Estimation of the Pesticide Exposure during Spraying among Applicators

Syamimi I[a], Tengku Hanidza TI[a], Puziah AL[a]
[a]*Department of Environmental Sciences, Faculty of Environment Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*

ABSTRACT: Pesticide exposure used in paddy farming was estimated using whole body dosimetry. The respondents were applicators from Sekinchan, Selangor who participated voluntarily in this study. They were given cotton coveralls to wear before spraying pesticide in the fields. After they had completed their task, the coveralls were collected from pesticide applicators immediately. The coveralls were cut into nine pieces representing parts of the body from shoulder to leg to assess the part of the applicator's body that will be exposed the most to pesticide during spraying. Each cutting pieces of the coveralls was extracted using acetone: hexane (1:1) solvent mixture followed by cleanup using C-18 Solid Phase Extraction. The solvent extracts were analyzed for chlorpyrifos using GCMS. The result indicated that different pieces of the coveralls have different concentrations of chlorpyrifos residues. The highest concentration of chlorpyrifos residues was found at the bottom left leg and bottom right leg of the body. Biomonitoring of pesticide exposure was also performed on the same applicators using their urine samples collected four times that is before and within two days after spraying. The result showed that 2,3,6 trichloro-2-pyridinol (TCP), a chlorpyrifos metabolite was detected in the urine samples.

Keywords: chlorpyrifos, residues, dermal exposure, paddy field, pesticide, GC/MS, cotton coveralls

Introduction

Exposure to pesticides during field applications can be estimated by measuring the contamination of the skin. Measurement of dermal exposure can be important in evaluating the hazard, in helping to characterize the exposure pathway, quantifying the magnitude and extent of contamination, and evaluating the variability in sources and work behaviour. Dermal exposure can be estimated using a range of techniques; direct removal of the contaminant from the skin by wiping or washing; recovery of contaminants from clothing (whole-body dosimetry); recovery of contaminants from patches (patch sampling); using gloves; visualization of contamination using a fluorescent marker; and biological monitoring (EH74/3). Each method has its relative merit and advantages and disadvantages with no one method being able to assess dermal exposure completely.

In the whole body method (Chester, 1995), workers were dressed in a suit that serves as the sampling medium.

After exposure, the coveralls were sectioned into several pieces, which were extracted and analyzed separately, to determine the concentration of pesticide deposited on the body and its distribution. In the patch method, absorbent cloth patches are attached to defined area of the applicator's body. After a period of exposure, the patches are removed and analyzed for pesticide content. The use of patch may lead to erroneous estimation, since splashes are by nature local and therefore may or may not be detected by the patch. Furthermore, patch estimation of contamination have to be extrapolated to the whole body. This may be done using standard surface areas of body parts such as those proposed by World Health Organization (1982) and Environmental Protection Agency (1987).

Assessing dermal exposure is always more difficult and intrusive than inhalation exposure. In inhalation exposure, the assessments rely on collecting samples from a well defined location, i.e. the breathing zone of the individual worker. For dermal exposure to be assessed accurately, the assessments must be in terms of the whole body. The variability in dermal exposure can be very large, with some parts of the body, such as hands and knees, being more proned to contamination than other parts.

Corresponding Author:
Syamimi I
Department of Environmental Sciences,
Faculty of Environment Studies,
Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia
Email: my_aphrodite85@yahoo.com

Published 31 Jan 2011

The whole body dosimetry method can be used to determine if there is a significant skin exposure and to what areas of the body it is occurring (Tanahill, 1997; Frenich et al., 2002; Wheeler and Warren, 2002). Disposable whole-body overalls have been recommended as a collection medium for contaminants during spraying operations and a procedure has been developed (WHO, 1982). Theoretically, all contaminants that contact the skin are collected. The method differs from the patches in that it does not require a surface area extrapolation. However, the problem with the method is that it is both time consuming and expensive, as each overall has to be cut into manageable pieces for chemical disposition.

According to Delgado et al. (2003), the arms or thighs are receiving much greater contamination than other areas of the body. Frenich (2002) also showed that lower left leg and lower right leg were on high exposure level during spraying. However, Soutar et al. (2000) argued that using whole body dosimeter does not mimic skin uptake. There are no standardized guidelines for the type of material that sampling suits should be absorbent. It should also be noted that, when whole body dosimetry are used to investigate the effectiveness of protective clothing, the whole suit method assume that all contamination beneath the protective clothing occurs as a result of penetration or permeation through the clothing and takes no account of contamination as a result of direct deposition to the skin contamination layer.

The objective of the study is to determine the part of the body that would be exposed to pesticide when the farmer is mixing, loading and spraying the chemicals. The whole body method was used to determine dermal exposure for a better understanding of the level of risk faced by the farmers.

Materials and Methods

Exposure assessment using coveralls

Pesticide applicators in Sekinchan, Selangor who volunteered to participate in this study in April, 2006 were given cotton coveralls to wear before handling pesticide starting with mixing, loading and spraying. The paddy field covers an area of 12000 m^2 (200 m-600 m). Twelve pesticide applicators were involved in this activity. All of them are males, experienced applicators. They sprayed pesticide following the wind direction so that the wind will not blow the pesticide into their faces. They were provided with requisite information about the study before the application of the pesticide. The participants were instructed to carry out work activities according to their normal practice. During the exposure period, the applicators wore rubber gloves and dressed in the given coveralls. During the application period, the applicators also wear either full-face respirators or cloths to cover their nose and mouth. The pesticide used by the applicators was Nurelle-D505 EC, which consist of 45.9% Chlorpyrifos and 4.6% Cypermethrin as active ingredients and 49.5% other substances.

Immediately after spraying, the coveralls were collected and hanged for a moment to allow air-dried before being cut into nine parts as shown in **FIG.1**. Note that the nine pieces represent parts of the body are: left hand (LH), right hand (RH), left chest (LC), right chest (RC), upper left leg (ULL), upper right leg (URL), bottom left leg (BLL), bottom right leg (BRL) and back (B) for subsequent analysis (Frenich et al., 2002). Then, each piece was placed in separate sampling bottles and soaked with acetone:hexane (1:1) solvent-mixture. To avoid contamination between samples, each sample was handled carefully and the bottle was labeled and stored at 4°C until analysis.

Biomonitoring using urine samples

Urine samples were also collected four times from each participant: baseline (before the chlorpyrifos application), one day after application (composite 24 hours), the second day after application (composite 24 hours) and the day after harvest. Samples were stored at -20°C prior to analysis.

Preparation of calibration standard solutions

Calibration standard solutions were prepared by taking known amount of the chlorpyrifos reference standard and diluting it with hexane (HPLC grade). The concentrations of the standard solutions used for calibration were 0.1 µg mL^{-1}, 0.3 µg mL^{-1}, 0.5 µg mL^{-1}, 0.8 µg mL^{-1} and 1.0 µg mL^{-1}.

Preparations of sample extracts

The extraction procedure for each cutting piece of the coverall was as follows: First, the coveralls were cut into nine pieces as shown in **FIG. 1**. Each piece was placed in a separate glass bottle and extracted using 300 mL of acetone:hexane (1:1) solvent-mixture. The bottles were closed and shaken with side arm shaker for 30 min. Then, the solvent extracts were transferred into a round bottom flask by passing through 6 g of anhydrous sodium sulphate placed on glass wool in a filter funnel to remove excess water. The whole process was repeated twice for each coverall cutting piece. Solvent extracts collected in the flask were concentrated with column rotary evaporator until almost dry. The flask was rinsed with 5 mL of hexane.

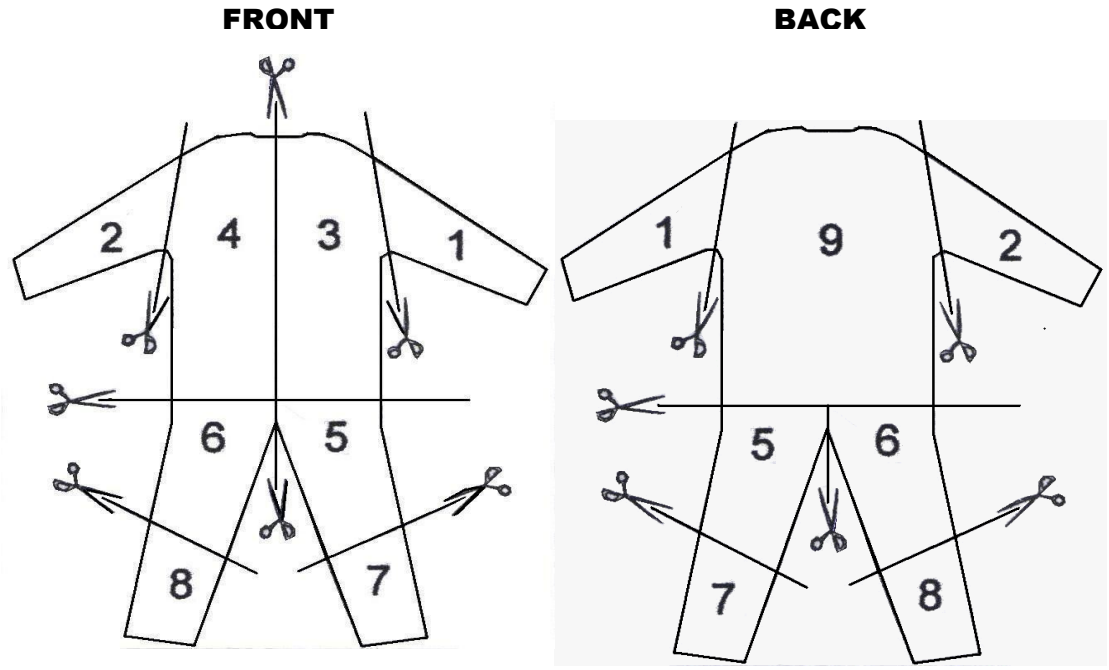

FIG. 1- Coverall sectioning for whole body analysis: 1: LH (left hand), 2: RH (right hand), 3: LC (left chest), 4: RC (right chest), 5: ULL (upper left leg), 6: URL (upper right leg), 7: BLL (bottom left leg), 8: BRL (bottom right leg), 9: B (back).

To remove unwanted interferences, the solvent extracts were subjected to cleanup process using Solid Phase Extraction (SPE) method. The extracts were made to pass through a C-18 cartridge using SPE manifold. Then, each solvent extract was concentrated using nitrogen blow-down to less than 1 mL. The solvent extract was transferred into a vial and made to a final volume of 1 mL with hexane. The extracts were analyzed for chlorpyrifos residues using Gas Chromatography-Mass Spectrometry.

Results and Discussion

In this study, twelve pesticide applicators were initially interviewed in the survey and seven of them participated in the dermal exposure study using coverall. The applicators used mist blower to spray pesticide in their fields. The results show that the highest concentration of chlorpyrifos was found at the bottom left leg and bottom right leg (**TABLE 1** and **FIG. 2**).

TABLE 1- Concentration of Chlorpyrifos in worker's body parts and urine.

Body Parts	**Concentration (µg mL^{-1})**							
	Applicator 01	**Applicator 02**	**Applicator 03**	**Applicator 04**	**Applicator 05**	**Applicator 06**	**Applicator 07**	**Applicator FB**
Left Hand	1.3	2.5	3.1	2.8	1.2	1.9	0.7	ND
Right Hand	1.4	2.8	2.5	3.3	1.8	1.5	2.0	ND
Chest Left	5.2	6.2	6.8	4.7	6.5	5.5	5.9	ND
Chest Right	5.3	6.6	7.5	4.5	6.8	5.4	6.0	ND
Upper Left Leg	6.5	6.8	7.0	6.4	6.0	7.1	7.1	ND
Upper Right Leg	6.2	6.5	6.7	5.9	6.0	6.8	6.9	ND
Bottom Left Leg	13.5	12.5	13.8	12.2	15.4	15.8	14.3	ND
Bottom Right Leg	13.8	12.4	14.2	13.0	15.2	15.9	14.8	ND
Back	1.2	0.9	1.0	0.9	1.3	1.1	1.2	ND
Urine	ND	ND	ND	ND	ND	ND	ND	-

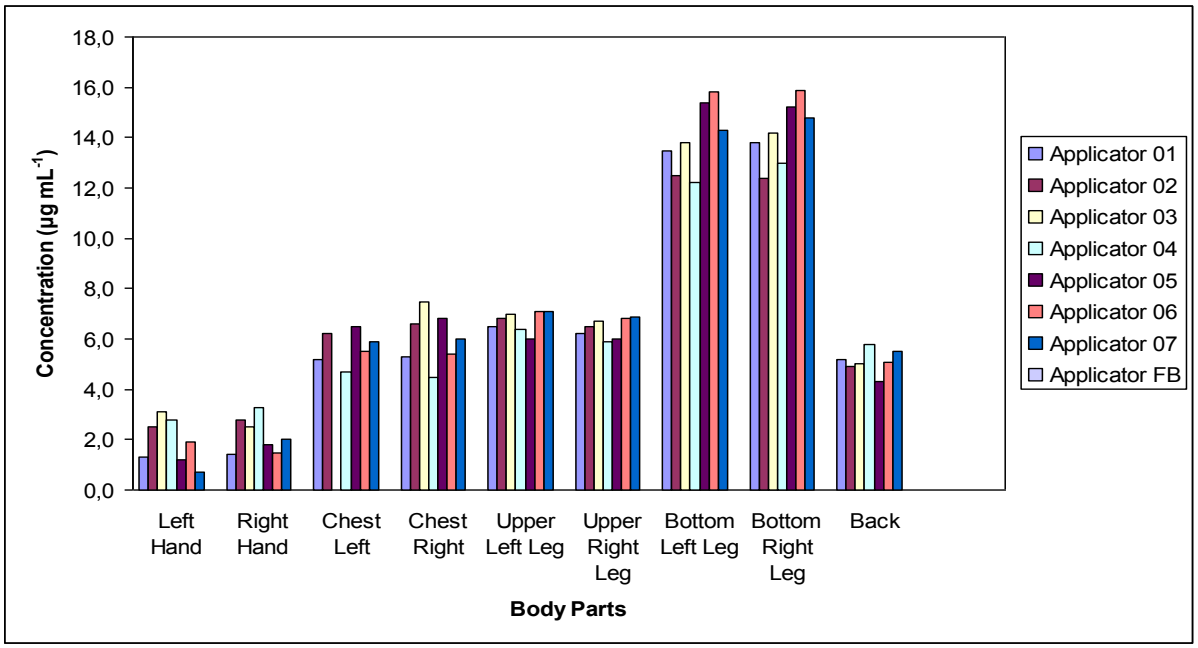

FIG. 2- Total concentration of chlorpyrifos residues in coveralls

Based on this observation, the bottom leg was heavily contaminated with pesticide. As expected, applicator's legs were submerged in the wet paddy field with plants at knee length high. During the spraying activities, the workers walked through the paddy field, therefore pesticide deposited on the paddy plants could easily be transferred onto the worker's clothes. **FIG. 3** shows the picture of a worker while spraying and the spraying equipment.

FIG. 3- Picture on the left shows a worker spraying pesticide and picture on the left shows the spraying equipment.

A study conducted by Tuomainen et al. (2002) found that lower limbs were the most contaminated body parts during spraying activity. This is because lower limbs were nearer to the mist blower. However, Tuomainen et al. (2002) used patch technique and conducted the study in greenhouses as compared to our study in the open field. It is likely that the deposition would be more in an enclosed environment.

Wheeler and Warren (2002) claimed that areas such as the front of the thighs, the inside of the ankles and lower legs and the forearms have much higher levels of dermal exposure than the back of the legs and torso. They used Dirichlet Tesselation – based sampling scheme for measuring whole-body exposure with respondents being workers from biocide-based companies. In the study, respondents were given coveralls to wear during their working hours. Ten contaminated coveralls were obtained:

nine from treating salmon fishing nets with biocide and one from boat painting. In a study conducted by Delgado (2003), workers spraying olive trees used hand held sprayers connected by hoses to the tractor mounted sprayer. The results show that there was much less contact between the applicator and the treated crop, the pattern of contamination tends to be more uniform.

The findings of our study, together with previous published studies, indicate that the pattern of pesticide deposition is influenced by the type of spraying equipment used and the type of crops sprayed. For applicators that went through the crops, the most contaminated areas of their body would be their legs. The type of crops also influences deposition pattern. For example, the study of pesticide exposure from spraying olive trees (Delgado 2003), minimal contact between the crop and the workers was observed. The height of crop also influences the pattern of deposition, as in the Frenich study for high vegetable crops where the legs were being heavily deposited with pesticides.

Conclusion

Based on the results obtained so far, it can be concluded that chlorpyrifos residues were detected in all coverall samples analyzed. The study also found that the parts of the body having the highest chlorpyrifos depositions were bottom left legs (BLL) and bottom right legs (BRL). No chlorpyrifos metabolite (TCP) was detected in the urine sample of the seven pesticide applicators.

References

1. Chester, G. (1995). Revised Guidance Document for the Conduct of Field Studies of Exposure to Pesticides in Use in P.B. Curry (ed.). Methods of pesticide exposure assessment. Plenum Press, New York, pp. 179-215.
2. EPA. (1999). ORGANOPHOSPHATE PESTICIDES SW–846 METHOD 8141 A. http://www.epa.gov/method/htm.
3. Fenske, R.A. (1993). Dermal Exposure Assessment Techniques. *Annals of Occupational Hygiene*, 37: 687-706.
4. Frenich, A.G., Aguilera, P.A., Gonzalez, F.E., Castro Cano, M.L., Galera, M.M., Martinez Vidal, J. L. and Soler, M. (2002). Dermal Exposure to Pesticides in Greenhouses Workers: Discrimination and Selection of Variables for the Design of Monitoring Programs. *Environmental Monitoring and Assessment*, 80: 51-63.
5. Gamón, M., Sez, E., Gil, J., and Boluda, R. (2003). Direct and Indirect Exogenous Contamination by Pesticides of Rice-farming Soils in a Mediterranean Wetland. *Archives of Environmental Contamination and Toxicology*, 44: 141-151.
6. Jenrich, R. and Sampson, P. (1993). Stepwise Discriminant Analysis, in W.J. Dixon (ed.), BMDP Statistical Software, University of California Press, pp. 519-537.
7. Kumar Singh, B., Walker, A. and Wright, D.J. (2002). Persistence of Chlorpyrifos, Fenamiphos, Chlorothalonil, and Pendimethalin in Soil and Their Effects on Soil Microbial Characteristics. *Bulletin Environmental Contamination and Toxicology*, 69: 181-188.
8. Liu, S. and Pleil, J. D. (2002). Human Blood and Environmental Media Screening Method for Pesticides and Polychlorinated Biphenyl Compounds using Liquid Extraction and Gas Chromatography – Mass Spectrometry Analysis. *Journal of Chromatography B*, 769: 155-157.
9. Soutar, A., Semple, S., Aitken, R.J. and Robertson, A. (2000). Use of Patches and Whole Body Sampling for the Assessment of Dermal Exposure. *Annals of Occupational Hygiene*, 44(7): 511-518.
10. Tuomainen, A., Kangas, J.A., Meuling, W.J. A. and Glass, R.C. (2002). Monitoring of Pesticides Applicators for Potential Dermal Exposure to Malathion and Biomarkers in Urine. *Toxicology Letters*, 134: 125-132.
11. Wheeler, J. P. and Warren, N.D. (2002). A Dirichlet Tesselation-based Sampling Scheme for Measuring Whole-body Exposure. *Annals of Occupational Hygiene*, 46(2); 209-217.
12. World Health Organisation. (1986). Field Survey of Exposure to Pesticides, Standard Protocol. *Toxicology Letter*, 33: 223-235.
13. Yücel, Ü., Ylim, M., Gözek, K., Helling C. S. and Sarykaya, Y. (1999). Chlorpyrifos Degradation in Turkish Soil. *Journal Environmental Science Health*, B34 (1): 75-95.