absolute quantity of chlorpyrifos was expressed as residues multiplied by the proportion in the corresponding medium. As shown in the bar chart (Fig. 1a), at the tillering stage, the initial distribution of chlorpyrifos (2 hr, day 0) in soil was 31.4% (proportion of total quantity). From 1 to 7 days, a gradual and continuous increase of the pesticide proportion in soil was observed. The chlorpyrifos distribution in soil reached 93.8% at 7 days. At the tillering stage, the initial chlorpyrifos distribution in water and straw was 35.1% and 33.5%, respectively. At 1 day after application, the distribution decreased along with time in

Table 1 – Dynamics of chlorpyrifos in straw, water and soil at tillering and jointing stage under field condition.

Trial	Compartment	First-order kinetic equation	Correlation coefficient (R^2)	Half-life (day)
Tillering stage	Straw	$C_t = 18.048e^{-0.4759t}$	0.9985	1.5
	Water	$C_t = 4.416e^{-0.7333t}$	0.9227	0.9
	Soil	$C_t = 0.825e^{-0.1946t}$	0.9703	3.6
Jointing stage	Straw	$C_t = 19.286e^{-0.4077t}$	0.9759	1.7
	Soil	$C_t = 1.556e^{-0.1824t}$	0.8404	3.8

water and plant samples. The proportion detected in water and straw at 7 days was low, at 0.4% and 5.8%, respectively. However, there was no water at the jointing stage (Fig. 1b). The initial distribution of chlorpyrifos in the straw was 54.2% 2 hr after application, which was higher than that in soil (45.8%). That might be attributed to the biomass of plants being at its maximum in this period, which led to the highest pesticide distribution. One day after application, the proportion increased with time in soil. The distribution of chlorpyrifos was mainly in soil, with the proportion 94.8% at 7 days. One of the major factors could be the high adsorption of chlorpyrifos on soil (Liang et al., 2011). Another important factor that influenced the distribution ratio of pesticides was the degradation rates. Chlorpyrifos showed shorter half-life in rice straw (1.6–1.7 days) than in soil (3.6–3.8 days). This might be due to strong light intensity on straw during the field experiments. Consequently, the high distribution of chlorpyrifos in soil might lead to adverse influences on soil microorganisms; for example, it was reported that the composition of the fungal community was obviously changed with chlorpyrifos treatment (Chen et al., 2014).

2.3. Ultimate residue of chlorpyrifos under field conditions

The final residues of chlorpyrifos in husk, rice, straw and soil at 14 days after final spraying are shown in Table 2. The residues ranged from 0.08 to 0.76 mg/kg for 2 applications. The maximum residue was found in husk, with the concentration of 0.76 mg/kg. The ultimate residues with 3 applications were in increasing order: 0.10 mg/kg (rice), 0.16 mg/kg (soil), 0.43 mg/kg (straw), 1.00 mg/kg (husk), respectively. For 2 applications, the chlorpyrifos residues ranged from 0.08 to 0.76 mg/kg. The results indicated that the higher application rate led to higher final residues. Similarly, Zhang et al. (2006) found that chlorpyrifos residues in cabbage were dependent on the frequency and rate of pesticide application. When the cabbages were treated with the pesticide once at normal rates, the residual levels were within the national standards. When

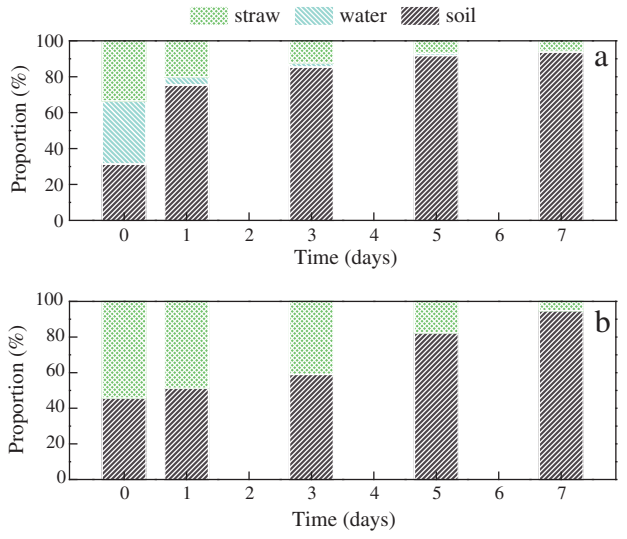

Fig. 1 – Distribution of chlorpyrifos at tillering (a) and jointing (b) stage in paddy ecosystem under field condition.

Table 2 – Ultimate residues of chlorpyrifos in paddy environment under field condition.

Sample spraying times	Residue (mg/kg)	
	Two time	Three time
Husk	0.76	1.00
Rice	0.08	0.10
Straw	0.29	0.43
Soil	0.13	0.16

the cabbages were treated four times at maximal rates at 5 day intervals, the residual levels of chlorpyrifos exceeded the national standards. Liu et al. (2014a) also observed that the bromothalonil residues in apples after 4 applications (0.05–0.17 mg/kg) were higher than residues after 3 applications (0.04–0.13 mg/kg). Those results strongly suggested that the pesticide residues mainly depended on the rate and frequency of application, and the residues positively correlated with increasing rate and frequency at the same dosage. When chlorpyrifos was sprayed at 1.5-fold the recommended dosage for 2 and 3 applications, the final residue in rice was 0.08–0.10 mg/kg.

2.4. Degradation of chlorpyrifos under laboratory conditions

The dissipation of chlorpyrifos in a paddy environment in the laboratory (flooded soil and liquid cultivation conditions) was investigated (Table 3). The estimated residues of chlorpyrifos in soil were found to be 2.02–6.17 mg/kg in the flooded soil condition. The DT_{50} value of chlorpyrifos in paddy soil was 6.3 days. From 3 to 14 days, the chlorpyrifos residues could be detected in water (flooded soil condition), with the concentrations ranging from 0.46 to 3.22 mg/kg. However, the residues detected in water (liquid cultivation conditions) were less, with the concentrations of 0.01–1.28 mg/kg. The difference was due to the applied amount of chlorpyrifos, which was increased from 80 mL to 120 mL for the larger rice plant biomass in the flooded soil condition. At the same time, the liquid culture condition had approximately 2-fold the volume of water compared to that under flooded soil conditions, which led to a diluting effect for chlorpyrifos. In our study, chlorpyrifos was dissipated relatively rapidly, with DT_{50} values of 2.8 days (flooded) to 4.2 days (liquid) in water. Chlorpyrifos was relatively persistent in straw, with DT_{50} of 6.2 days in the flooded condition and 10.3 days in the liquid cultivation condition. Obviously, compared with the results from the field study, chlorpyrifos showed a slower dissipation rate in the laboratory experiment. This discrepancy could be attributed to the lower temperatures in the laboratory experiment (28 ± 1°C) compared to the temperatures in the field experiment (24°C–38°C). A recent study has showed that hydrolysis, volatilization and microbial degradation could be more significant in the field (Tsochatzis et al., 2013). The hydrolysis rate of chlorpyrifos was increased with increasing temperature (Pablo et al., 2008). In the present study, the slightly higher temperature under field conditions could result in higher hydrolysis and consequently a shorter half-life for the field tests, compared to the laboratory study. In addition, the high temperature may permit increased volatilization. Bozlaker et al. (2009) showed that chlorpyrifos

Table 3 – Dynamics of clorpyrifos in straw, water and soil at submerged soil and liquid under laboratory condition.

Trial	Compartment	First-order kinetic equation	Correlation coefficient (R^2)	Half-life (day)
Flooded soil	Straw	$C_t = 36.687e^{-0.1126t}$	0.9908	6.2
	Water	$C_t = 3.372e^{-0.2474t}$	0.8610	2.8
	Soil	$C_t = 8.702e^{-0.1095t}$	0.8908	6.3
Liquid	Straw	$L = 22.903e^{-0.0673t}$	0.9262	10.3
	Water	$C_t = 4.938e^{-0.1654t}$	0.9384	4.2

had higher atmospheric levels in summer due to increased volatilization and seasonal local application. Moreover, in the field, with intense solar radiation, the loss of chlorpyrifos can be faster than in the laboratory due to the high level of solar radiation, which accelerates the photolysis process (Zeng and Arnold, 2013). Therefore, the hermetic environment in the laboratory may thus result in longer DT_{50} values.

2.5. Distribution of chlorpyrifos under laboratory condition

The distribution of chlorpyrifos in the paddy ecosystem under laboratory conditions is presented in Fig. 2. Chlorpyrifos was mainly distributed in soil for the flooded soil condition, with the percentages of 77.0%, 83.0%, 74.4%, 67.8% and 79.5% after 3, 5, 7, 10, 14 days, respectively (Fig. 2a). The distribution was decreased along with time in water samples at 3 days after application, with only 0.1% proportion after 14 days. The percentages of the chlorpyrifos in root and straw were significantly different from those in water, which increased along with time and reached the highest proportion (15.1% and 16.4%) at 10 days after application. At the end of the experiment period, the percentages exhibited the same trend as observed in the field distribution. Chlorpyrifos was mainly persistent in soil, with 93.8% and 79.5% percentages under field and laboratory conditions, respectively. In the liquid cultivation condition, the distribution in water was 50.1%, 56.5%, 51.2%, 38.2% and 25.0% after 3, 5, 7, 10, 14 days, respectively (Fig. 2b). In keeping with the flooded soil condition, the distribution decreased along with time in water samples, while the distributions in straw and root increased. The proportions were 33.7% and 41.3% in root and straw after 14 days of application, and chlorpyrifos mainly persisted in root and straw. Agrochemicals accumulate in plant tissues *via* uptake and adsorption from the soil, especially organics with high K_{ow} (Pereira et al., 2008). Contaminants such as hexachlorocyclohexane accumulate in plant tissues, mainly by root uptake (Yi et al., 2013). Combined with the higher relative distribution of chlorpyrifos in root and straw than that in water, it could be inferred that the dominant accumulation of the pesticide was in the root.

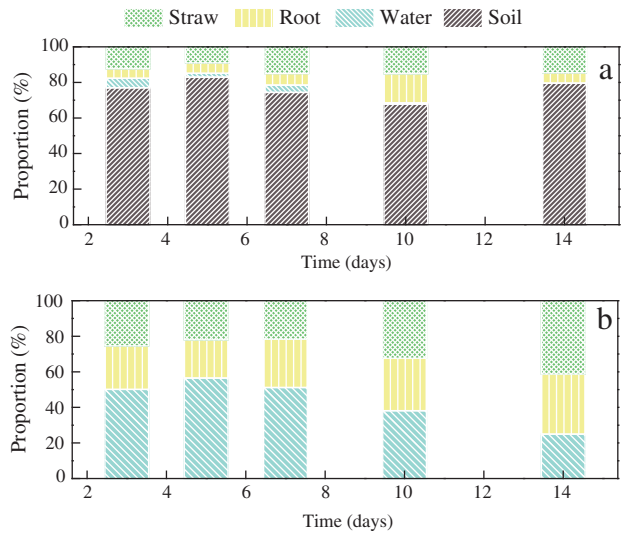

Fig. 2 – Distribution of chlorpyrifos in rice ecosystem at flooded soil (a) and liquid (b) under laboratory condition.

2.6. Ultimate residues of chlorpyrifos under laboratory conditions

To check the universality of results obtained from outdoor residues, complementary indoor experiments were conducted. The ultimate residues of chlorpyrifos in husk, rice, straw and soil under laboratory condition are shown in Table 4. When chlorpyrifos was applied 2 times, the residues were 0.86, 0.57, 0.07 and 0.02 mg/kg in soil, straw, husk and rice, respectively. With 3 applications, the residues were 0.03–1.27 mg/kg. The ultimate residue levels of chlorpyrifos in rice at 14 days after application were 0.02 mg/kg when sprayed twice, and 0.03 mg/kg when sprayed three times, respectively. The residues of chlorpyrifos in rice following both spraying times were all below Maximum Residue Limit (MRL) values, which was consistent with the field experiment. On the other hand, the residue level of chlorpyrifos in soil under laboratory conditions was slightly high, which could be attributed to the high initial deposition and low dissipation rate. Moreover, throughout the paddy system, chlorpyrifos residues in the edible part (rice grain) were the lowest, consistent with the field experiments. The ultimate residues of chlorpyrifos were far below the MRL value of 0.50 mg/kg set by CAC (Codex Pesticide Residues Limits in Food, 2005) and China (GB2763, 2014).

Table 4 – Ultimate residues of chlorpyrifos in paddy environment under laboratory condition.

Sample spraying times	Residue (mg/kg)	
	Two times	Three times
Husk	0.07	0.12
Rice	0.02	0.03
Straw	0.57	0.79
Soil	0.86	1.27

Table 5 – Dietary risk assessment for acute and chronic effects with chlorpyrifos residues.

Trails	Chronic				Acute			
	Residue (mg/kg)	ADI (mg/kg bw)	EDI (mg/kg bw)	RQ ($\%_c$)	HR (mg/kg)	ARfD (mg/kg bw)	ESTI (mg/kg bw)	RQ_a (%)
Field	0.09	0.01	0.59×10^{-3}	5.90	0.12	0.1	0.78×10^{-3}	0.78
Laboratory	0.02	0.01	0.13×10^{-3}	1.30	0.04	0.1	0.25×10^{-3}	0.25

ADI: Acceptable Daily Intake; EDI: Estimated Daily Intake; RQ_c: chronic risk quotient; HR: high residue; ARfD: Acute References Doses; ESTI: Estimate of Short-Term Intake; RQ_c: acute risk quotient.

2.7. Risk assessment of chlorpyrifos

In this study, the pesticide intakes were estimated using the average and highest detected pesticide residue levels in field and laboratory trials, to determine long and short-term dietary risks to consumers based on methods recommended by the WHO (GEMS/FOODS, 2012). The risk from pesticide residues in food commodities was evaluated on the basis of two toxicological limit values: the ADI and the ARfD (JMPR, 2012). The intake at the cluster level was weighted by the population size of the reporting country. GEMS/Food Cluster Diets are based on similarities between dietary patterns, and China belongs to G09: Bangladesh, Indonesia and Viet Nam et al. (GEMS/FOOD, 2012). Rice is a representative model of a cereal in China and contributes 24% (391.9 g/day) to the total daily food consumption (1612 g/day) (GEMS/Food, 2012). Intakes of pesticide residues from rice may contribute a major part to the total intakes of chlorpyrifos. The chronic and acute risk assessments for intake based on the reported calculations are presented in Table 5. Long-term exposure was expressed as a chronic risk quotient (RQ_c). Based on the EDI values, the chronic intakes of chlorpyrifos residues were rather low compared to the ADI (RQ_c ranged from 1.30% to 5.90%). An acute risk assessment was also performed by calculating the acute risk quotient (RQ_a). The ESTI of rice represented 0.78% and 0.25% of the ARfD (ARfD = 0.10 mg/kg bw). That meant that the dietary risk from chlorpyrifos was fairly low for the general Chinese population. These results on risk assessment were consistent with previous studies (Chen et al., 2012). The evaluation of consumer dietary risk connected with pesticide residues at the highest concentrations in rice samples showed that it did not pose a serious health problem. However, chlorpyrifos showed a larger effect in a market monitoring study conducted between 2007 and 2010 compared to our study. It was reported that the estimated daily intakes (EDIs) of chlorpyrifos for the most sensitive age group (2–6 year-olds) based on the probabilistic assessment at high percentile (P99.9) amounted to 48.99% of ADI and was 20.02%–23.56% of ADI for people ≥ 18 years (Yuan et al., 2014).

3. Conclusions

Our results provided the first comprehensive field-to-laboratory assessment of the dissipation and distribution of chlorpyrifos in rice paddy ecosystems. The field experiments showed that the half-lives of chlorpyrifos were 0.9–3.8 days, which were shorter than the results under laboratory conditions (2.8–10.3 days). The results suggested that the application of this insecticide was not likely to pose a threat for the contamination of receiving surface water resources in rice basins due to the limited persistence. With high percentages of the total chlorpyrifos distribution, soil was characterized as the major absorber. Furthermore, the ultimate residues were found to be below the MRLs of chlorpyrifos in rice grain (0.50 mg/kg) in CAC and China. In terms of chronic exposure, chlorpyrifos constituted 5.90% and 1.30% of ADI in field and laboratory conditions, respectively. The short-term hazard (acute exposure) stemming from chlorpyrifos amounted to 0.78% and 0.25% of ARfD. The chronic and acute risk quotient values of chlorpyrifos were significantly less than 100%, which demonstrated that the use of chlorpyrifos could be considered safe for humans. Based on the investigated data, the application of chlorpyrifos at the recommended dose on rice is quite safe in China from the point of view of crop protection and human health.

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