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Assessment of potential dermal and inhalation exposure of workers to the insecticide imidacloprid using whole-body dosimetry in China

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ABSTRACT

In China, although improvements to the pesticide registration process have been made in last thirty years, no occupational exposure data are required to obtain a commercial license for a pesticide product. Consequently, notably little research has been conducted to establish an exposure assessment procedure in China. The present study monitored the potential dermal operator exposure from knapsack electric sprayer wheat field application of imidacloprid in Liaocheng City, Shandong Province and in Xinxiang City, Henan Province, China, using whole-body dosimetry. The potential inhalation exposure was determined using a personal air pump and XAD-2 sample tubes. The analytical method was developed and validated, including such performance parameters as limits of detection and quantification, linear range, recovery and precision. The total potential dermal and inhalation exposures were 14.20, 16.80, 15.39 and 20.78 mL/hr, respectively, for the four operators in Liaocheng and Xinxiang, corresponding to 0.02% to 0.03% of the applied volume of spray solution. In all trials, the lower part (thigh, lower leg) of the body was the most contaminated, accounting for approximately 76% to 88% of the total exposure. The inhalation exposure was less than 1% of the total exposure. Such factors as the application pattern, crop type, spray equipment, operator experience and climatic conditions have been used to explain the exposure distribution over the different parts of the body. As indicated by the calculated Margin of Exposure, the typical wheat treatment scenarios when a backpack sprayer was used are considered to be safe in terms of imidacloprid exposure.

Introduction

Pesticides are a class of products essential for sustainable agriculture and good public health. However, a general misunderstanding of the difference between the toxicity of a pesticide and the actual risk has heightened public anxiety over the use of such materials. The risk presented by a pesticide depends on its inherent toxicity and the level of exposure. Therefore, the importance of reliably assessing human exposure to pesticide risk has been growing worldwide (Palis et al., 2006). The developed countries, such as the European Union and North American countries, who have established exposure data requirements, do not allow a pesticide to be authorized unless there are specific data or adequate model predictions to show that, in normal use, the operator exposure levels would be below the acceptable operator exposure level (Hughes et al., 2006). In many developing countries, including China, no occupational exposure data

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are required to obtain a commercial license for a pesticide product, and consequently, very little research has been performed to establish exposure assessment in China.

Assessment of operator exposure to a pesticide is a very complicated task for which the difficulty fluctuates greatly depending on multiple factors, such as the application equipment (*e.g.*, hand-held or vehicle-mounted sprayer, airplane, helicopter), application rate and duration, the type of pesticide formulations (*e.g.*, powders, granules, micro-encapsulates), the climatic conditions (*e.g.*, temperature, humidity, wind speed and direction), the type of job performed by the operator, the personal protective equipment (*e.g.*, coveralls, gloves, face mask), and the training and aptitude of the applicator. All these sources of variability are grouped into "use scenarios" (Fenske and Day, 2005). The EU and USA have taken the lead in the field of occupational exposure assessment for pesticides. Under defined-use scenarios, the most important independent exposure databases, also called predictive exposure models, have been established and amended in the formal pesticide registration process. These are the Pesticide Handlers Exposure Database in the United States (PHED, 1998), the German model (Lundehn et al., 1992), the UK Predictive Operator Exposure Model (UK-POEM, 1992), the Dutch model (Van Hemmen, 1993) and the European model (Van Hemmen, 2001), which are used to estimate operator exposure.

Due to the characteristics of the small-scale farmer household economy in China, large-tonnage mechanical spraying equipment is not popular, and manual (backpack) pesticide spraying prevails in general plant protection practices in most regions of China. Moreover, the low education levels of the rural population, poor awareness of occupational hygiene, lack of information and training on pesticide safety and inadequate personal protection equipment during pesticide use place many Chinese farmers into the high pesticide exposure risk category. A large amount of attention should be paid to this situation. However, the pesticide use scenarios are different from those in developed countries, and the general exposure data cannot be readily extrapolated from the existing international predictive exposure models mentioned above. Therefore, it is imperative to carry out occupational exposure assessment for pesticides based on the fundamental realities of our own country. However, the relevant research in this field is just at the very beginning in China (Li et al., 2010; Chen et al., 2012), and research on wheat field pesticide exposure has not been reported.

The dermal route is usually the main route of exposure during the handling of pesticides, and it is considered to contribute to the greatest proportion of systemic exposure (Machera et al., 2003). In the absence of actual data on dermal absorption, most work in this field has focused on characterizing potential dermal exposure (PDE) using passive dosimetry that measures the amount of pesticide that comes into contact with the skin and clothing of workers. The measurement of PDE is a key component of risk evaluation and in helping to characterize the exposure pathway, quantifying the magnitude and extent of contamination, and evaluating the variability in sources and pesticide handler behavior (Garrido Frenich et al., 2002).

It is well known that the exposure data itself cannot be used as a risk indicator because it must be related to the acceptable exposure limits. For this, the Margin of Exposure (MOE) formula has been proposed as a useful and simple risk indicator (US EPA, 2002) that relates the acceptable exposure to the quantity absorbed by the body, which can be evaluated from values of potential exposure. The target MOE is 100 for occupational handlers. Scenarios with MOEs greater than 100 do not exceed the administrative department's level of concern.

As large agricultural provinces, the current pesticide exposure situation in Shandong and Henan provinces is representative and can generally reflect the situation in China. In the present study, field trials were conducted in farmland by four local farmers as pesticide operator volunteers. Imidacloprid, which is used for the control of many insect pests, was selected for these studies. The analytical method used for imidacloprid determination was established, and the performance parameters were fully validated. Finally, the methodology was applied to evaluate the potential dermal and inhalation exposure using whole-body dosimetry with custom-made cotton coveralls as sampling medium. The variability of the pesticide exposure and distribution pattern and evaluation of MOEs will be presented.

1. Materials and methods

1.1. Reagents and materials

Imidacloprid analytical standard (98.9% purity) was purchased from the National Pesticide Quality Supervision and Testing Center (Shenyang). The solid standard was dissolved in methanol to obtain primary stock solutions (1120 mg/L). Other working solutions were prepared by dilution with methanol. Chromatographic purity methanol was obtained from Fisher Scientific (Pittsburgh, USA), and the acetone used for extraction was analytical grade purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). A commercial formulation of 15% imidacloprid soluble liquid (SL) was provided by Jiangsu Rotam Chemistry Co. Ltd. (Kunshan, China). Cotton gloves (100% cotton, 200 g/m^2) were from Beijing Kuailu Knitting Co., Ltd. (Beijing, China). An OVS tube with XAD-2 sorbent and tube holder were purchased from SKC Inc. (Eighty Four, PA, USA).

1.2. Instrumentation

All chromatographic analysis was performed on an Agilent 1200 Series HPLC (Agilent Technologies, Santa Clara, CA, USA) with an autosampler, equipped with a diode array detector and Venusil XBP C_{18} reversed-phase column (5 μm × 4.6 mm × 250 mm). For instrumentation control and data analysis, Agilent 1200 Chemstation software (Agilent Technologies, Waldbronn, Germany) was used. Standard laboratory glassware and equipment, such as a rotary evaporator (Shanghai Yarong Biochemical Instrument Factory, Shanghai, China) and overhead shaker (Shanghai Yiheng Scientific Instruments Co., Ltd., Shanghai, China), were used in the extraction procedure. The personal air sampler was AirChek 2000 from SKC Inc. (Eighty Four, PA, USA). A knapsack electric sprayer was obtained from Chaoda Instrument Co., Ltd. (CD-16B, Taizhou, China).

1.3. Field experiment

1.3.1. Application conditions

One field experiment on imidacloprid application for wheat was conducted in Liaocheng City of Shandong Province. The climatic conditions were recorded as follows: the temperature was between 21 and 22°C, relative humidity 35%–37% and average southwest wind velocity 5 km/hr. The crop was 70–80 cm high. The spray liquid was prepared by dispersing 15 g of 15% imidacloprid SL in a hydraulic knapsack electric sprayer containing 15 L of water with a single cone nozzle operating at a typical working pressure 300,000 Pa. Two experienced local farmers (operator A: female, 45 years old; operator B: male, 48 years old) performed the field experiment as volunteers. The operators started spraying, using their usual technique, with no other instructions. With the lance in front of them, approximately

30 cm above the top of the crop, the operators swung the lance from side to side, walking forward into the spray aerosol. The treatment was finished after 15 min. Approximately halfway through the procedure, a 10–20 mL tank sample was sprayed into a bottle for the determination of the actual imidacloprid concentration in the field spray tank (FST) solution. Each sample was analyzed in triplicate. The typical field application scenario is presented in Fig. 1.

Another field experiment on imidacloprid application for wheat was conducted in Xinxiang City of Henan Province. The climatic conditions were recorded as follows: the temperature was between 25 and 26°C, relative humidity 48%–50% and average south wind velocity 2 km/hr. The crop was approximately 70–80 cm high. The spray liquid was prepared by dispersing 15 g of 15% imidacloprid SL in a hydraulic knapsack electric sprayer containing 15 L of water with a single cone nozzle operating at a typical working pressure of 300,000 Pa. The treatment was finished after 15 min. Two experienced local farmers (operator A: male, 50 years old; operator B: male, 46 years old) performed the field experiment as volunteers with a similar spraying technique as that used for wheat treatment in Liaocheng as discussed above.

1.3.2. Monitoring of potential dermal exposure

The most-frequently reported PDE sampling method in the literature is the surrogate skin technique, which includes the patch method (Durham and Wolfe, 1962; WHO, 1986; Soutar et al., 2000) and whole-body dosimetry (Fenske, 1993; Castro Cano et al., 2000). Compared with the patch method, whole-body dosimetry is more suitable because it is not necessary to assume uniform deposition or to extrapolate from small target areas to large body regions. As a result, the US EPA recommends that registrant studies be conducted using whole-body dosimetry to assess pesticide handler dermal exposure. In the present study, the PDE was measured using the whole-body dosimetry technique. As there were no 100% cotton coveralls commercially available, we designed a custom-made cotton coverall with hood and commissioned the processing in a specialized company. For this, a series of different cotton materials were tested in the laboratory for water retention and pesticide recovery. All the cotton coveralls had been prewashed in a conventional washing machine without detergent. Before the spraying application, the operators were dressed with the custom-made cotton coveralls, cotton gloves and disposable face masks. Following the pesticide application, the coveralls and gloves were removed carefully by assistants wearing new disposable nitrile gloves. The coveralls were then cut into nine sections each using clean scissors following the procedure described by Castro Cano et al. (2000) with slight modification (Fig. 2). The coverall sections as well as the gloves and the inhalation sampling tubes were packed individually in polythene bags adequately labeled and maintained in refrigeration until extraction and analysis. All the extractions were completed not later than 7 days after sampling collection.

Fig. 1 – Typical imidacloprid field application scenario in Liaocheng.

1.3.3. Monitoring of potential inhalation exposure

For the determination of potential inhalation exposure, a personal air sampling pump (SKC Inc., Eighty Four, PA, USA) was used, operating at a flow rate of 2 L/min, equipped with an OVS sampling tube using XAD-2 sorbent. The tube was located in the breathing zone of the operator and connected to the pump. Following the application, the tubes were closed with two plastic caps at either end and transported to the laboratory for analysis.

1.4. Analysis

1.4.1. Extraction procedure

The step-by-step extraction procedures of coverall sections, gloves and air sampling medium were as follows. The coverall sections and gloves were extracted with acetone in 1 L capacity closed bottles, 500 mL for piece numbers 1, 2, 3, 6, 7, 8 and 9, 700 mL for 4 and 5 and 150 mL for each glove. The air sampling medium was extracted with 20 mL of acetone. The extraction was placed in the overhead shaker for 30 min at 200 r/min. After extraction, the final mixture was evaporated to dryness and re-dissolved in 5 mL of methanol to ready it for HPLC analysis.

1.4.2. HPLC conditions

The optimized HPLC operating conditions were as follows: a mobile phase of methanol–water containing 0.1% formic acid (V/V, 40:60), flow rate of 0.8 mL/min, injection volume of 5 μL and detection wavelength at 270 nm.

1.4.3. Determination of imidacloprid in the sampling medium

A calibration curve derived from measurement of imidacloprid analytical standard solutions was used for the quantitative determination of contamination levels in the sampling medium. The calibration curve was plotted using a least-square regression technique on 7 points corresponding to seven concentration levels ranging from 0.05 to 56.0 mg/L. Thus, the residues in each sampling medium were calculated by Eq. (1):

$$c = (y - b)/a \quad (1)$$

where, c (mg/L) is the imidacloprid concentration in the concentrated sample (HPLC vial); y is the sample (imidacloprid) peak area; a is the slope of the linearity graph; and b is the intercept of the linearity graph. If the imidacloprid concentration c is beyond the linearity range, further dilution with methanol is necessary. The imidacloprid amount deposited on each sampling medium in micrograms (m, μg) is then calculated by Eq. (2):

$$m = c \times V \quad (2)$$

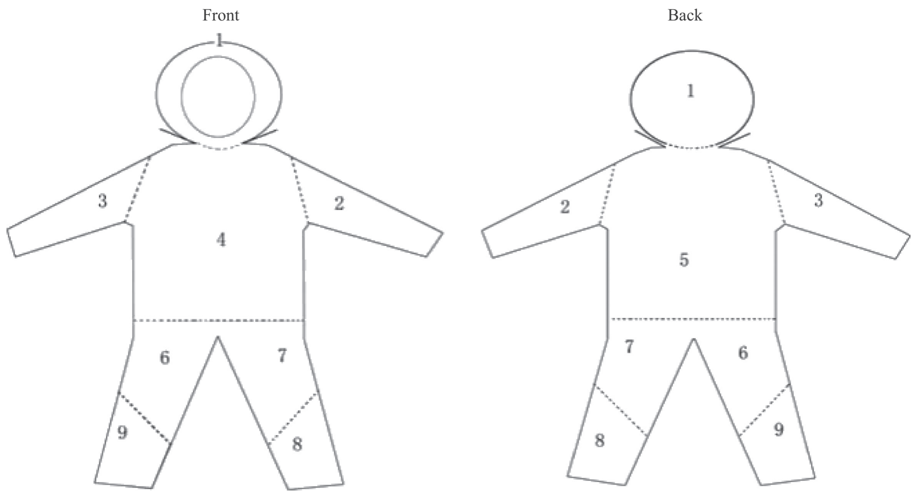

Fig. 2 – Coverall sectioning for whole-body dosimetry analysis. 1: head, 2: left arm, 3: right arm, 4: chest, 5: back, 6: right thigh, 7: left thigh, 8: left lower leg, 9: right lower leg.

where, V (mL) is final solution volume being ready for HPLC analysis.

1.4.4. Determination of imidacloprid in the FST and LST solutions

The FST and laboratory spray tank (LST) solutions were analyzed to determine the actual imidacloprid concentration. An aliquot of 1 mL of spray solution was transferred to a 10 mL volumetric flask and diluted to a constant volume with methanol for HPLC analysis.

1.5. *MOE calculation*

The MOE (US EPA, 2002) is defined as follows:

$$MOE_{total} = 1/(1/MOE_{dermal} + 1/MOE_{inhalation}) \quad (3)$$

$$MOE_{dermal} = POD_{dermal}/Exposure_{dermal} \quad (4)$$

$$MOE_{inhalation} = POD_{inhalation}/Exposure_{inhalation} \quad (5)$$

where point of departure (POD), traditionally the no observed adverse effect level, is used to mark the beginning of extrapolation for risk assessment with different endpoints. In this study, the imidacloprid POD values for both dermal and inhalation exposure were 0.057 mg/(kg·day), including the uncertainty factor 100 (US EPA, 2013a). $Exposure_{dermal}$ was obtained by multiplying the total potential dermal exposure (mg) resulting from the present study by the dermal absorption factor and then dividing by the body weight (kg) and one day. Determination of $Exposure_{inhalation}$ followed the same procedure. For imidacloprid, the dermal absorption factor (7.2%) and inhalation absorption factor (100%) were adopted (US EPA, 2013a). For all calculations, an average of 70 kg was considered for all workers.

2. Results

2.1. *Validation of the method*

The selectivity of the chromatographic methods was assessed by examination of peak purity using diode array detector. All the purity factors of imidacloprid peaks in the extract of the sampling medium, LST and FST solutions were within the set threshold limit 990.00, which indicates that the imidacloprid chromatographic peak was not attributable to more than one component.

Seven calibration working solutions were prepared from the stock solution by dilution with methanol. The detector response was linear for the imidacloprid concentration range 0.05–56.0 mg/L (r^2 = 0.9999).

Limit of detection (LOD) and quantification (LOQ) were determined as the lowest imidacloprid concentration injected that yielded a signal-to-noise (S/N) ratio of 3 and 10 respectively. For the present established method, the LOD and LOQ for imidacloprid were 0.02 and 0.05 mg/L, respectively.

The recovery and precision studies were carried out by spiking six replicates of each sampling medium (coveralls, sampling tubes and gloves) with LST solutions with three concentration levels, 3, 6 and 9 μg, of imidacloprid. The LST solutions were prepared from the commercial 15% imidacloprid SL at a concentration of 150.5 mg/L. The extraction and quantification methods used were the same as with that for the determination of the sampling medium. At the low concentration level, the percentages of recovery and precision (expressed as RSD% and supplied in parenthesis) were 86.26% (4.07), 87.25% (2.17) and 84.36% (2.49) for coveralls, sampling tubes and gloves, respectively. For the middle concentration level, the values were 87.63% (2.71), 90.09% (2.33) and 92.93% (1.22), respectively, whereas for the highest concentration levels, the values were 92.60% (1.83), 97.97% (1.33) and 93.45% (0.91), respectively.

2.2. *Potential dermal and inhalation exposure*

During the analysis procedure, the real exposure amount expressed in weight units (μg) was calculated first. The exposure values were related to the duration of each application. Thus, normally the potential dermal and inhalation exposures of pesticide found are expressed as mL/hr (mL of spray solution deposited on sampling media per hour of application). The average imidacloprid concentrations in the field spray tank for two trials performed in Liaocheng were 145.2 and 148.5 mg/L, respectively. In the two Xinxiang trials, these values were 151.4 and 152.3 mg/L, respectively.

The coveralls were sectioned in nine pieces, along with gloves and air sampling medium to obtain the distribution of the contamination over the body. The levels of potential dermal and inhalation exposure to applicators in Liaocheng are presented in Table 1. As seen, the total potential dermal and inhalation exposure was 14.20 and 16.80 mL/hr, respectively, for the two trials. These amounts correspond to 0.02% of the applied volume of spray solution. The amount of spray solution reaching the lower part (thigh, lower leg) of the body was much higher than the amount reaching the upper part (head, chest, back and arm) in both trials, accounting for 79% and 76%, respectively, of the total exposure to the insecticide. Considering the upper body, the back of both operators was found to be the most exposed, with 8.7% and 10% of the total exposure.

The levels of potential dermal and inhalation exposure to applicators in Xinxiang are presented in Table 2. Because of the similar crop height and density, spray application technique and operators' experience, the exposure distribution was quite similar to that in for the Laiocheng application study. The total potential and inhalation exposure were 15.39 and 20.78 mL/hr, respectively, for the two trials, corresponding to 0.02% and 0.03% of the applied volume of spray solution. Exposure of the lower body represented 88% and 77%, respectively, of the total exposure. The exposure of the right hand of the operator B was abnormally high, reaching 2.96 mL/hr with 14% of the total exposure. This may be due to a leak in the hand lance as well as to an accidental spill in this trial.

A very interesting phenomenon is lateralization. There was greater exposure on the right half of the body in both cases, especially for hand exposure. Considering the arm, thigh, lower leg and glove, the exposures measured on the right half of the body for the four operators were 49%, 50%, 53% and 61%, respectively, of the total exposure, whereas for the left half of the body, the corresponding contributions were 36%, 37%, 43% and 35%, respectively.

The potential inhalation exposures of the two operators in Liaocheng application were determined to be only 0.05 and 0.04 mL/hr, respectively, based on the ventilation rate of 2 mL/min. These amounts correspond to 0.3% and 0.4% of the total exposure. In the Xinxiang application, however, inhalation exposure was not detected for either of the two operators. These results are in accordance with the opinion of Machado-Neto (2001), who mentioned that ≥99% of the total exposure occurs *via* the dermal route.

The MOE calculation results for the exposure risk analysis are presented in Table 3. In the present scenarios, the total deposition on the exterior dosimeter was considered to be very conservative and the worst case of dermal exposure for risk refinement. All the MOEs for dermal and inhalation were far greater than the target MOE 100, which indicates that the single-case exposures under the present scenarios were safe.

3. Discussion

The analytical methodology applied for the qualitative and quantitative determination of imidacloprid was fully validated, including LOD/LOQ, linearity, recovery and precision assays, to ensure that the results were statistically controlled. A possible matrix effect on the analytical parameters from different media types was studied using LST solution containing the same ingredients as the FST solution. The average recoveries ranged from 84% to 98%, and the RSD% ranged from 0.9 to 4.1, indicating no obvious detection of a matrix effect for the different three matrices (coveralls, sampling tubes and gloves) for the present analytical method.

The level of operator exposure is known to be very variable, depending on many different factors. These variables critically affect the amount of pesticide that comes into contact with the operator's body. In both the Liaocheng and Xinxiang trials, the lower-body exposures were much higher than those of the upper body. This could be due to the wheat height (70–80 cm) and density or the operator's movements, as they all walked forward, moving into the spray cloud, and also had frequent contact with the recently sprayed very dense foliage and stalks. The dramatic influence of crop type (maize, broccoli, apple,

Table 1 – Potential dermal and inhalation exposure to imidacloprid in Liaocheng field spray trial.

Body region	Operator exposure					
	Op. A (μg)	Op. A (mL/hr)	Op. A [a] (%)	Op. B (μg)	Op. B (mL/hr)	Op. B [a] (%)
Head	4.76	0.14	1.0	6.25	0.18	1.1
Chest	24.50	0.72	5.1	12.14	0.35	2.1
Back	41.87	1.24	8.7	58.25	1.68	10.0
Left arm	3.83	0.11	0.8	10.25	0.30	1.8
Right arm	7.06	0.21	1.5	14.58	0.42	2.5
Left thigh	74.04	2.19	15.4	95.56	2.76	16.4
Right thigh	94.84	2.80	19.7	114.32	3.30	19.6
Left lower leg	89.47	2.64	18.6	100.45	2.90	17.3
Right lower leg	120.70	3.56	25.1	135.21	3.90	23.2
Left glove	6.79	0.20	1.4	8.54	0.25	1.5
Right glove	11.62	0.34	2.4	24.21	0.70	4.2
Inhalation	1.67	0.05	0.3	2.35	0.07	0.4
Total	481.15	14.20	100.0	582.11	16.80	100.0

Op. A: operator A; Op. B: operator B;
[a] Relative contribution (%) of each part of the body in the total potential dermal and inhalation exposure.

Table 2 – Potential dermal and inhalation exposure to imidacloprid in Xinxiang field spray trial.

Body region	Operator exposure					
	Op. A (μg)	Op. A (mL/hr)	Op. A [a] (%)	Op. B (μg)	Op. B (mL/hr)	Op. B [a] (%)
Head	2.92	0.09	0.6	1.04	0.03	0.1
Chest	4.1	0.12	0.8	6.03	0.17	0.8
Back	14.58	0.44	2.9	26.14	0.74	3.5
Left arm	10.11	0.31	2.0	13.27	0.37	1.8
Right arm	13.36	0.41	2.6	9.12	0.26	1.2
Left thigh	88.95	2.71	17.6	95.74	2.69	13.0
Right thigh	107.29	3.27	21.2	130.75	3.68	17.7
Left lower leg	112.66	3.43	22.3	140.59	3.96	19.0
Right lower leg	135.16	4.12	26.8	204.34	5.75	27.7
Left glove	5.21	0.16	1.0	6.25	0.18	0.8
Right glove	10.54	0.32	2.1	105.24	2.96	14.2
Inhalation	<LOD	<LOD	0	<LOD	<LOD	0
Total	504.92	15.39	100.0	738.61	20.78	100.0

[a] Relative contribution (%) of each part of the body in the total potential dermal and inhalation exposure.

cucumber, green pepper and paddy) on the exposure amount and distribution has recently been investigated (Hughes et al., 2008; Choi et al., 2013). The total exposures, mainly originating from contact with sprayed foliage, are closely related with the spray liquid deposition efficiency on crop leaves. The low critical surface tension of wheat leaf, 36.9 mN/m, makes the wetting and spreading of the spray droplets on wheat leaves difficult (Gu et al., 2002), which obviously affects the retention of spray liquid. As a consequence, the total exposures of the four operators in Liaocheng and Xinxiang of 14.20, 16.80, 15.39 and 20.78 mL/hr, respectively, were relatively low.

The higher contamination of the right half the body than that of the left one can be attributed to the fact that the operators held the spray lance with the right hand, therefore, the spray was closer to the right half of the body. In addition, any leaks from the lance, trigger handle and hose were generally over the right half of the body.

The hand exposure merits considerable consideration because of the fact that hands are always indispensable to the manipulation of the spray application, which increases the contact risk of hands to pesticide. Hand exposure is dramatically spray application technique- and treated-plant-dependent. The hand exposure can vary from 1.4% to 58% of the total exposure when the spray application technique is switched from spray gun to Fumimatic (Nuyttens et al., 2009). The hand exposure can also change from 3.1% to 35% when the treated plants are changed from apple to green pepper plants (Choi et al., 2013). In the present wheat field application, the left and right hands were all above the top of the crop, resulting in the hands having less contact with the sprayed foliage. Most sources for hand exposure came from spray droplets in the air and any leaks that can come into contact with hands. In the Liaocheng application, the hand exposures were 3.8% and 5.7%, respectively, of the total exposure for the two operators, whereas in Xinxiang, operator A had 3.1% exposure, and operator B displayed a marked increase to 15%. The reasons for this abnormality, *i.e.*, the leak in the sprayer lance and the accidental spill, appear to reflect common farm practices, where heavy hand contamination is often the case due to general worker carelessness and the resulting poor maintenance of the application equipment.

Table 3 – The calculation results of margin of exposure for four operators to imidacloprid exposure.

Operator	Liaocheng		Xinxiang	
	Op. A	Op. B	Op. A	Op. B
MOE_{dermal}	11558	9559	10975	7503
$MOE_{inhalation}$	2.4×10^6	1.7×10^6	ND	ND
MOE_{total}	11024	9049	10975	7503

ND: Not determined.

Concerning the upper body, the back was the most contaminated section, with 8.7% and 10% of the total exposure for the two operators in Liaocheng. Back contamination was partly caused by sprayer tank leaks as a consequence of incorrect assembly and checking of the equipment before use. During outdoor wheat spray application, the major chest and head exposures come from contact with the spray droplets in front of the operator. Therefore, wind velocity and direction can obviously affect the head and chest exposure. In the Liaocheng and Xinxiang applications, the wind velocity was 5 and 2 km/hr, respectively. For the first half of the application, operators walked with the wind, and for the second half of the application, the operators turned around and walked against the wind. As a result, all the head, chest and back exposures increased in Liaocheng compared with those in Xinxiang due to the greater wind speed.

Potential inhalation exposure occurs when airborne spray droplets or vapor is present in working areas. The amount of inhalation exposure in Liaocheng corresponded to 0.3% and 0.4% of the total exposure, whereas in the Xinxiang application, inhalation exposure of the two operators was not detected. The very low contribution of inhalation exposure can be attributed to low spray droplet concentration in the breathing zone of the operator due to the low application pressure (300,000 Pa) and outdoor application. On the contrary, higher inhalation exposure occurs indoors (greenhouse) because of the closed system. The climatic conditions can also affect the inhalation exposure.

The wind velocity in Liaocheng (5 km/hr) was higher than that in Xinxiang (2 km/hr). The spray droplets could last a longer time in air and have a greater tendency to remain in the breathing zone of the operator due to blowing wind. As a consequence, the inhalation exposure in Liaocheng was higher than that in Xinxiang.

In addition to the objective factors, the operator's application experience plays an important role in exposure assessment. During captan application, an inexperienced operator was 13–17 times more contaminated than a more experienced one (Hughes et al., 2006). In the present study, all four operators are local farmers with years of spray experience who have established spray habits. Thus, the exposure amount and distribution pattern over the body were more or less similar. Abnormal exposure is always the result of an accidental splash or spray tank solution liquid leak. Therefore, regular checking and maintenance of the spray equipment is necessary to avoid unexpected exposure.

In the United States, the Environmental Protection Agency utilizes the unit exposures (UE) as the basis for assessing handler exposures to pesticides. The UE are expressed as mass of pesticide active ingredient (ai) exposure per unit mass of ai handled (*e.g.*, μg/lb ai). The UE under different scenarios referring to a specific type of application equipment, formulation type, job function, and level of personal protective equipment (PPE) can be listed on the "Occupational Pesticide Handler Unit Exposure Surrogate Reference Table" (US EPA, 2013b). The US EPA then uses these UE generically, irrespective of chemical identity, to estimate the exposure for each pesticide used in the scenario for calculation of average daily dose. In China, occupational pesticide exposure research is just at the very beginning, and a corresponding database is absent. In the present study, only an exterior dosimeter was used to mimic the very conservative and worst dermal exposure case. The UEs calculated from the backpack spray application in this study ranged from 1.0×10^5 to 1.5×10^5 μg/lb ai, which are beyond the maximum UE for a backpack spraying scenario from the UE database (US EPA, 2013b). However, if appropriate PPE was used, the UE value would decrease markedly and fall into an acceptable UE range.

For exposure risk assessment, the dermal and inhalation absorption factors are crucial. There is no such information available about imidacloprid. Recently, the European Food Safety Authority Panel on Plant Protection Products and their Residues agreed on dermal absorption values of 0.3% for the concentrate and 8% for the diluted formulation based on an *in vitro* study on human skin with Confidor OD 200, with a default value of 100% for Gaucho FS 600 (EFSA, 2008). The US EPA suggests 7.2% for dermal absorption (US EPA, 2013a). In this study, the dermal absorption value of 7.2% and inhalation absorption value of 100% were adopted. With this valuable information in hand, the MOE could be easily calculated. The MOE values for the four operators in Liaocheng and Xinxiang are presented in Table 3. All the MOEs were much higher than the target 100, indicating that all activities can be considered safe in terms of imidacloprid exposure. Even if the conservative 100% dermal absorption was used, the MOEs were still greater than 100. The present MOE obtained described the situation of a single backpack. For those situations in which more than one backpack would be necessary, the MOE is extrapolated by dividing the present MOE value by the number of backpacks applied. In this sense, the MOE is inversely proportional to the number of applied backpacks.

4. Conclusions

A whole-body dosimetry method to analyze the potential dermal and inhalation imidacloprid exposure using custom-made cotton coveralls, an air sampling medium and cotton gloves have been proposed based on trials carried out in Liaocheng and Xinxiang. The analytical method was validated, and performance parameters established using blank sampling media spiked with LST solutions indicated no obvious matrix effect on the present analytical methodology. In both field trials, under the present typical wheat treatment scenarios, the lower body exposure was much higher than that of upper body and the inhalation exposure was less than 1% of the total exposure. Factors such as application pattern, crop height, density and foliage surface characteristics, spray equipment, operator experience and climatic conditions were used to explain the total and distribution of the exposure on the different parts of the body. As indicated by the calculated MOEs, which are far greater than the target MOE 100, these single-case imidacloprid exposures under the present typical wheat treatment scenarios are considered to be very safe. When the exposure scenario parameters, such as application duration, environmental conditions and aptitude of the applicator, are changed, the methodology developed can be utilized for imidacloprid exposure risk assessment. In addition, it is important to note that this research can further bring pesticide exposure to the forefront of pesticide risk assessment and attract greater attention to this field, which has recently begun in China.

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