J. Toxicol. Pub. Health
Vol. 21, No. 4, pp. 297-301 (2005)

Official Journal of
Korean Society of Toxicology
Available online at http://www.toxmut.or.kr

Risk Assessment of Human Exposure to Methidathion during Harvest of Cucumber in Green House

Ji-Youn Byoun[1], Hoon Choi[1], Joon-Kwan Moon[1], Hee-Won Park[1], Kwang-Hyeon Liu[2], Yang-Bin Ihm[3], Byeoung-Soo Park[1] and Jeong-Han Kim[1]

[1]*School of Agricultural Biotechnology, Seoul National University, Shillim-dong, Gwanak-gu, Seoul 151-742*
[2]*Department of Pharmacology and PharmacoGenomics Research Center, Inje University College of Medicine, Busan 614-735*
[3]*Department of Crop Life Safety, Natural Institute of Agricultural Science and Technology, Rural Development Administration, Suwon 441-707, Korea*

Received November 24, 2005; Accepted December 12, 2005

ABSTRACT. Farmers are generally expressed to pesticides through mixing loding, application activity and harvesting of crop after application of pesticides. The present work investigated the exposure and risk of furathiocarb to workers when harvesting of cucumber was carried out in green house after application of furathiocarb EC. Glove was used for the hand exposure assessment, socks for foot and dermal patches for the other parts of body. Personal air monitor equipped with a XAD-2 resin was used for the respiratory exposure assessment. During the harvest of cucumber in green house, the initial rate of potential dermal exposure (Day 1) for methidathion was 1.3 mg/hr. The major exposure parts were hand (78~83%), thigh (5~7%) and arms (6~9%) during 3 days' harvest. No exposure was detected from the respiratory monitoring. For risk assessment, the potential dermal exposure (PDE), the absorbable quantity of exposure (AQE) and the margin of safety (MOS) and margin of exposure (MOE) were calculated. In risk assessment of harvester exposure for 7 days, all MOS was > 1 and MOE was > 100 indicating that possibility of risk was little.

Keywords: Exposure, Risk assessment, Methidathion, Dermal, Inhalation, Cucumber.

INTRODUCTION

Human exposure to pesticides can occur during manufacture, mixing/loading, spraying, harvest, and by consumption of treated crops. During harvest, the representative routes of human exposure are dermal deposition and inhalation. By far the greatest potential exposure is through the dermal absorption during spraying and harvest operations, and the importance has been confirmed by many studies (Durham and Wolfe, 1962; Fenske and Elkner, 1990). Such studies have raised concerns about the need for greater protection of workers, since levels of pesticide deposited on exposed skin were found to be 20~1700 times the amount reaching the respiratory tract (Feldman and Maibach, 1974).

Direct contact with pesticides by workers during harvest can result in harmful effects. Therefore the importance of field surveys and assessment of exposure of harvest worker to pesticides under actual harvest conditions is paramount. Such surveys provide essential data for risk assessment and are the only alternative to extrapolation from animal exposures (Calumpang, 1996). Dermal exposure is represented in direct measurements by the total amount of pesticide retained.

Methidathion is a non-systemic organophosphorous insecticide and acaricide with stomach and contact action. The compound is used to control a variety of insects and mites in many crops such as fruits, vegetables, and also in green houses.

Cucumber is one of the favorite vegetable worldwide and in Korea. Farmers prefer to wear long sleeved shirts and long trousers instead of protective garments while harvesting. Therefore, there may be significant dermal exposure to workers and accidental field-poisoning may also occur.

Recently expose and risk assessment of spray operator was reported by Choi *et al.* (2005) and Liu *et al.*

Correspondence to: Jeong-Han Kim, School of Agricultural Biotechnology, Seoul National University, Shillim-dong, Gwanak-gu, Seoul 151-742, Korea
E-mail: kjh2404@snu.ac.kr

(2003).

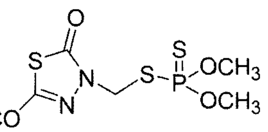
However, no study on exposure and risk assessment of methidathion during harvest of cucumber has been carried out so far. Thus, this study attempted to evaluate the exposure rates via different exposure route by monitoring harvester's work activities. Based on the evaluation results, risk assessment was conducted by calculating MOS to ascertain the status of pesticide exposure to harvesting worker and to obtain information for health protection measures for those workers.

MATERIALS AND METHODS

Chemicals. Pesticide used in field study was commercial insecticide methidathion (methion, EC 40%, Bayer). The chemical structure and properties of methidathion are reported in Table 1. Analytical standard of methidathion (95%) was obtained from Rural Development Administration (RDA), Korea. All solvents were HPLC grade, and purchased from Fisher Scientific Korea Ltd.

Dermal patches. Patches were used for dermal exposure measurement. Dermal patch was made by putting cellulose TLC paper (Whatman 17CHR, 46 × 57 cm, Cat. No. 3017-915, 1 mm thickness) in the patch pocket (10 cm × 10 cm) having circular exposure part (50 cm^2). Safety pins were used to attach patches on protective garment (SP protective, KleenGuard, Yuhan-Kimberly, USA).

Table 1. Physicochemical properties of methidathion

Class	Organophosphosphate
Structure	
IUPAC Name	S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-ylmethyl *O,O*-dimethyl phosphonodithioate
Mol. Wt.	302.3
M.p.	39~41 degrees Celsius
V.p.	2.5×10^{-1} mPa (20 degrees Celsius)
K_{ow}	logP = 2.2
NOEL	(2 y) for dogs 0.25, rats 0.2 mg/kg daily.
NOAEL	20 mg/kg/day (21 days) in rabbits
Formulation	EC

Gloves and socks. Hand exposure was monitored with cotton gloves. Foot exposure was evaluated using cotton socks.

Personal air monitor. Inhalation exposure was measured using a personal air monitor equipped with air pump (Gillian Model 224-PCXR7, MSA, USA) and solid sorbent (ORBO™ 609 Amberlite XAD-2 400/200 mg, Supelco, USA) which traps pesticides in air. The flow rate was 2 l/min.

Analytical conditions

A Hewlett-Packard (HP) model 5890 series II gas chromatograph, equipped with a capillary column (DB-5, 15 m × 0.53 mm i.d., d_f = 1.5 mm) (Hewlett-Packard, CA, USA) and a nitrogen-phosphorous detector (NPD), was used for quantification of methidathion. The injector and detector temperatures were 250°C. The oven temperature was isothermal at 200°C. The flow rate of the nitrogen carrier gas was 8 ml/min at a splitless mode.

Fields and application

Exposure measurement was conducted in cucumber green house in Nonsan, Chungnam, Korea. Application was performed by stepping backward and moving the lance up and down. During the harvest, protective garments (SP protective, KleenGuard, Yuhan-Kimberly, USA) and dermal patches were used. The harvest was conducted for 7 days.

Analytical procedures

Analysis of methidathion from patches, gloves, and socks. The patches were placed into a 100 ml vessel with 60 ml of ethyl acetate, while gloves were placed into a 500 ml vessel containing 300 ml of ethyl acetate. Each matrix was then shaken for 1 hr at 200 rpm in shaker (Wooju Scientific, Korea). After filtration with nylon filter (45 μm, Target®), aliquots (1 μl) were analyzed with GC-NPD. The recovery of methidathion was determined by fortification of methidathion on the

Table 2. Recoveries and limit of detection for the pesticides and matrices used in the study

	Patch	Glove	XAD-2	Socks
Recovery (%)				
LOQ	99.3 ± 0.1	110.0 ± 0.1	76.5 ± 9.5	92.9 ± 0.03
10LOQ	92.4 ± 4.1	102.1 ± 0.1	90.5 ± 6.0	110.4 ± 0.04
100LOQ	94.7 ± 0.7	88.3 ± 0.02	83.2 ± 3.9	100.8 ± 0.04
Limit of detection	0.05*	0.05*	0.05*	0.05*
Limit of quantitation	0.25	0.25	0.25	0.25

* ng per sample (patch, glove, XAD-2 and socks).

different matrices (Table 2).

Analysis of Methidathion from XAD-2 resins. To measure the inhalation exposure, the 1°- and 2°-part of XAD-2 resins were separated after cutting a tube. Then, each XAD-2 resin was placed into a 20 ml vial and shaken in ethyl acetate (10 ml) for 1 hr. The extract was concentrated by rotary evaporator, dissolved in 2 mlof acetone, and concentrated to 100 μl by purging with nitrogen gas using reacti-vap™ (PIERCE, Rockford, IL) before analyzed (1 μl) using GC-NPD.

Method Validation

LOD (Limit of Detection) & LOQ (Limit of Quantitation). Aliquots (1 μl) of standard solution from 0.005 ppm to 1 ppm were analyzed for LOD determination before LOQ calculation.

Matrix extraction efficiency (recovery) test. Three levels (LOQ, 10 times of LOQ and 100 times of LOQ level) of pesticide were spiked on patches, gloves, socks and XAD-2 resin.

Field recovery test. A certain amount (10 times of LOQ) of pesticide was spiked on patches, gloves, socks and XAD-2 resin in field. They were exposed to outdoor during harvest in order to simulate field study conditions.

Trapping efficiency test. An aliquot of standard solution (100 times of LOQ) was spiked at the bottom of U-shape glass tube which is connected with XAD-2 resin tube, and air was passed through the system at 2 l/min for 4 hr for trapping of evaporated pesticide. To help the volatility of compounds, U-shape glass tube was heated to 70 degrees Celsius. The residue in U-shape glass tube and the amount trapped in XAD-2 resin were analyzed for mass balance.

Breakthrough test. This was conducted by adding standard solution (100 times of LOQ) in the 1°-part of XAD-2 resin and passing air through the tube at 2 l/min for 4 hr. And then, 1°- and 2°-part of resin were analyzed separately.

Risk assessment

The potential dermal exposure (PDE) values were obtained by extrapolated to a 4-hr time period of effective exposure per day with the actual harvesting time (about 3~4 hr). The AQE (absorbable quantity of exposure) value was based on assumptions of 10% skin absorption (Jensen, 1984) after 10% of penetration through clothes was considered (POEM, 1992). The margin of safety (MOS) was calculated by an adaptation of the formula of Severn (Severn, 1984): MOS = (NOEL × BW)/(AQE × SF) where, NOEL (no observable effect level) is 0.2 mg/kg/day (rats) for methidathion (Tomlin, 2000), BW (body weight) is 60 kg (Jensen, 1984) and SF (safety factor) is 100 (Renwick, 2003). Alternative concept: NOAE/Exposure where NOALE (no observed adverse effect level) of methidathion is 20 mg/kg/day from short term (21 days) dermal toxicity test is rabbits, and exposure is AQE/BW.

RESULTS AND DISCUSSION

Method validation

Method validation is a important procedure to secure the reliability of analytical results. LOQ was calculated as 5 times greater than LOD and the values were low enough for the analysis (Table 2). The correlation of detector response with the concentration of methidathion was linear over the range of 0.05~10 mg/l. Matrix extraction efficiency (Recovery) test (Table 2) was to measure recovery of pesticides from various matrices while field recovery test (Table 3) was conducted in the same manner except spiking pesticide in the field because pesticides on various exposure matrices may degrade when exposed to sunlight during application time or storage and transportation. The small relative standard deviation values of 0.7~2.4% indicate the analytical procedures are reliable (Liu *et al.*, 2001). To validate the sampling methods in inhalation exposure monitoring, trapping efficiency test was conducted. This test was to measure the efficiency of XAD-2 resin for the trapping of pesticide in air. This experiment allowed a mass balance of about 107% by adding up the pesticide trapped in XAD-2 resin and residue at the bottom of U-shape glass tube (Table 4). Another test is breakthrough test which is to evaluate the capacity of XAD-2 resin to retain a pesticide. The result of 109% recovery from 1°-part of resin without escaping

Table 3. Field recoveries of the pesticides and matrices used in the study

Matrices	Added amounts (ug)	Recovery (%)
Patch	10LOQ	99.0 ± 0.06
Glove	10LOQ	102.1 ± 0.05
XAD-2	10LOQ	80.3 ± 0.03
Socks	10LOQ	110.4 ± 0.04

Table 4. Breakthrough test and trapping efficiency test of XAD-2 resin

	Recovery (%)		Total
Breakthrough	1°-XAD	2°-XAD	
100LOQ	109.9 ± 5.0	0.0 ± 0.0	109.9 ± 5.0
Trapping efficiency	Residue	XAD	
100LOQ	96.4 ± 19.8	11.0 ± 6.2	107.4 ± 13.7

over to 2°-part suggested that 1°-part of resin has enough capacity to retain the corresponding amount of pesticide (Table 4). Through the various experiments, the analytical and sampling methods of this study were fully validated.

Potential dermal and inhalation exposure

During the harvest of cucumber in the field, the initial amount (exposure amount for time of exposure test) and rate (exposure amount per hour) of potential dermal exposure (Day 1) for methidathion was 3.3 mg and 1.3 mg/hr, respectively, and they decreased with time, as expected, degradation with various factors such as photolysis, hydrolysis, co-evaporation and etc. (Fig. 1. and Fig. 2.) The major exposure parts were hand (78~83%), thigh (5~7%) and arms (6~9%) for 3 days' harvest.

Table 5. Potential dermal exposure amounts for worker during harvesting after application of methidathion on cucumber in green house

	Potential dermal exposure amounts (unit, μg/hr)				
	Day 1	Day 2	Day 3	Day 5	Day 7
Head	7.9	6.3	1.7	0.0	0.0
Shoulder	7.1	1.7	0.5	0.0	0.0
Front of neck	0.4	0.3	0.2	0.0	0.0
Back of neck	0.0	0.4	0.0	0.0	0.0
Chest	23.6	7.6	2.6	0.0	1.7
Back	16.8	3.5	0.0	0.0	0.0
Upper arms	53.3	40.2	14.9	0.0	6.7
Forearms	57.7	29.9	9.6	0.0	0.0
Thigh	95.2	45.3	21.0	0.0	0.0
Shins	12.4	5.1	3.5	0.0	0.0
Foot	23.8	18.9	18.2	10.8	5.6
Hand	1045.4	669.5	355.6	69.4	20.7
Total	1343.5	828.6	427.7	80.2	34.8

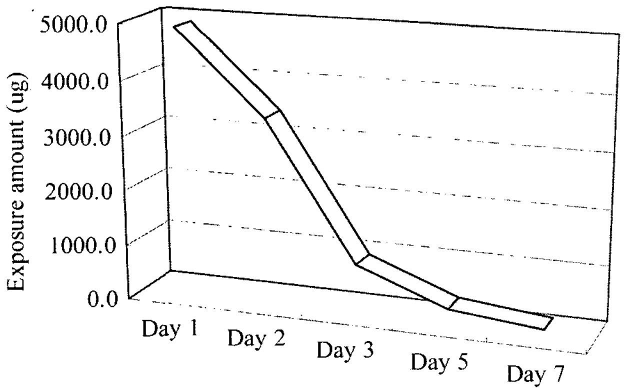


Fig. 1. Total dermal exposure amounts of worker during harvest on cucumber greenhouse after application of methidathion.

Hands of the harvester were mainly exposed due to the direct contact with pesticides on crop foliage or cucumber because of the working type. It is, therefore, extremely important that some form of hand protection be used.

Between the two dermal and inhalation exposure routes during spraying, inhalation exposures were found to be 20~1700 times less than dermal exposure (Feldman and Maibach, 1974), suggesting much less significant. As predicted based on the work by Choi *et al.* (2005) and Liu *et al.* (2003), inhalation exposure was not observed (below LOD) in all cases.

Risk assessment

The actual dose provides the most precise estimate of exposure that can be practically obtained for humans and is important for risk assessment and management (Krieger *et al.*, 2000). The actual dose, AQE was calculated from PDE and then MOS and MOE were determined (Table 6) indicating that the harvesting situation

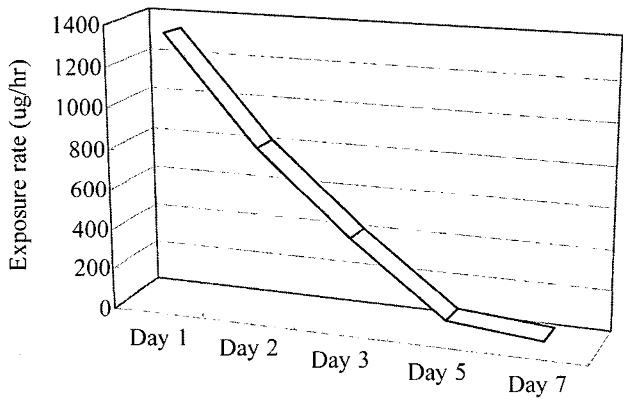


Fig. 2. Dermal exposure rate of worker during harvest on cucumber greenhouse after application of methidathion.

Table 6. Estimates of potential dermal exposure (PDE), absorbable quantity of exposure (AQE), margin of safety (MOS), exposure control need (ECN), and safe work time (SWT) of harvesters on cucumber crops sprayed methidathion

	DER[a] (mg/hr)	PDE[b,c] (mg/day)	AQE[d]	MOS	MOE	ECN[e] (%)	SWT[f] (hr)
Day 1	1.3	0.5	0.1	2.23	223	-	8.93
Day 2	0.8	0.3	0.03	3.62	362	-	14.48
Day 3	0.4	0.2	0.02	7.01	701	-	28.05

[a]DER : Dermal Exposure Rate.
[b]Exposure time : 4 hr/day.
[c]10% skin absorption after 10% of penetration through clothes.
[d]AQE = PDE + PIE (Potential Inhalation Exposure).
[e]Exposure control need (ECN, %) = (1-MOS) × 100.
[f]Safe work time (SWT, hr) = MOS EWT.

was considered to be of less risk (all MOS > 1 and MOE >100). If MOS is < 1 or MOE is < 100, the working condition could pose some risk (Kieczka, 1993), then ECN (exposure control need) and SWT (safe work time) values proposed by Machado-Neto (Machado-Neto, 2001) may be very effective tools for selecting safety measures to manage the risk of workers. These results provide useful data for incorporation in farmer training programs on the proper use of pesticides.

ACKNOWLEDGMENTS

This work was supported by Agricultural R & D promotion center.

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