Gas Chromatographic Method for Assessing the Dermal Exposure of Greenhouse Applicators to Dimethoate and Malathion

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Abstract

An analytical method is developed to determine potential and actual dermal exposure to dimethoate and malathion for agricultural workers using whole body dosimetry. The methodology described includes three different aspects: the validation of the analytical method incorporating a matrix effect for establishing performance parameters such as recovery rates (between 92% and 103% for both pesticides), limits of detection and quantitation, and precision of measurements (RSD < 10%); a field sampling strategy developing a procedure for collecting samples and carrying out field spikes and field blanks in order to ensure the stability of samples during transport, storage, and analysis; and finally, a quality control procedure for ensuring that data are under statistical control. The method is applied to evaluate the potential and actual dermal exposure as well as its distribution for a pesticide applicator and the applicator's assistant after a greenhouse application. Operator exposure levels of approximately 68 mL/h, and 25 mL/h in the case of the assistant, are found. The body areas most exposed are the lower body and hands.

Introduction

Pesticide use is associated with risk derived from exposure, which occurs during mixing, loading, application of the pesticides, and re-entry. The legislative basis for the regulation of plant protection products in the European Community is Directive 91/414/EEC. In annex III of this directive are related exposure data requirements. Modeling of exposure for different scenarios is often the first step in the exposure assessment. A number of predictive operator exposure models exist in Europe (1,2) and North America (3). However, wherever appropriate realistic data are available, the risk assessment is based on these in preference to modeling (4).

Several methods have been reported to determine potential and actual exposure of agricultural workers to pesticides, with the "patch" method and the "whole body" method being the most used. Durham and Wolfe (5) proposed the patch method, which was adopted by the World Health Organization and the Environmental Protection Agency. This method distributes absorbent patches of a known surface on different places of the worker's body, analyzes the amount of pesticide deposited on it, and extrapolates the amount found in the patches to the body area that represents each one. Several authors (6,9) agree on some of the limitations inherent to this methodology, which may give significant under- or overestimation of exposure mainly derived from the assumption that the spray liquid deposits uniformly on the body. These limitations also exist when the method is applied for determining re-entry exposure in which contact with the crop is not a uniform process. Despite its limitations, the patch method is a cost-effective method for determining pesticide exposure in comparative studies.

In the whole body method (10), the worker dresses in a suit of a material such as cotton or polyester that is used as the sampling medium. After that, the garment is sectioned into several pieces, extracted, and then analyzed by determining the amount of pesticide deposited on the body and its distribution. In a practical sense this method is more convenient because it is not necessary to assume the uniform deposition and that the suit retains most of the pesticide. It is not necessary to extrapolate from small target areas to larger body regions, and finally, the method is compatible with biological monitoring.

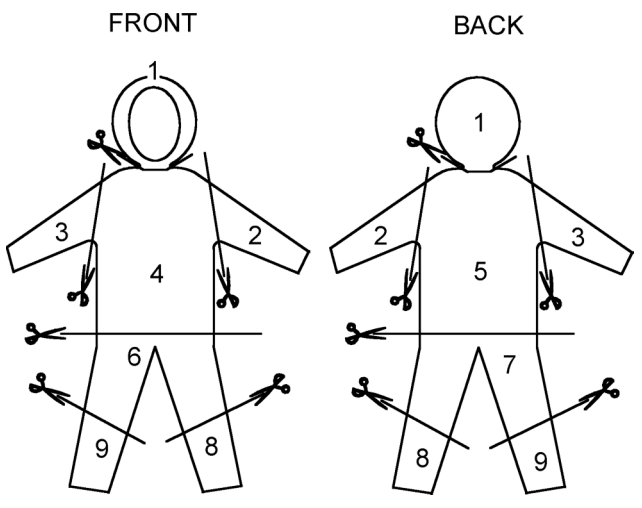

Figure 1. Coverall sectioning for whole body analysis.

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Several authors have reported potential dermal exposure data using patch or whole body methods. Machado Neto et al. (11) have found potential exposure levels ranging between 166 and 1800 mL/h after two applications on a tomato crop. Spencer et al. (12) found levels of exposure to chlorothalonil between 60 and 500 mg/L in a tomato crop's applicators. Calumpang (13) studied the likely influence of four application patterns on dermal exposure to parathion-methyl. Popendorf (14,15) used the whole body method combined with patches attached underneath to evaluate potential and actual dermal exposure of workers and found a high variability in the results. In the same address, recent studies (16) showed that the use of an absorbent garment together with a relatively impermeable suit underneath is a good sampling strategy to collect the spray liquid during pesticide applications for potential and actual dermal exposure evaluation.

Dermal exposure evaluation methods reported in the literature showed different sampling and analytical methods such as differences in the number and location of patches and (in the whole body method) differences in the material used, sectioning of the coveralls, and extraction procedures of the analytes.

Three reviews on pesticide exposure assessment (6–8) report that analytical methods should be validated because few papers incorporate the validation of sampling and analytical methods or quality control procedures to ensure the quality of the results. In this sense, recent studies incorporating the matrix effect in the quantitation of pesticides and quality control criteria have been carried out (17).

The European Union (EU) is concerned by the assessment of the pesticide exposure of agricultural workers in Southern Europe, and the European Committee for European Standardisation is the organization that is to decide upon the analytical requirements for this purpose. The work reported in this study has been conducted in the frame of the EU Standard Measurement and Testing Programme (reference SMT4-CT96-2048) with the aim of reporting an analytical method for assessing the dermal exposure of greenhouse applicators to dimethoate and malathion. Several aspects of the analytical procedure rarely considered in exposure assessment (such as the likely effect of the coextractives from the matrix in the quantitation of pesticides, the validation of the analytical method calculating performance parameters, and a sampling and quality control procedure for routine analysis) have been established in this study. Finally, the method has been applied to evaluate potential and actual dermal exposure of a greenhouse applicator and an assistant worker to dimethoate and malathion during an application.

Experimental

Chemicals

The solvent used for extraction was acetone (residue-analysis grade, Panreac, Barcelona, Spain). Dimethoate and malathion standards (< 99% pure, pestanal quality) obtained from Riedel de Haën (Seelze, Germany) were dissolved separately in acetone (200 mg/mL) in order to obtain the primary calibration solutions. Other solutions of lower concentration were prepared from these by dilution with acetone or the matrix extract when appropriate.

Perfekthion S (50% dimethoate, w/v) (Basf Española, Madrid, Spain) and Ultration 90 (90% malathion, w/v) (Lainco, Barcelona, Spain) were used for treating plants in the greenhouse.

Mojante (AgrEvo, Valencia, Spain) was used as the surfactant.

Absorbent cotton gloves and the disposable coveralls Tyvek Pro-Tech (DuPont Engineering Products, Luxembourg) and Sontara were used in the field experiment.

Instrumentation

A Hewlett-Packard (Palo Alto, CA) gas chromatograph (GC) 5890 equipped with a Nitrogen–Phosphorus Detector (NPD) was used. A 1-µL sample volume was injected using an HP 7673 autosampler in a fused-silica capillary (HP-1) column containing a 100% methylpolisiloxane stationary phase (60-m length, 0.25-mm i.d., 0.25-µm film thickness). HP 3365 Chemstation software was used for instrument control and data treatment. An HP Model 5890 Series II GC coupled with an HP 5971 mass spectrometer (MS) detector on a column injector and an HP 7673 autosampler with HP-UX Chemsystem software were used for GC–MS analysis using a Chrompak (Middelburg, The Netherlands) CP-Sil 5 capillary column (25-m length, 0.25-mm i.d., 0.25-µm film thickness) connected to a deactivated fused-silica uncoated precolumn (1-m length, 0.53-mm i.d.).

An overhead mixer (Agitaser, Sirem, S.A., Barcelona, Spain) that was needed for holding containers was used for the cold extraction of contaminated clothes (1-L capacity with lid).

GC–NPD operating conditions

The injector temperature was 250°C, the detector temperature 300°C, and the splitless time 2 min. The initial temperature was 90°C. It then rose at 20°C/min to 200°C, at 10°C/min to 250°C, and then was held at 250°C for 20 min. The carrier gas was nitrogen at 0.85 mL/min.

GC–MS operating conditions

Upon column injection, the initial oven temperature was 60°C for 1 min. It then rose from 10°C/min to 270°C and then was held for 5 min. The initial injector temperature was 63°C, and then it was held at the same rate as the oven. The helium carrier gas with column head pressure was 8 psi. The MS was set in the electron-impact ionization mode with a 70-eV electron energy and a scan mass range from 40 to 440.

Precleaning of clothes

The coveralls and cotton gloves were prewashed in order to eliminate possible interfering substances using 10 L of a water–acetone (9:1, v/v) mixture in a conventional washing machine. The cleaned clothes were dried at room temperature and stored in clean plastic bags in the dark until use.

Extraction and analysis of pesticides from clothes

Coveralls were sectioned into nine pieces (Figure 1) and placed in separate containers with acetone as the extract. The section name (and extraction volume) for each one were as follows: head and neck (250 mL), left arm (250 mL), right arm (250 mL), chest

(350 mL), back (350 mL), thighs and waist front (350 mL), thighs and waist back (350 mL), lower leg left (250 mL), lower leg right (250 mL), glove left (150 mL), and glove right (150 mL). In the next stage, containers were closed and placed in the overhead shaker for 30 min for the extraction of pesticides. In order to obtain a blank matrix extract, uncontaminated coveralls were extracted following the same procedure. An aliquot of each extract was transferred to a 10-mL volumetric flask containing 3.5 µg of caffeine as the internal standard. Finally, these solutions were injected into the GC–NPD (1 µL) and GC–MS (5 µL).

Field experiment

A field experiment was conducted in a flat-roof experimental greenhouse of polyethylene (200-mm thickness; 15- × 40- × 2.50-m volume) located in Almería (Spain), which was in use for the growth of green beans. The crop was 2.5-m high with rows separated by 1.5 m. Lateral windows remained closed during the experiment. Perfekthion S (50% dimethoate, w/v) and Ultration 90 (90% malathion, w/v) were applied at a rate of 1235 L/h, corresponding to a dose of 0.617 Kg/h dimethoate and 2.223 Kg/h malathion as the active ingredient. Formulations were dissolved in a tank containing 300 L of water and 300 mL Mojante as the surfactant.

A semistationary high-volume two-stroke sprayer with one circular nozzle operating at a flow rate of 3.9 L/min was used for the spraying application from ground level up to a height of 2.5 m for 19 min. Droplet sizes ranged from 40 to 180 µm at an application pressure of 20 atm. Climatic conditions were monitored and registered. During application the applicator held the spray lance with his right hand while walking between the rows spraying the crop on one side of the row and then returning along the same row spraying the plants on the other side of the row from ground level upwards in both cases.

An assistant helped the operator with the application, remaining always in the central alleyway without walking between the cropped area. Both the operator and assistant wore cotton gloves, a disposable respirator, and Sontara and Tyvek coveralls. The absorbent Sontara was worn over the Tyvek to collect the liquid landing on the worker. The Tyvek undergarment collected any liquid penetrating the Sontara.

Field quality control and sampling procedure

A quality control procedure was established for ensuring the performance of the method. A section of the quality control procedure included a field sampling strategy for assessing the sample and analyte stability during sampling, the transport and storage, and the performance of the analytical method.

The quality control procedure consisted of the following steps. An aliquot of the spray tank was taken from the nozzles and stored separately from the rest of the samples for testing its concentration. Field spikes were prepared for checking the recovery rates and precision of the routine analyses and for spiking three pieces (30 × 30 cm) of the uncontaminated coveralls and three cotton gloves with 100 µL of the spray tank (which contained 50 µg and 180 µg of dimethoate and malathion, respectively). In addition to these steps, three pieces of uncontaminated coveralls and three cotton gloves (field blanks) were also stored as a check for accidental contamination or sample decomposition during sampling, transport, storage, and analysis.

After application, coveralls and cotton gloves worn by the applicator and assistant were carefully removed and dried in the shade. Samples, field spikes, and field blanks were kept in single bags adequately labeled, and the spray tank sample was stored separately from the samples in order to avoid accidental contamination. All samples were stored in the laboratory in darkness at 4°C until extraction and analysis.

Results and Discussion

Figure 2 shows the GC–NPD chromatogram of dimethoate and malathion for an acetone extract of Sontara containing both compounds at a 0.3-µg/L concentration level and caffeine as the internal standard. It can be observed that there were no interfering signals at the retention time of the analytes.

Calibration

The retention time window (RTW), defined as the average of ten measurements of retention times plus or minus three times the corresponding relative standard deviation (RSD) (18), was determined for each pesticide by injecting a solution containing 1 µg/mL of dimethoate and malathion into the GC–NPD and 4.0 µg/mL of each pesticide into the GC–MS. The RTW values obtained for dimethoate were 13.38–13.46 and 13.99–14.05 using the HP-1 and CP-Sil 5 capillary columns, respectively, and 16.09–16.14 and 16.46–16.53, respectively, for malathion.

Calibration curves were prepared from four experimental points containing caffeine as the internal standard and plotting the height ratio versus the amount ratio for each analyte. Blank matrix extract was used for filling up to volume in order to avoid a matrix effect (matrix-matching calibration). The determination coefficients obtained for both pesticides were greater than 0.99 and the standard deviation of the slope, intercept, and residuals was 0.008, 0.007, and 0.01, respectively. Dynamic ranges (19) were calculated by obtaining the RSD of the response factors

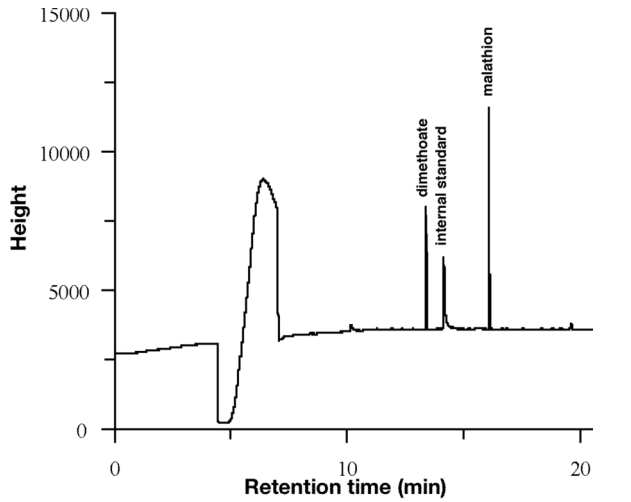

Figure 2. NPD chromatogram of a Sontara extract containing dimethoate and malathion.

measured between 1–10 and 10–100 times the quantitation limit (LOQ) of dimethoate and 1–20 and 20–200 times the determination limit (LOD) of malathion, which were lower than 8%. The LODs and LOQs were calculated as 3 and 10 times the respective standard deviation of the baseline signal corresponding to the blank matrix extract chromatogram at the analyte retention time divided by the slope of the calibration curve. The LODs for dimethoate and malathion were 19.5 and 5.8 µg/L and the LOQs were 64.3 and 19.2 µg/L, respectively.

Validation of method

In order to carry out the validation studies, the composition of the field spray tank was reproduced for recovery and precision studies, preparing a "standard laboratory spray solution" by dispersing 50 mg and 180 mg of dimethoate and malathion standards, respectively, and 0.3 mL of a placebo of emulsifiable liquid formulation in 50 mL of water. Finally, 0.1 mL of Mojante was added as the surfactant. The solution was homogenized and the volume was filled up with water to 100 mL in a volumetric flask. The concentration of this solution was 0.5 g/L dimethoate and 1.8 g/L malathion. In order for the validation of the analytical method, recovery studies and precision were determined.

Recovery

The standard laboratory spray solution was used for spiking ten pieces of each clothing (30 × 30 cm) at two concentration levels, 50 and 1000 µg for dimethoate and 180 and 3600 µg for malathion. Pieces were extracted, analyzed, and quantitated as explained in the Experimental section. When dilution was necessary it was carried out using blank matrix extract. The values of percent recovery for dimethoate and malathion at the two levels of concentration for Sontara, Tyvek, and gloves are given in Table I. The RSD of the measurements were lower than 10% in all cases. The influence of the matrix in the quantitation of the analytes can be observed when the coextractives from the matrix are included in the calibration solutions (matrix-matched calibration). Under these conditions the recovery rates are closer to 100% compared with those obtained when solvent calibration is used.

Precision

The standard laboratory spray solution was used for spiking ten pieces of each clothing (30 × 30 cm) with 50 µg of dimethoate and 180 µg malathion. These pieces were extracted, analyzed, and quantitated in the previously stated method, obtaining RSDs less than 10%. In order to test the intermediate precision, 12 pieces of each garment and 12 cotton gloves were spiked at the previously stated concentration levels and stored. Batches of three pieces and cotton gloves were analyzed every two weeks for four months, obtaining similar recovery rates as in the previous cases and a slightly higher RSD (< 15%). The calculated intermediate precision included some sources of variability such as time, changes in the reagents and standards batches, and the usual maintenance operations in the GC.

Table I. %Recovery and Precision of Dimethoate and Malathion at Two Concentration Levels for Sontara, Tyvek, and Gloves

	Spiking	Sontara		Tyvek		Cotton gloves	
Pesticide	level (µg)	SC*	MMC†	SC	MMC	SC	MMC
Dimethoate	50	115.3 (8.4)	92.3 (7.4)	115.9 (7.7)	95.6 (8.7)	84.3 (8.4)	98.6 (9.1)
	1000	112.6 (8.1)	92.8 (8.3)	116.1 (7.5)	94.4 (9.1)	87.4 (7.9)	97.6 (8.4)
Malathion	180	80.3 (8.0)	93.3 (7.1)	116.2 (7.0)	96.4 (6.5)	80.2 (6.2)	103.2 (6.9)
	360	83.4 (7.8)	92.7 (7.7)	115.7 (6.4)	97.0 (8.7)	83.4 (6.6)	98.4 (9.1)

* SC, solvent calibration.
† MMC, matrix-matched calibration.

Table II. Potential and Actual Dermal Exposure of Applicator and Assistant to Dimethoate and Malathion

	Applicator exposure (mL/h)				Assistant exposure (mL/h)	
	Sontara*		Tyvek†		Sontara	
Body Region	Dimethoate	Malathion	Dimethoate	Malathion	Dimethoate	Malathion
Head/neck	0.73	0.98	–	–	–	–
Left arm	4.53	4.72	0.28	0.23	0.39	0.43
Right arm	5.33	5.19	0.69	0.72	2.21	2.13
Chest	2.12	2.35	0.17	0.11	1.43	1.54
Back	1.18	1.48	–	–	–	–
Thighs (front)	6.49	6.55	0.56	0.66	3.98	4.12
Thighs (back)	4.53	4.69	–	–	0.26	0.22
Lower leg (left)	17.17	17.36	3.33	3.47	3.79	3.73
Lower leg (right)	19.66	19.55	3.61	3.52	2.69	2.72
Total body	61.74	62.87	8.64	8.71	14.75	14.89
Left hand	3.38	3.41	–	–	4.22	4.12
Right hand	2.59	2.56	–	–	6.65	6.53
Total hands	5.97	5.97	–	–	10.87	10.65
Total (body and hands)	67.71	68.84	8.64	8.71	25.62	25.54

* Sontara beneath.
† Tyvek underneath.

Stability

In order to study the stability of dimethoate and malathion on different clothes and cotton gloves, 36 pieces (30 × 30 cm) of each garment were spiked with 50 and 180 µg of dimethoate and malathion, respectively, using the laboratory spray solution and stored in darkness at 4°C for four months. A set of three samples of each sampling medium was extracted and analyzed on the first day and every fourth week. The percent recovery (besides the storage time that was calculated by comparing the amount recovered with the amount recovered on the first day after spiking) was found to be > 91% in all cases during the period studied.

Analytical quality control and analysis of field samples

A quality control was established for the analysis and quantitation of analytes, including each set of samples, field blanks, calibration curves, and field spikes. Results were tested to be under statistic control when comparing the recovery

rates obtained from field spikes and those obtained during the validation of the method using spikes carried out in the laboratory. The assumed criteria were that the recovery rates of field spikes should be between 70% and 120% and precision less than 15%, the field blanks should not show evidence of any contamination nor sample decomposition, and calibration curves should not differ more than 25% from those obtained in validation studies.

Dermal exposure levels

Once the analytical procedure was established, potential and actual dermal exposure of the agricultural workers to dimethoate and malathion were determined after a greenhouse application. The concentration of both pesticides expressed as the milliliters of spray tank deposited on the garment per hour of application for the operator (top and underwear) and assistant (top wear) are summarized in Table II.

Spray tank concentration was calculated obtaining 453 mg/L of dimethoate and 1748 mg/L malathion. The total volume of spray liquid deposited on the top suit of the operator (Sontara) was 61.74 and 62.87 mL/h for dimethoate and malathion, respectively. Although the concentration of both pesticides in the field spray tank was different (approximately 0.5 g/L for dimethoate and 1.8 g/L for malathion), the amount (expressed in milliliters per hour) was almost the same because the concentration of the tank was homogenous and the pesticides were applied together.

When considering the distribution on the body, approximately 78% of the total potential exposure was found on the lower body (thighs and lower leg), with both of the lower legs being the most contaminated sections (17.17–19.66 mL/h for dimethoate on the left and right leg, respectively, and 17.36–19.55 mL/h for malathion). The highest amount of pesticide in these regions was because the operator directed the spray-gun downwards pointing to the legs without cutting the flow when he passed from one row to another. On the upper body (head, torso, back, and arms) the amount found was 22% (dimethoate) or 23% (malathion) of the total, with the right arm (5.33 mL/h dimethoate and 5.19 mL/h malathion) and left arm (4.53 mL/h dimethoate and 4.72 mL/h malathion) being the most exposed areas.

The inter-row distance (1.5 m) contributed to the exposure, mainly the arms that came into frequent contact with the sprayed plants. The exposure of the total body was also because of the application pattern of the operator, the design of the spray lance, and the height of the crop. The actual total body exposure of the operator (Tyvek undergarment) was 14% (8.6 mL/h dimethoate and 8.71 mL/h malathion) of the volume of spray found on the Sontara outer garment. No contamination was found in the head, back, and thighs (back). In the other sections, exposure ranged between 0.17 mL/h (dimethoate) and 0.11 mL/h (malathion) for the chest and 3.61 mL/h (dimethoate) and 3.52 mL/h (malathion) for the lower leg (right).

The body exposure of the hoseman was likely because of the airborne droplets in the cloud produced by the nozzles, and there was high contamination on his hands resulted from contact with the hose. In this case the potential dermal exposure was 25.62–25.54 mL/h for dimethoate and malathion, respectively, with the hands having exposure at 40% of the total.

Conclusion

A whole body method using an outer absorbent garment (Sontara) and an inner garment (Tyvek Pro-Tech) allowed for the majority of the liquid contamination to be retained by the outer garment, with the inner garment collecting any liquid penetrating the Sontara.

The use of blank matrix extracts to establish performance parameters for the validation of the method established an LOD of 5.8 and 19.5 µg/L and an LOQ of 19.2 and 64.3 µg/L for malathion and dimethoate, respectively. Linear dynamic ranges were also established using blank matrix extracts to prepare calibration curves and resulted between 1–10 and 10–100 times the LOQ of dimethoate and between 1–20 and 20–200 times the LOQ of malathion. The use of a spray liquid with the same composition as the field spray tank for spiking samples and the incorporation of the matrix coextractives in the calibration curves gave recovery rates higher than 90% and precision less than 10% for both pesticides in the different garments tested.

A sampling methodology including field spikes and field blanks was proposed in order to establish quality control criteria for routine analysis such as recovery rates, precision, and the absence of contamination and the evidence of sample decomposition during transport, storage, and analysis of field blanks.

The potential dermal exposure of the applicator was approximately 68 mL/h (including hands), and the exposure of the hoseman was 25 mL/h. The exposure of the hands was approximately 9% of the total in the case of the applicator and approximately 40% for the assistant. Actual dermal exposure of the applicator was approximately 12% of the potential dermal exposure, with the lower legs being the areas most exposed. Factors such as the application pattern, application equipment, and crop may affect the distribution of the contamination on the different parts of the body.

Acknowledgments

This work was financially supported by the European Union Standard Measurement and Testing Programme Project SMT4-CT96-2048, "The Assessment of Operator, Bystander and Environmental Exposure to Plant Protection Products", and by the CICYT Project AMB97-1194-CE.

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Manuscript accepted May 14, 2001.