Dermal Exposure of Applicators to Chlorpyrifos on Rice Farms in Ghana

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ABSTRACT

Studies evaluating dermal exposure to pesticides among applicators in tropical countries have largely been conducted using the patch dosimetry and hand wiping/washing techniques. This study used the more accurate whole-body dosimetry technique to evaluate dermal exposure to chlorpyrifos among applicators on rice farms in Ghana. The exposure levels were plotted as Cumulative Probability Distribution (CPD). Total Dermal Exposure (TDE) of chlorpyrifos among the median exposed and the 5% highly exposed groups during a spray event were 24 mg and 48 mg, respectively. When these were converted as a percentage of the quantity of active ingredient applied (Unit Exposure, UE), UE values of 0.03% and 0.06% were found among the median exposed and the 5% highly exposed groups, respectively. Overall, the hands were the most contaminated anatomical regions of the applicators, both in terms of proportion of TDE (39%) and skin loading (13 $\mu\text{g}/\text{cm}^2$). Also, the lower anatomical region was more contaminated (82% of TDE) compared to the upper anatomical region (18% of TDE). The levels of chlorpyrifos TDE among the applicators were found to be influenced by the quantity of insecticide applied and the height of the crops sprayed ($p < 0.05$). The pesticide UE data of the present study can be used to estimate the levels of dermal exposure under similar pesticide

use scenarios among applicators. The findings of the present study suggest that protecting the hands and the lower anatomical regions with appropriate PPE may significantly reduce exposure among applicators.

Key Words: dermal exposure, chlorpyrifos, pesticides, whole-body dosimetry, Ghana

1. INTRODUCTION

The dermal route generally constitutes the major exposure pathway for agricultural pesticide applicators (Van Hemmen and Brouwer, 1995; Vitali *et al.*, 2009; Fenske *et al.*, 2012; Macfarlane *et al.*, 2013). Studies on dermal pesticide exposure are needed to enhance understanding of the contribution of the dermal route to total exposure, the patterns of dermal exposure, as well as help to identify effective exposure prevention and control strategies (Leckie and James, 1998; Marquart *et al.*, 2001).

Pesticide applicators in tropical countries do not usually use Personal Protective Equipment (PPE) during pesticide application activities, mainly due to the discomfort associated with the use of PPE under hot and humid climatic conditions (Clarke *et al.*, 1997; Adjrah *et al.*, 2013; Jepson *et al.*, 2014). Also contributing to the limited use of PPE in most tropical countries are financial constraints and inaccessibility of PPE (Clarke *et al.*, 1997; Issa *et al.*, 2010; Stadlinger *et al.*, 2011). Consequently, these applicators are more vulnerable to dermal exposure than their counterparts in temperate countries. In addition, under tropical conditions applicators easily sweat, which may enhance dermal absorption of pesticides (Williams *et al.*, 2004; Blanco *et al.*, 2005).

Studies have been conducted in some tropical countries to evaluate dermal exposure to chlorpyrifos, a commonly used insecticide, among applicators (Farahat *et al.*, 2010; Pan and Siri Wong, 2010; Syamimi *et al.*, 2011; Fenske *et al.*, 2012; Lappharat *et al.*, 2014). Generally, these studies have employed the patch dosimetry (Farahat *et al.*, 2010; Fenske *et al.*, 2012; Lappharat *et al.*, 2014) or hand wiping (Pan and Siri Wong, 2010) techniques. The patch

dosimetry technique involves extrapolation from the level measured on a patch to the whole body, thus exposure may be incorrectly estimated. Similarly, the hand wiping technique does not account for exposure on other parts of the body. Whole body dosimetry provides a more accurate means of evaluating dermal exposure to pesticides because it does not involve extrapolation

Only Syamimi *et al.* (2011) has employed the whole body dosimetry technique to evaluate chlorpyrifos exposure in a tropical country, where spraying practices differ from more temperate climates. While Syamimi *et al.* (2011) focused on the patterns of dermal exposure, the present study applied the whole-body dosimetry to investigate a broad range of parameters regarding dermal exposure to chlorpyrifos. Also, the present study involved a relatively larger number of subjects and thus allowed a probabilistic evaluation of the levels of dermal exposure. The objectives of the present study were to evaluate the magnitude, patterns and determinants of dermal exposure to chlorpyrifos among applicators on rice farms in Ghana, a tropical country where use of chlorpyrifos is high and use of PPE is limited.

2. METHODS

2.1 Study Area and Participants

The study was conducted among applicators ($n = 24$) growing rice with irrigation from a typical farming community in the southern part of Ghana, where small scale farming is the main source of livelihood. The use of pesticides to control farm insect pests was predominant, with chlorpyrifos being one of the commonly used insecticides. Participants for the study were selected among 214 farmers who had previously taken part in a pesticide-use survey in the study area and had expressed interest in the present study. The pesticide spraying schedules of the potential participants were obtained and those with schedules coinciding with the sampling period of the present study were included in the study. The protocol for the study was reviewed and approved by the Ghana Health Service Ethical Review Committee (GHS-ERC: 10/07/15) and Griffith University Human Ethics Committee (GU Ref. No: ENV/24/15/HREC). The approved protocol, detailing the study objectives, activities, and rights of the participants was explained to the participants in both the local and English languages prior to recruitment. Written informed consents were obtained from those that volunteered to take part in the study.

2.2 Field Observations and Pesticide Application Method

Data for the study were collected between December, 2015 and January, 2016. It involved a single pesticide spraying event for each applicator on each separate occasion. During each spray event, field factors were observed and documented. The information collected included PPE usage, type of clothing worn, duration of spraying, quantity of insecticide applied, crop height, farm size, as well as incidences of spills, and leakages. The applicators were asked to carry out their pesticide spraying activities the normal manner. Chlorpyrifos (Dursban - 480g/L Emulsifiable Concentrate) was the insecticide applied, using hand-pressurized knapsack

spraying devices that were carried on the back. The sprayings were done with the lance positioned in front of the applicators while they walked forward through the area being sprayed. The spraying activities were all carried out in the morning between the hours of 6 to 8 am. The applicators preferred to spray in the morning, when the temperature was cooler. By observation, there was no significant variation in the weather conditions that could impact the exposure levels that was investigated.

2.3 Dermal Sampling Procedure

Dermal sampling was based on the protocols of the World Health Organisation (WHO, 1982) and Organisation for Economic Co-operation and Development (OECD, 1997). On the day of spraying, each applicator was given a new set of Tyvek under-wear garment made of flash-spun, high-density polyethylene (DuPont™ Tyvek®), white cotton hand gloves, and socks. These sampling media were worn by the applicators with their usual farm clothes worn over the sampling media before beginning any pesticide spraying activity. The purpose of this sampling procedure was to capture pesticide residues that penetrated applicators' clothing during spraying activities and potentially reaching their skin, as well as residues adhering to body areas of the applicators not covered by their farm clothing. These exposed areas included the face, neck, hands and feet. Tyvek under-wear garments and cotton sampling media have been found to satisfactorily trap and retain chlorpyrifos-methyl (Castro Cano *et al.*, 2000) and other organophosphate insecticides (Castro Cano *et al.*, 2001; Machera, 2003).

Immediately after spraying, the Tyvek underwear garment and the rest of the sampling media were carefully removed from the applicators and dissected into nine anatomical regions (Figure 1). The head, front abdomen, back abdomen, upper arms, lower arms, hands, upper legs, lower

legs, and the feet were labelled as 1, 2, 3, 4, 5, 6, 7, 8, and 9, respectively. The face and neck of each applicator were wiped with 2 pieces of 8-ply dry sterile surgical cotton gauze (10 cm by 10 cm) and added to the sampling media of the head section (anatomical region 1). Each section was folded, wrapped with aluminium foil, placed in a pre-labelled zip-lock plastic bag and then kept in an ice chest packed with ice, away from direct sunlight. The label on the bag consisted of the code of the applicator, anatomical region, and the date of sampling. The samples were transported to the laboratory within one hour and stored at -25°C until analysed.

Figure 1: Tyvek Under-wear Garment, Hand Gloves and Socks Sectioned into Nine Anatomical Regions.

2.4 Extraction of Tyvek Under-wear Garments, Cotton Hand Gloves, Socks and Gauze

The extraction and analysis of the samples for chlorpyrifos were carried out at the Pesticide Residues Laboratory of Ghana Standards Authority, using a modified version of the analytical methods for agricultural chemicals of Japan's Department of Food Safety (Department of Food Safety, 2006). The pesticide sampling media (Tyvek garments, cotton hand gloves, socks and gauze) were placed in pre-washed glass bottles of various volumes depending on the size of the sampling media. Pesticide grade ethyl acetate (Fisher Scientific, UK) (150mL to 1,150mL) was then added to each sample until fully submerged. The bottles were placed in ultrasonic water bath (Decon FS400B) and sonicated for 45 minutes at room temperature (25°C). The extracts were then filtered with anhydrous sodium sulfate (5g) (Glass World, South Africa). Aliquots of the extract (70 to 200mL, depending on the quantity of the initial volume) were taken and concentrated with a rotary evaporator (Büchi Rotavapor R-210, USA) at 39°C at 79 mbar to dryness. The residues were redissolved with ethyl acetate (1 mL) and transferred to vials (2 mL) for Gas Chromatography (GC) analysis. After sectioning, the dermal samples obtained from 20 of the applicators (Table 1) were analysed as one composite sample for each applicator, while samples from the remaining four applicators (Table 1; Applicator 1 or A, 2 or B, 9 or C, and 10 or D) were analysed separately according the anatomical regions shown in Figure 1.

2.5 Analysis for Chlorpyrifos

A Varian CP 3800 Gas Chromatograph (Varian Associates Inc, USA) equipped with Pulsed Flame Photometric Detector (PFPD) and a CombiPAL auto sampler was used for the analysis. Chromatographic separations for chlorpyrifos were performed with a capillary column coated with VF-1701ms (30 m, 0.25 mm, 0.25 µm film thickness). The carrier gas was nitrogen at a

flow rate of 2.0 mL/min, while hydrogen (14 mL/min), air 1(17 mL/min) and air 2 (10 mL/min) were used for the detector. The injector (splitless mode) and PFPD temperatures were held at 270°C and 300°C, respectively. The column oven temperature was programmed as follows: 70°C for 2 minutes, increased steadily at a rate of 25°C/minutes to 200°C, then at 20°C/minutes up to 250°C and held for 4.3 minutes. The injection volume was 2.0 µL and the total run time for each sample was 15 minutes. Instrument control, data acquisition and processing were done with the Star Chromatography Workstation software (Version 6.4.1).

Chlorpyrifos standard (Dr. Ehrenstorfer GmbH, Germany) calibration mixtures were prepared for PFPD detection at six concentration levels in ethyl acetate (0.01, 0.02, 0.05, 0.10, 0.50 and 1.0 mg/L). These were run in the GC to obtain their corresponding peak areas. The calibration mixtures with the corresponding peak areas were used to derive a calibration curve with R^2 value of 0.99. The peak areas of the samples were used to calculate the respective concentrations. Further dilution of the extracts was done, when appropriate, to ensure that the concentrations were within the linear range of the calibration curve. The concentration of chlorpyrifos in each extract and the final solution volume after preparation for GC analysis were used to calculate the mass of chlorpyrifos residues in the sampling media.

Sample matrices were spiked with standard chlorpyrifos at 0.05 mg/L and analyzed with each extraction batch. The recovery rates (%) from the spiked matrices were 94%, 88%, 88%, and 96%, for Tyvek garment, cotton socks, cotton hand gloves, and cotton gauze, respectively.. The quantities of chlorpyrifos obtained were adjusted based on the recoveries of the spiked samples. The Limit of Detection (LOD) and Limit of Quantification (LOQ) were determined using the formulae, $LOD = S \times t$ and $LOQ = S \times 10$, where, S is the standard deviation of the

replicate analysis, and t , the student's t -value for the 99% confidence interval with $n-1$ degrees of freedom (Wisconsin Department of Natural Resources, 1996; USEPA, 2012). The limit of detection and limit of quantification were determined to be 0.005 mg/L and 0.01 mg/L, respectively.

2.6 Quality Control

Quality control and quality assurance measures consisted of solvent blanks, matrix blanks, and standards which were analyzed alongside each extraction batch and found to be satisfactory. To ensure high laboratory testing and calibration standards, the Pesticide Residues Laboratory of Ghana Standards Authority, where the laboratory analysis of the present study was carried out, participates in international accreditation schemes. It is ISO/IEC 17025:2005 compliant and accredited by Deutsche Akkreditierungsstelle GmbH (DAKKS) for analysis of organophosphate insecticides including chlorpyrifos, with certificate No. D-PL-15209-01-02.

2.7 Calculation of the Applicators Exposure to Chlorpyrifos

The magnitude of dermal exposure was measured by three parameters: Total Dermal Exposure (TDE, mg), Unit Exposure (UE, % active ingredient handled), and Skin Loading (SL, $\mu\text{g}/\text{cm}^2$ of skin area). TDE was calculated as the sum of the chlorpyrifos obtained from all sections of the body (head, front abdomen, back abdomen, upper arms, lower arms, hands, upper legs, lower legs, and the feet) for each applicator. To determine the proportion of the active ingredient that the applicators were exposed to, UE was calculated by expressing TDE as a percentage of the quantity of Active Ingredient (AI) applied by each applicator [$\text{UE \%} = (\text{TDE mg} / \text{AI mg}) * 100$]. SL was calculated to evaluate the level of exposure per unit skin area by expressing TDE for each anatomical region as a ratio to the skin surface area of the respective

anatomical region. The average skin surface areas of the anatomical regions determined and applied were as follows: head (1,200 cm²), front abdomen (3,950 cm²), back abdomen (3,950 cm²), upper arm (1,700 cm²), lower arm (1,200 cm²), hands (680 cm²), upper legs (2,300 cm²), lower legs (2,000 cm²), and feet (750 cm²).

2.8 Data Analysis

Descriptive statistics such as frequencies, means and ranges were determined to summarize the field factors. TDE and UE, were described with Cumulative Probability Distribution (CPD) plots, which were obtained using Microsoft Excel. The Cumulative Probabilities (CPs) of TDE and UE values were calculated using the equation below, after ranking the data points from the lowest to the highest:

$$CP (\%) = (i/n+1) \times 100 \quad \text{Equation 1}$$

where, CP is cumulative probability (%), i, the ith point and n, the total number of data points.

CPD plots allow the flexibility of determining the exposure level at any percentile of interest. Also, with the use of the Statistical Package for the Social Sciences (SPSS) (Version 20), the association between TDE and independent variables were assessed with independent t-test.

3. RESULTS AND DISCUSSION

3.1 Observed Field Factors during Application

All of the applicators were male aged between 23 to 53 years (mean, 40 years). Fifty eight percent of the applicators were educated up to Junior High School (JHS) level, whereas the rest (42%) had education above this level. The applicators had used insecticides for between 5 and 32 years with a mean of 16 years.

The observed field factors during application are outlined in Table 1. The majority of the applicators (54%) had received training on pesticide safety from Ghana's Ministry of Food and Agriculture and/ or non-governmental organisations through seminars. Short sleeve shirts with long trousers made with cotton were the predominant form of apparel (58%). Only one applicator (4%) used any form of PPE. This consisted of safety glasses to protect the eyes. Incidences of pesticide leakage and spillage were recorded among 63% and 83% of the applicators, respectively. The farm size and the height of crops sprayed ranged from 0.2 to 1.0 ha (mean, 0.5 ha) and 10 to 85 cm (mean, 42 cm), respectively. The duration and insecticide quantity during one spray event ranged from 21 to 110 minutes (mean, 57 minutes) and 100 to 325 mL (mean, 182 mL), respectively.

Table 1: Observed Field Factors during Spraying of Rice Crops with Chlorpyrifos by Applicators in Ghana

Applicator ID	Trained on pesticide safety	Type of Shirt*	Type of PPE	Leaky tank	Spillage	Farm size(ha)	Crop height(cm)	Quantity of Insecticide (mL)	Spraying Duration(min)
1 or A**	Yes	Short sleeved	None	No	Yes	1.0	80	275	85
2	Yes	Long sleeved	None	No	Yes	0.2	65	100	24
3 or B**	Yes	Short sleeved	None	Yes	No	0.9	50	300	83
4	No	Short sleeved	None	No	No	0.3	16	100	21
5	No	Short sleeved	None	No	Yes	0.5	20	150	47
6	Yes	Short sleeved	None	Yes	No	0.9	50	300	110
7	Yes	Short sleeved	None	No	No	0.6	15	150	50
8	Yes	Long sleeved	None	No	Yes	0.3	60	200	27
9 or C**	Yes	Long sleeved	None	No	Yes	0.4	12	125	44
10 or D**	No	Short sleeved	None	Yes	Yes	0.9	30	275	82
11	Yes	Short sleeved	None	Yes	Yes	0.5	40	150	48
12	Yes	Long sleeved	None	Yes	Yes	0.2	55	200	21
13	No	Long sleeved	None	No	Yes	0.2	35	100	21
14	Yes	Long sleeved	Safety glasses	No	Yes	0.5	60	150	55
15	No	Short sleeved	None	Yes	Yes	0.8	65	325	94
16	No	Short sleeved	None	No	Yes	0.3	30	150	45
17	No	Short sleeved	None	No	Yes	0.8	65	150	75
18	No	Short sleeved	None	No	Yes	0.4	10	100	69
19	No	Short sleeved	None	Yes	Yes	0.3	85	200	36
20	Yes	Long sleeved	None	No	Yes	0.4	45	150	47
21	No	Long sleeved	None	Yes	Yes	0.4	45	150	44
22	Yes	Long sleeved	None	Yes	Yes	0.4	35	200	51
23	No	Short sleeved	None	Yes	Yes	0.4	20	163	69
24	Yes	Long sleeved	None	No	Yes	0.8	30	200	110
Summary	Yes (54%) No (46%)	Long sleeved (42%) Short sleeved (58%)	Used PPE (4%) No PPE (96%)	Yes (63%) No (37%)	Yes (83%) No (17%)	Mean (0.5) Range (0.2-1.0)	Mean (42) Range (10-85)	Mean (182) Range (100-325)	Mean(57) Range (21-110)

0 * All of the applicators wore long pants.

1 ** A,B,C, and D - The four applicators whose samples were analysed separately according the body sections shown in Figure 1 with dermal exposure in Table 2.

3.2 Total Dermal Exposure and Unit Exposure

The Cumulative Probability Distribution (CPD) plots of TDE and UE values of chlorpyrifos found with the applicators studied are provided in Figure 2 (A and B). The linear part of the CPD plots of environmental pollutant levels, when normal distribution occurs, is usually determined to lie between 20% or below (lower bound) and 80% or above (upper bound) of the CPD (Edokpolo *et al.*, 2015; Sadler *et al.*, 2016). In this study the linear part of the CPD for TDE and UE were determined to be between 4% - 96% and 12% - 88% of the CPD, respectively, based on the coefficient of determination (R^2) values. The corresponding regression equation for the linear part of the CPD plots, respectively were:

$$CP (\%) = 150\log TDE - 156 \quad (R^2 = 0.94) \quad \text{Equation 2}$$

$$CP (\%) = 189\log UE + 340 \quad (R^2 = 0.99) \quad \text{Equation 3}$$

Figure 2A shows that TDE at the 50th percentile cumulative probability (CP₅₀) was 24 mg, while TDE at the 95th percentile cumulative probability (CP₉₅) was 48 mg. Likewise, Figure 2B indicates that the UE value at CP₅₀ and CP₉₅ were 0.03% and 0.06%, respectively. CP₅₀ is the level of exposure among the median exposed group, whereas CP₉₅ is the level of exposure among the 5% most highly exposed group.

The UE values (0.01 – 0.06%) from the present study is similar to reported UE values (Choi *et al.*, 2013; Moon *et al.*, 2013) ranging from 0.01 – 0.04% and 0.01 - 0.05%, respectively, during the application stage. Choi *et al.* (2013) evaluated the UE values from imidacloprid exposure among applicators who sprayed green pepper, cucumber, rice and apple crops, while Moon *et*

al. (2013) evaluated fenvalarate exposure among applicators who sprayed apple crops. However, during the mixing and loading stage, both Choi *et al.* (2013) and Moon *et al.* (2013) reported lower UE values (0.001 to 0.008% and 0.001 to 0.002%, respectively). This implies that the exposure levels during the mixing and loading stage were less than those during the application stage. It is noteworthy that, unlike the studies conducted by Choi *et al.* (2013) and Moon *et al.* (2013), the UE values obtained in the present study were for both mixing/loading and spraying stages.

Figure 2: Cumulative Probability Distribution Plot of Total Dermal Exposure (A) and Unit Exposure (B) of Chlorpyrifos with Applicators on Rice Farms in Ghana.

In contrast to the findings of the present study, a relatively higher UE value (0.10%) has been reported by An *et al.* (2015) in a study conducted among applicators who sprayed cucumbers in greenhouses with chlorpyrifos and chlorothalonil. The differences in the UE values between the study by An *et al.* (2015) and the present study could be due to the different types of knapsack sprayers used by the applicators in the two studies. Whereas hand-pressurized knapsack sprayers were used by applicators in the present study, the applicators in the study by An *et al.* (2015) used powered knapsack sprayers. Powered knapsack sprayers usually produce higher spray pressure and could therefore lead to higher levels of exposure on applicators.

Information on UE values of pesticides in different handling scenarios from the USA and Canadian pesticide field conditions have been used by the United States Environmental Protection Agency (USEPA) and Health Canada to develop a Pesticide Handlers Exposure Database (PHED)(Nielsen *et al.*, 1995). The database has two main assumptions: (1) exposure is proportional to the quantity of AI applied; and (2) exposure dose depends mainly on the method of application and the formulation type, but not the physico-chemical properties of the AI applied (Sielken Jr, 2005; Beauvais *et al.*, 2007). However, the second assumption regarding physico-chemical properties is only valid for AIs with vapour pressures below 7.5×10^{-4} mmHg(1×10^{-4} kPa) for outdoor use at 20 to 30°C (Norman, 2005). These include chlorpyrifos, which has a vapour pressure of 1.0×10^{-3} Pa at 25°C (WHO, 2009). Using the PHED and more recent databases such as the Agricultural Handlers Exposure Database (AHED), the USEPA has created an Occupational Pesticide Handler Unit Exposure Surrogate Reference Table (OPHUESRT) (USEPA, 2016). With appropriate absorption factors, this unit exposure information can be used to estimate pesticide exposure for a particular use scenario, when actual exposure data are not available.

The UE value (0.03%) obtained in the present study among the median exposed group (CP₅₀) of the applicators was thrice the dermal UE value of 0.01% (when converted to metric mass units from the stated 58,400µg /pound AI) for a similar pesticide use scenario of the USEPA's unit exposure surrogate reference table (USEPA, 2016). The UE value (0.06%) found among the 5% highly exposed group of the present study was six times higher than the USEPA's UE value stated above. These results suggest that applicators of the present study were at risk of excessive levels of exposure compared to applicators in North American countries. In addition, the applicators had used pesticides for about 16 years with consequent repeated high exposure. The high UE values obtained in the present study, compared to that of the USEPA's unit exposure surrogate reference table, OPHUESRT, could be due to differences in the safety practices between pesticide applicators of North American countries and applicators in the present study.

3.4 Pattern of Pesticide Exposure

3.4.1 Individual Anatomical Regions of the Applicators

The patterns of chlorpyrifos exposure on the anatomical regions was evaluated with four randomly selected applicators (Table 1) from the study group as presented in Table 2. Some differences were observed regarding the patterns of chlorpyrifos deposition at the level of individual applicators. These differences probably reflected the field factors reported in Table 1. Applicators A, C, and D had the highest proportion of exposure on the hands (27.7 %, 87.5 %, and 23.3 % of TDE, respectively), compared to applicator B whose hand exposure was 16.1 % of TDE. This might be due to spillage that was observed during mixing and loading of pesticides by applicators A, C, and D, but not with applicator B. Also, Table 1 shows that the height of the crops sprayed by applicators A and B (80 cm and 50 cm, respectively), were greater than those of the crops sprayed by applicators C and D (12 cm and 30 cm, respectively).

Consequently, the proportions of exposure on the upper legs of applicators A and B (28% and 21%, respectively) were higher than those of applicators C and D (0.4% and 14%, respectively) since taller crops may allow contaminated leaves to reach the upper legs of applicators. In addition, the applicator who wore a long sleeve shirt (applicator C) had a relatively lower proportion of exposure (0.1%) on the lower arms than applicators A, B and D (about 1.5% and 1.1%, and 12%, respectively), who wore short sleeve shirts. Moreover, incidence of spray tank leakage affected the proportion of exposure at the back abdomen of the applicators. The applicators whose spray tank leaked (applicators B and D), had the highest proportion of exposure (18.7% and 12.8%, respectively) at the back abdomen, compared to applicators A (0.5%) and C (0.7%). Interestingly, applicators B and D also had the highest proportion of exposure on the front abdomen (16% and 11%, respectively), compared to applicators A (1.7%) and C (0.3%). The reason for this finding is not immediately clear but may suggest that leaked insecticide may have reached the front abdomen.

Table 2: Pattern of Chlorpyrifos Deposition on the Anatomical Regions of Individual Applicators on Rice Farms in Ghana.

Body Section*	Proportion of Total Dermal Exposure (%)			
	Applicator A**	Applicator B**	Applicator C**	Applicator D**
Head	1.1	0.7	3.9	1.3
Front abdomen	1.7	16.0	0.3	11.0
Back abdomen	0.5	18.7	0.7	12.8
Upper arm	0.2	1.6	0.1	2.2
Lower arm	1.5	1.1	0.1	12.4
Hands	27.7	16.1	87.5	23.3
Upper legs	28.4	21.0	0.4	14.2
Lower legs	28.4	18.1	4.6	16.4
Feet	10.6	6.7	2.4	6.5

*see Figure 1

**see Table 1 for the observed field factors with these applicators

The general pattern of chlorpyrifos deposition on the anatomical regions, evaluated with the four applicators, is presented in Figure 3. Overall, the anatomical region that received the highest proportion of exposure with the applicators studied was the hands. Contamination on the hands constituted about 39% of TDE. The next highly exposed anatomical regions were the lower legs (17%), upper legs (16%), back abdomen (8%), front abdomen (7%), and the feet (7%). The least exposed anatomical regions were the lower arms (4%), head (2%), and the upper arms (1%).

Figure 3: General Patterns of Chlorpyrifos Deposition on the Anatomical Regions of Applicators on Rice Farms in Ghana.

With the exception of the feet and the lower arms, the chlorpyrifos skin loading of the anatomical regions of the applicators followed a similar pattern to that of the general proportion of exposure described above. The hands were the primary site of contamination in terms of

chlorpyrifos skin loading ($13.1 \mu\text{g}/\text{cm}^2$). The feet ($3.0 \mu\text{g}/\text{cm}^2$), lower legs ($2.9 \mu\text{g}/\text{cm}^2$), upper legs ($2.5 \mu\text{g}/\text{cm}^2$) and lower arms ($1.4 \mu\text{g}/\text{cm}^2$) were secondary sites of exposure, with the lowest levels of exposure being found on the back abdomen ($0.85 \mu\text{g}/\text{cm}^2$), front abdomen ($0.75 \mu\text{g}/\text{cm}^2$), head ($0.34 \mu\text{g}/\text{cm}^2$) and upper arms ($0.25 \mu\text{g}/\text{cm}^2$). None of the applicators used any form of hand gloves, which might have contributed to the relatively high level of exposure of the hands found with applicators in the present study. Activities during the mixing and loading stages with the applicators in the present study involved the use of the hands. Also, the hands were used to adjust and clear the nozzle of the spray device.

A similar study conducted among applicators who sprayed malathion on greenhouse tomato plants revealed that contamination on the hands was about 76% of the total dermal exposure (Machera, 2003). Likewise, hand contamination represented between 85% - 99% of total dermal exposure among agricultural subcontractors who did not use hand gloves (Vitali *et al.*, 2009). Also, among applicators in vineyards, hand contamination was the highest and accounted for 49% and 56% of total dermal exposure during mixing and spraying stages, respectively (Baldi *et al.*, 2006). Evaluation of exposure to acetamiprid with applicators in a greenhouse watermelon farm revealed that the highest level of contamination was on the hands during mixing and loading of pesticides into the spray tank (Kim *et al.*, 2014). Related outcomes have also been found with applicators who used chlorpyrifos on maize crops (Gao *et al.*, 2014); procymidone and deltamethrin on greenhouses tomato crops (Ramos *et al.*, 2010); and fenvalerate on apple crops (Moon *et al.*, 2013). Compared to the left hand, the right hand which usually held the spray lance, was the most contaminated (An *et al.*, 2014; Gao *et al.*, 2014).

However, hand contamination was less prominent in another study (Cao *et al.*, 2015). This study evaluated exposure of imdacloprid to applicators who sprayed wheat crops using knapsack sprayers. The upper and lower legs contributed the most (76% to 88%) to total exposure. The legs were also identified as the site of highest exposure (48% of total exposure) in a study conducted among applicators who sprayed rose plants in greenhouse with malathion (Tuomainen *et al.*, 2002). The higher proportion of exposure found on the legs in the studies by Cao *et al.*, (2015) and Tuomainen *et al.* (2002), compared to the present study, could be due to the relatively taller crops sprayed in those two studies. The crop heights had means of 75 cm and 110 cm, respectively, compared to mean crop height of 42 cm in the present study (Table 1). Also, the pesticide in the present study was sprayed under irrigation conditions compared to the non-irrigation conditions with the studies by Cao *et al.*(2015) and Tuomainen *et al.* (2002). Consequently, part of the legs of applicators in the present study might have been protected from pesticide exposure by the irrigation water.

3.4.2 Upper and Lower Anatomical Regions of the Applicators

The present study revealed that the upper anatomical region of the body (head, upper arms, lower arms, front abdomen and back abdomen) were the least contaminated (18% of TDE) (Figures 4). The lower anatomical region (hands, upper legs, lower legs, and feet) accounted for 82% of TDE. With a maximum crop height of 80 cm (Table 1), it would be expected that less of the spray cloud would penetrate to the upper anatomical regions. In addition, the applicators walked through densely planted crops that had been recently sprayed and the lower anatomical region would have had significant contact with pesticide soaked leaves.

The findings of the present study is consistent with similar studies (Castro Cano *et al.*, 2000; Castro Cano *et al.*, 2001; Tuomainen *et al.*, 2002; Cao *et al.*, 2015). The study reported by Cao *et al.* (2015) revealed that the level of exposure on the lower anatomical region (upper and lower legs) was about 76 - 79% of total exposure, compared to 9 – 10% for the upper anatomical region (head, chest, back, and arm). Similarly, the lower anatomical region received 64 to 79% of of total exposure among applictors who sprayed green peas (Castro Cano *et al.*, 2000; Castro Cano *et al.*, 2001). Tuomainen *et al.*(2002) also found among applicators who sprayed rose plants that exposure on the lower anatomical region constituted about 78% of total exposure. Conversely, exposure on the upper anatomical region could be higher than the lower anatomical regions, when spraying crops that are taller, as well as having more dense foliage in the upper portion. For instance, Hughes *et al.* (2008) found among applicators who sprayed maize crops, that exposure to deltamethrin on the upper anatomical region (head, torso, arms, and hands) was about 170 mL/h, compared to 140 mL/h on the lower anatomical region (upper and lower legs).

Figure 4: Proportion of Exposure (% of TDE) of the Upper and Lower Anatomical Regions of Applicators on Rice Farms in Ghana.

3.5 Factors Associated with Total Dermal Exposure

The results of the independent t-test analysis are reported in Table 3. Applicators who handled more insecticides (at least 150 mL) had significantly higher TDE (28 ± 9.4 mg) compared to those that handled less than 150 mL of the insecticide (18 ± 8.0 mg) ($p < 0.05$). Similar to this finding, a previous study (Hines *et al.*, 2011) showed that the quantity of captan applied was a significant determinant of exposure. Comparable results have been reported by Phung *et al.* (2012) and Aponso (2002). Applicators of the present study who sprayed taller crops (at least 35 cm) received significantly higher levels of exposure (29 ± 12.5 mg) compared to those that sprayed crops less than 35 cm (20 ± 6.2 mg) ($p < 0.05$). Tall rice crops were usually dense, allowing more contact with applicator's clothing and body. Also, such crops required more pesticide to be sprayed, in order to effectively control pests, compared to shorter crops. Gao *et*

al. (2014) has similarly reported in a study which assessed chlorpyrifos exposure among applicators who sprayed maize crops, that spraying taller crops were significantly associated with higher levels of exposure.

Contrary to expectation, there was no significant difference in the exposure levels between applicators with at least Junior High School level of education and those that were not educated up to Junior High School ($p > 0.05$). In addition, applicators who had been trained on pesticide safety had similar levels of exposure as applicators that had not received any training on pesticide safety ($p > 0.05$). These findings suggest that being educated or trained on pesticide safety may not necessarily translate into reduced pesticide exposure. Fan *et al.* (2015) found that, because of fear of economic loss, vegetable and fruit farmers who were more knowledgeable and aware of pesticide safety used higher levels of pesticides, compared to their counterparts. It was similarly reported that, exposure prevention behaviours were poor among a group of tobacco farmers, although awareness of pesticides hazards was high (Damalas *et al.*, 2006).

The type of shirt (long or short sleeve) worn by the applicators did not also influence the exposure levels significantly ($p > 0.05$), in contrast to the findings of previous studies (Blanco *et al.*, 2005; Phung *et al.*, 2012) that showed that wearing long sleeve shirt was more protective against exposure. The clothing worn by most of the applicators in the present study were in relatively poor conditions, as have previously been reported elsewhere (Okello and Okello, 2010; Christie *et al.*, 2015). Consequently, such clothing may not provide adequate protection against pesticide exposure.

Other factors that were not significantly associated with exposure were age of applicator, years of application, spraying duration, farm size, and whether or not there was spillage and leakages ($p > 0.05$).

Table 3: Factors Associated with Total Dermal Exposure (TDE) of Chlorpyrifos among Applicators on Rice Farms in Ghana (n = 24).

Variable	Mean TDE(mg)	SD	<i>t</i>	<i>p</i> (2-tailed)
<i>Age(years)</i>				
Less than 25	26	10.2	0.35	0.73
At least 25	24	7.8		
<i>Years of applying pesticides</i>				
Less than 10	33	15.6	-1.30	0.21
At least 10	25	8.9		
<i>Educational level</i>				
Less than Junior High	25	7.5	-0.54	0.60
At least Junior High	27	12.8		
<i>Trained on pesticide safety</i>				
Yes	27	8.0	0.43	0.67
No	25	12.1		
<i>Type of shirt</i>				
Short sleeve	25	11.2	-0.38	0.71
Long sleeve	27	8.1		
<i>Duration of spraying(minutes)</i>				
Less than 60	26	9.4	0.17	0.87
At least 60	26	11.1		
<i>Incidence of leaky tank</i>				
Yes	28	7.8	1.02	0.32
No	24	11.1		
<i>Incidence of spillage</i>				
Yes	26	7.9	0.24	0.81
No	25	15.3		
<i>Farm size (ha)</i>				
Less than 0.5	25	9.6	0.70	0.50
At least 0.5	28	10.8		
<i>Insecticide Quantity(mL)</i>				
Less than 150	18	8.0	2.20	0.04
At least 150	28	9.4		
<i>Crop height(cm)</i>				
Less than 35	20	6.2	2.40	0.03
At least 35	29	12.5		

3.6 Conclusion

The present study used the whole-body dosimetry technique to evaluate dermal exposure to chlorpyrifos among applicators on rice farms in a typical farming community in Ghana. Chlorpyrifos TDE among the median exposed and the 5% highly exposed groups were 24 mg and 48 mg, respectively. These translated into percentage UE values of 0.03% and 0.06% among the median exposed and the 5% highly exposed groups, respectively. These were much higher than the UE value of a comparable pesticide handler scenario of USEPA's unit exposure surrogate reference database. In many developing countries such as Ghana, pesticide exposure and risk assessment studies are usually not carried out as part of the processes for registering new pesticides for a number of reasons including financial and logistical challenges. Such countries may therefore rely on exposure models and databases from developed countries to evaluate pesticides. However, the findings of the present study clearly demonstrate that such an approach for pesticide exposure and risk assessment could be problematic because of differences in pesticide UE values between developed and developing countries.

Overall, the hands were the most contaminated anatomical region of the applicators both in terms of proportion of exposure (39% of TDE) and skin loading ($13 \mu\text{g}/\text{cm}^2$). Also, the lower anatomical region was more contaminated (82% of TDE) compared to the upper anatomical region (18% of TDE). However, these results should be interpreted with caution owing to the small sample ($n=4$) used to determine the pattern of exposure. The levels of chlorpyrifos exposure among the applicators were significantly influenced by the quantity of insecticide applied and the height of the crops sprayed. These findings suggest that actions that may be taken to significantly reduce pesticide exposure among applicators may include protecting the hands and the lower anatomical regions with appropriate PPE; and reducing the quantities of

pesticides handled by applicators. Also, other practices such as washing the hands, changing farm clothing, and bathing immediately after spraying may help to reduce exposure.

With the use of the whole-body dosimetry technique, the present study has provided important information on the magnitude, pattern, and determinants of dermal exposure to chlorpyrifos in a tropical country. The pesticide UE data of the present study can be used to estimate dermal pesticide exposure under similar pesticide use scenarios.

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Conflict of Interest: None

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