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Applicator Exposure to Imidacloprid while Spraying Mangoes

S. M. F. Calumpang, M. J. B. Medina

National Crop Protection Center, College of Agriculture, University of the Philippines Los Baños, Laguna 4031, Philippines

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Mango leafhoppers (*Idioscopus clypealis* and *I. niveosparsus*) are major economic pests of mangoes and crop protection management include chemical control. Spraying of mango trees involves the use of power sprayers, knapsack sprayers or improvised devices. Applicator exposure may at times be extremely high as this involves direct body contact with the spray solution while it sloughs off from overhead foliage (Ambridge and Haines, 1987). Pesticides commonly used in mango production are cypermethrin, deltamethrin, carbaryl, diazinon and imidacloprid. Imidacloprid 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine is a newly registered systemic insecticide used for the control of mango leafhoppers in the Philippines (Palis et al, 1994, Dupo et al, 1993). It has a broad spectrum of activity with long residual and systemic effect and low toxicity to non-target organisms (BAYER, 1993).

Attention has been drawn to the need for the assessment of exposure of spraymen to pesticides while spraying mangoes, a major export of the Philippines. An assessment of the exposure of sprayers while wearing a set of recommended protective garment recommended by the Fertilizer and Pesticide Authority of the Philippines was therefore conducted to evaluate the extent of their exposure to imidacloprid.

MATERIALS AND METHODS

The exposure study was conducted in farmer-cooperators' mango farms in Dasmariñas, Cavite and Sta. Rosa, Laguna, Philippines on October 15 and 26, 1994, respectively.

Correspondence to: S. M. F. Calumpang

Six workers used a set of recommended personal protective equipment over the usual worker attire of cotton shorts and cotton polyester T-shirt while spraying (Fig 1). Applicators sprayed imidacloprid, Confidor 100 SL (Bayer Phils, Inc.) on mango trees at the rate of 2.0 tbsp/100L for approximately 3 hrs/day.

Skin was swabbed twice using gauze soaked in 80% ethanol over a 46 cm^2 template. Each gauze pad was extracted with acetonitrile (1 x 100 ml, 1 x 50 ml) by shaking for 30 and 15 min, respectively. The organic extract was concentrated and taken up in 2 ml of acetonitrile.

Protective garment swatches (46 cm^2) were extracted with acetonitrile (100 and 50 ml) through standing for 1 hr each time. The combined extracts were concentrated under slight vacuum and taken up in 2 ml of acetonitrile.

Cellulose absorbent pads (46 cm^2) were placed under the protective garment of selected body parts (WHO). These were extracted with acetonitrile (2 x 100 ml) using a tissumizer for 2 min and standing for 1 hr, respectively. The organic extract was dried over sodium sulfate, concentrated and taken up in 2 ml of acetonitrile.

Inhalation exposure was assessed using a portable pump (Gilian Instrument Corp. NJ) strapped on the applicator's body. This was set at 2 L/min after calibration using a bubble flowmeter. Residues were extracted from the Tenax adsorbent material and analyzed for imidacloprid residues.

Urine samples were collected from each worker in sterile wide-mouthed bottles stored in ice in styrofoam boxes at various time intervals. All samples were collected in the field and kept in ice in a styrofoam box while in transit.

Urine (100 ml) was extracted for imidacloprid residues by shaking with methylene chloride (2 x 150 ml, 1 x 100 ml). The combined organic layer was dried over sodium sulfate, evaporated and taken up in 2 ml of acetonitrile. Urine (100 ml) was likewise extracted for 6-chloronicotinic acid (6-CNA) residues by shaking with acetonitrile (1 x 100 ml) and hexanes (1 x 100 ml). The aqueous layer was re-extracted with methylene chloride (1 x 100 ml) and the

combined organic layers were dried over anhydrous sodium sulfate, evaporated and made up to 5 ml in acetonitrile. The extract was passed through a Florisil column (4.5 g., 5% deactivated; 19 mm id x 185 mm) topped with a 1 cm layer of anhydrous sodium sulfate. The column was pre-wet with 20 ml of ethyl acetate and the sample flushed with 100 ml of ethyl acetate. Imidacloprid was eluted in 20 ml of acetonitrile. The final extract was evaporated and taken up in 2 ml of acetonitrile.

Analysis of imidacloprid and 6-CNA was done by high pressure liquid chromatography using a Tracor Model 950 pump equipped with a Tracor 970A variable wavelength detector set at 270 nm. The Whatman Partisil 10 ODS-1 column was eluted with 40:60 (v/v) acetonitrile:water at a flow rate of 0.6 ml/minute.

The efficacy of the extraction, clean-up and estimation procedures was checked from recovery experiments for imidacloprid by fortifying the respective samples.

Loss of imidacloprid due to storage, transit conditions and exposure to light was determined by pipetting 1 ml of spray formulation on garment patches (46 cm'). These were exposed to sunlight for the duration of spray application and stored in the same manner as the other samples. Unexposed patches served as controls.

Calculations:

$$\text{Specific exposure (head) (mg/person x kg AI)} = \frac{\text{Sum of nose and forehead (mgL}}{\text{Kg AI handled}}$$

$$\text{Specific exposure (body) (mg/person x kg AI)} = \frac{\text{Sum of all body parts (mg)}}{\text{Kg AI handled}}$$

$$\text{Estimated exposure} = \frac{\text{sum spec. exposure}}{\text{(inner body)}} \times \frac{\text{area sprayed } (m^2)}{10{,}000\ (m^2/ha)} \times \text{rate}$$

RESULTS AND DISCUSSION

The recovery values of treated pads, protective garment, gauze and urine ranged from 89 to 110% (Table 1). A substantial amount of the residues were lost through the effect of weather conditions prevalent on the day of spraying. Field recovery of imidacloprid residues

Table 1. Imidacloprid recovery from fortified samples.

Sample Type	Fortification Range	Mean Recovery	n
Absorbent pads	13 μg	89	3
Protective garment	13 μg	110	3
Gauze	13 μg	97	3
Urine	10 μg	90	3

showed an average reduction of 52% due to effects of weather conditions and storage.

Outer exposure of the workers was assessed through the amount of residues found on the prescribed white cotton outer wear. Most body parts did not contain any detectable residues or trace levels only (Fig 2).

Very low residue levels were detected in some body parts of five out of the six test workers. Residue levels detected on the garment were within the range of 11 to 54 ng/cm^2. Residues detected were found in the upper torso parts such as, forearms, upperarms and shoulders. This is indicative of the spraying regimen required for tall trees like mangoes. Sprayers have to spray overhead and sometimes climb the trees.

Imidacloprid residues found on the facial area could only be detected in three out of the six workers. Residues ranged from 146 to 260 ng imidacloprid/cm^2 over the unprotected facial area which was essentially the forehead and a portion of the cheeks. Worker 1 had some imidacloprid residues on the covered facial area. The front neck portion of two workers also had detectable residues. These can be attributed to the movement of residues through sweat, not only through the natural vertical movement due to gravity but through the act of wiping the face. It was observed that the workers were perspiring profusely not only in the face but throughout the whole body. They found the prescribed protective

Table 2. Exposure (ug/body area) of applicators to imidacloprid while spraying mangoes.

Body part	Worker Number 1	2	3	4	5	6	MDL[1]
1. Face	1.19	1.57	4.98	0.06	0.06	0.06	0.06
2. Neck	2.20	0.02	1.20	0.02	0.02	2.49	0.02
3. Forearms	0.11	0.11	0.11	0.11	0.11	0.11	0.11
4. Upperarms	0.27	0.27	0.27	0.27	0.27	0.27	0.27
5. Shoulders	0.02	1.56	0.02	0.02	0.02	0.02	0.02
6. Chest	0.33	0.33	0.33	0.33	0.33	0.33	0.33
7. Back	0.33	0.33	0.33	0.33	0.33	0.33	0.33
8. Thighs	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Total (ug)	4.79	4.54	7.59	1.49	1.49	3.96	

[1] Minimum detection limit

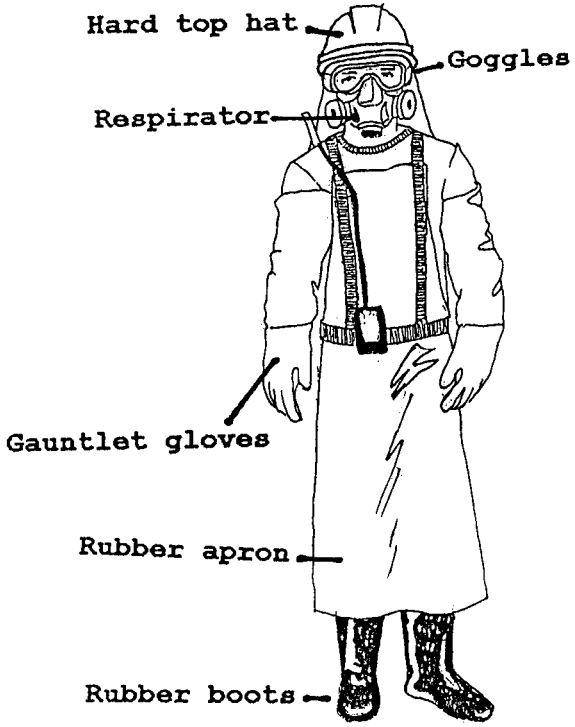

Figure 1. Applicator wearing recommended personal protective equipment.

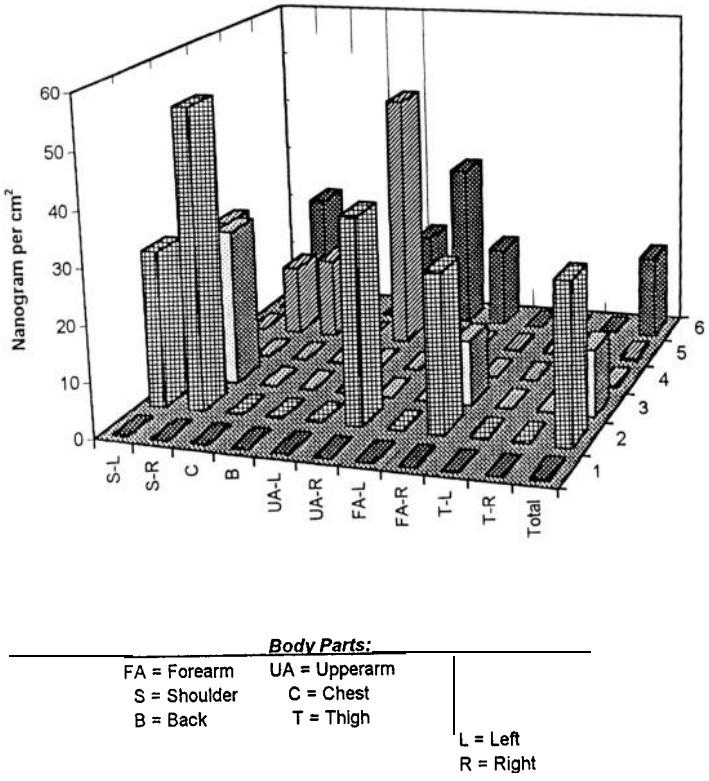

Figure 2. Imidacloprid residues in protective garment worn by pesticide applicators of mango.

garment most uncomfortable. Imidacloprid residues were not detected on the hair of the workers except for one worker. This is entirely due to exposure when the hat was removed due to extreme discomfort brought about by sweating.

Imidacloprid residues that penetrated through the protective garment could not be detected except on the right shoulder of Worker 2. Worker 2 had the highest level of imidacloprid residues (397 ng/cm^2) on the right shoulder of the protective garment and a percentage (25%) of these residues penetrated through the clothing material. Residues did not penetrate through the boots and socks for all workers. Imidacloprid residues were detected in the hands of five out of six workers. While their hands were protected by gauntlet gloves, it could not be avoided that they would have to remove their gloves even for just a short time during the entire 3-hr spraying period. Again, this was due to extreme discomfort brought about by sweating. Contamination came from the act of wiping their sweating hands on the cotton garment or accidental contact with the rubber apron. These resulted in residues ranging from 25 to 182 ng/cm^2.

Imidacloprid residues could not be detected in Tenax adsorbent cartridges used to assess inhalation exposure. Assessment of dermal absorption showed that urine did not through the effect of weather conditions prevalent on the day of spraying. Field recovery of imidacloprid residues contain any detectable imidacloprid and 6-CNA residues. The detection limits of the methods employed were 0.025 and 0.20 mg/L for imidacloprid and 6-CNA, respectively.

Estimated exposure for all six workers did not exceed the tolerable dermal exposure for imidacloprid. Values obtained for all six workers ranged from 0.0015 to 0.0076 mg/(person x day)(Table 1). Calculation for tolerable dermal exposure was based on a subacute dermal study in rabbits which established a NOEL of 1,000 mg/kg b.w. (Flucke, 1990).

$$D_{tol} = \frac{\text{NOEL x 50 kg b.w.}}{25\ (SF)} = 2{,}000 \text{ mg/(person x day)}$$

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