

EVALUATION OF PESTICIDES APPLICATORS
EXPOSURE TO DIMETHOATE UNDER PLASTIC
HOUSES IN THE JORDAN VALLEY

BY

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Dedicated

TO

MY FAMILY

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1. INTRODUCTION

Most of Jordanian agricultural production is concentrated in the Jordan Valley (JV). Nearly 66% of the total irrigated area in Jordan is located there, due to the sufficient water supplied by the King Abdallah Canal (Anonymous, 1985). Since plastic covers provide optimum conditions for plant growth during the period from October to June in the JV. Vegetables became the most important crop in economic and strategic terms. They occupied about 76% of the cultivated area in the JV (Anonymous, 1985). Also, plastic houses provide optimum conditions for a variety of insects and diseases.

In Jordan, as well as in many other developing countries, the use of pesticides forms the backbone of controlling these pests. It was estimated that 61.5% of the total imported insecticides to Jordan were organophosphorus (OP) during the year 1988. Dimethoate alone (66.4 tons) consisted about 48% of the total OP insecticides for that year (Anonymous, 1988). This chemical is extensively used because it is effective against a wide range of insects and certain mites and has a relatively moderate mammalian toxicity.

Because of the increased use of OP insecticides human poisoning became a problem (Davies, 1981). Several cases of poisoning have been reported in Jordan (Khoury and Abdul Wali, 1980; Fattaleh, 1984).

The exposure of spraymen to pesticides usually occurs during the spraying operation. Because of high temperature and humidity prevailing under plastic houses, spraymen are usually applied not to use protective measures while spraying. Under these working conditions the possibility of exposure to

the spray solution either dermally or through respiration is high. In Jordan, Fattaleh (1984) pointed out that the rate of poisoning was 10 persons per 100,000. This rate is considered high compared with records from other countries (Davies and Freed, 1981).

This striking differences in the poisoning cases in Jordan raised high concern among officials as well as civilians. Also, the lack of documented information concerning the dermal and respiratory exposure to pesticides prompted this study to be undertaken.

The objectives of this study are:

1. Measuring the exposure of different body parts of applicators to dimethoate under plastic houses in the Jordan Valley.
2. Measuring respiratory exposure of applicators to dimethoate under plastic houses in the Jordan Valley.
3. Measuring the percentage activity of plasma cholinesterase in the applicators before and after exposure to dimethoate under the circumstances described above.
4. To find out if the recommended health-based limits in occupational exposure to pesticides has been exceeded.

1. ORGANOPHOSPHORUS INSECTICIDES

Organic compounds of phosphorus are essential constituents of protoplasm, nucleotide coenzymes, metabolic intermediates, and phosphatides. Synthetic organophosphorus (OP) compounds are used as lubricants, plasticizers, and pesticides (Eto, 1977).

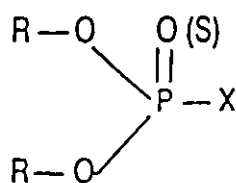
Research in the field of organic chemistry of phosphorus was first undertaken by Lassaigne, in 1820. The great advancement in agricultural practice and scientific knowledge on the structure-activity relationship of OP insecticides were achieved by the discovery of parathion in 1944 (Eto, 1977).

The earliest members of OP group were highly toxic to vertebrates. Later, many less toxic insecticides have been developed by slight structural modifications e.g. malathion, fenitrothion, and fenitrothion were discovered in 1951, 1958, and 1959, respectively (Eto, 1977).

An important feature of OP group is that different members possess different physiochemical properties, chemical stability and variable toxicity to mammals. They have overtaken OC pesticides because of their relatively low persistency and high efficiency. This wide variation enables appropriate substances of OP group to possess a wide range of uses in agriculture, public and animal hygiene (Hassall, 1982).

2. STRUCTURAL DIVERSITY OF ORGANOPHOSPHORUS INSECTICIDES

Most of OP insecticides have the following general structural formula:



The two R groups are usually methyl or ethyl and are usually identical in each insecticide, while X is frequently a rather complex aliphatic, homocyclic or heterocyclic group. Some of the more important variants of the basic molecular structure, chemical naming system and some examples are shown in Table (1).

The structural variation of OP insecticides is reflected by their range of physical properties and mechanisms by which they are liable to enzyme attack. This has two important consequences :

1. Species selectivity is sometimes achieved because of the amounts or the activities of different enzymes vary from species to another.
2. A multiplicity of possible types and positions of attack by enzymes minimizes the risk of a uniform development of tolerance to all OP insecticides (O'brien, 1967; Hassall,1982).

3. MODE OF ACTION AND TOXIC EFFECTS OF ORGANOPHOSPHORUS INSECTICIDES

Organophosphorus insecticides exert their acute effects on mammals by inhibiting cholinesterases (ChE's) which are present in the nervous system with subsequent accumulation of toxic levels of acetylcholine (ACh).

ACh is a neurotransmitter carrying the nerve signals across a synapse or neuromuscular junction. Once it transmits the signal, it must be immediately hydrolyzed by the enzyme acetylcholinesterase (AChE).

ChE's belong to the very large group of enzymes called hydrolases which split the substrate by hydrolysis. ChE's are divided into two groups : acetylcholinesterase (3.1.1.7) and cholinesterase (3.1.1.8).

Tabel 1 : Main chemical groups of organophosphorus insecticides*

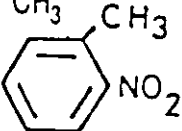
Group	General formula	Example
1. Phosphates	$ \begin{array}{c} \text{R-O} \quad \text{O} \\ \quad \quad \parallel \\ \quad \quad \text{P-O-X} \\ \text{R-O} \quad / \end{array} $	Dichlorvos $\text{R} = \text{CH}_3$ $\text{X} = \text{CH}=\text{CCl}_2$
2. Phosphonates	$ \begin{array}{c} \text{R-O} \quad \text{O} \\ \quad \quad \parallel \\ \quad \quad \text{P-X} \\ \text{R-O} \quad / \end{array} $	Trichlorphon $\text{R} = \text{CH}_3$ $\text{X} = \text{CHOH}-\text{CCL}_3$
3. Phosphorothiolates	$ \begin{array}{c} \text{R-O} \quad \text{O} \\ \quad \quad \parallel \\ \quad \quad \text{P-S-X} \\ \text{R-O} \quad / \end{array} $	Demeton-S-methyl $\text{R} = \text{CH}_3$ $\text{X} = \text{C}_2\text{H}_4\text{-S-C}_2\text{H}_5$
4. Phosphorothionates	$ \begin{array}{c} \text{R-O} \quad \text{S} \\ \quad \quad \parallel \\ \quad \quad \text{P-O-X} \\ \text{R-O} \quad / \end{array} $	Fenitrothion $\text{R} = \text{CH}_3$ $\text{X} = $ 

Table 1 (Continued).

Group	General formula	Example
5. Phosphorodithioates	$ \begin{array}{c} \text{R}-\text{O} \quad \text{S} \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{P}-\text{S}-\text{X} \\ \\ \text{R}-\text{O} \end{array} $	Dimethoate $\text{R} = \text{CH}_3$ $\text{X} = \text{CH}_2\text{-CONHCH}_3$
6. Pyrophosphoramides		Schradan $\text{R} = \text{CH}_3$

* O'brien (1967), Hassall (1982), WHO (1986).

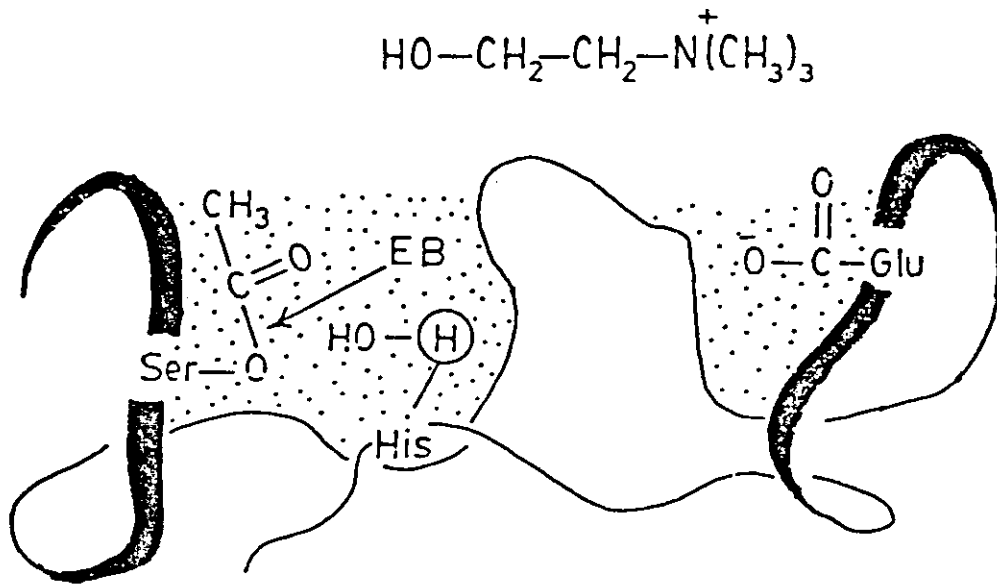
ACh binds to ChE's at two attachment sites. One of these, the ester forming site, containing a serine residue in protein chain. The other, the negative or anionic site contains a glutamic acid residue. The enzyme and the substrate combine at first to form enzyme-substrate complex. The acetyl group transfers to the esteratic site to form acetylated enzyme (Fig.1 a). The acetylated enzyme is then rapidly hydrolyzed and the active enzyme is recovered with a half-life of 2.3×10^{-6} min. or less (Vandekar, 1980).

The inhibition of ChE's with OP insecticides is based on the phosphorylation of the esteratic site (Fig. 1 b). The phosphorylated enzyme is much more stable by a factor 10^6 - 10^9 higher than that for normal substrate (Aldridge, 1985). Usually, an acute exposure will depress the ChE level before depressing the AChE; plasma levels of ChE will usually recover first (California Department of Food and Agriculture, 1983).

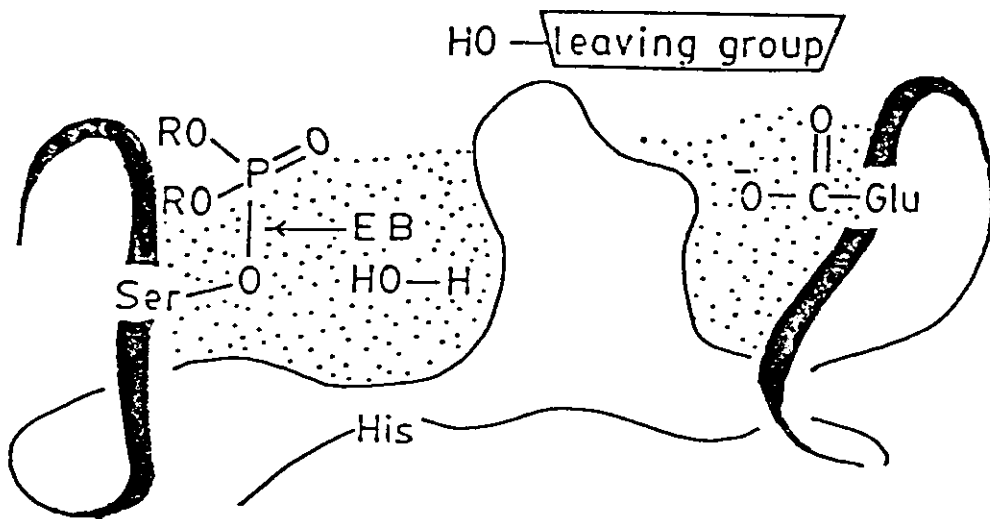
Levels of erythrocyte AChE are satisfactory guide to the level of acute intoxication since erythrocyte AChE are assumed to reflect the effect in target organs (WHO,1986).

Plasma ChE has no known physiological function and can be inhibited in similar way to erythrocyte AChE without causing a toxic response. Levels of plasma ChE are only useful as indicators of exposure (O'brien, 1976; WHO,1986).

Depression of AChE or ChE in excess of 20-25% is considered diagnostic of exposure, but not necessarily indicative of hazard. A depression of 30-50% or more of plasma ChE or erythrocyte AChE is considered as an indicator of clinically sick person. Removal of an exposed individual from further contact with pesticides until enzyme level returns to normal is



a. After splitting the (ACh) the enzyme is acetylated to every short time.



b. after splitting an organophosphate a much more stable phosphorylated enzyme remains.

Fig. 1 : Schematic structure of AChE to illustrate how it is (a) acetylated (b) phosphorylated. Ser, serine; Glu, glutamic acid; His, histidine; EB, esteratic bond.*

* Hassall (1982).

necessary (WHO, 1975; Vandekar, 1980; WHO, 1986).

Symptoms of acute cholinergic poisoning by OP insecticides which result from accumulation of ACh at nerve endings, were described in several references (Davies and Freed, 1981; Health and Safety Executive, 1987).

The symptoms of poisoning with OP insecticides are summarized in three groups (Stimman, 1980; WHO, 1988) :

1. Mild poisoning (include muscarinic and nicotinic only) :
fatigue, headache, dizziness, blurred vision, sweating, salivation, nausea and vomiting, abdominal cramps, diarrhea, and bradycardia.
2. Moderate poisoning :
unable to walk. weakness, chest discomfort, and constriction of pupil eye.
3. Severe poisoning (central nervous system (CNS) involvement) :
unconsciousness, severe constriction of pupil eye, muscle twitching, secretions from mouth and nose, breathing difficulty, coma, and death.

Continuous long-term exposure to high levels of OP insecticides may cause typical cholinergic symptoms, though most of the compounds do not accumulate extensively in the body (Ngatia and Megni 1980; WHO, 1986).

4. ROUTES OF EXPOSURE TO ORGANOPHOSPHORUS INSECTICIDES

The most common routes of OP insecticides entering to human body are dermal, inhalation and ingestion (Levine and Davies, 1980; Stimann, 1980; Freed and Chiou, 1981). Under normal conditions of use, ingestion is rare

(Cottus, 1980). In agricultural practices, the major route of absorption is via the skin (Health and Safety Executive, 1987; WHO, 1986). Inhalation is being less important as a route of exposure during work in open fields (Health and Safety Executive, 1987).

Emulsifiable Concentrate (EC) is considered as one of the most widely used formulation in agriculture. It is based on organic solvents with good skin permeability and generally promote the penetration of insecticides through the skin (Dedek, 1980; Speight, 1980).

Organophosphorus insecticides have different vapour pressure (10^{-2} - 10^{-7} mmHg). Consequently, hazard due to inhalation of vapour varies from compound to another. The vapour pressure of the active ingredient is reduced upon dilution with solvents and emulsifiers. Consequently, inhalation hazard is reduced vastly. On the other hand, these additives facilitate absorption of insecticides through the skin (WHO, 1986).

5. DIMETHOATE

5.1 Chemical And Physical Properties

5.11. Chemical

5.1.1.1. Nomenclature

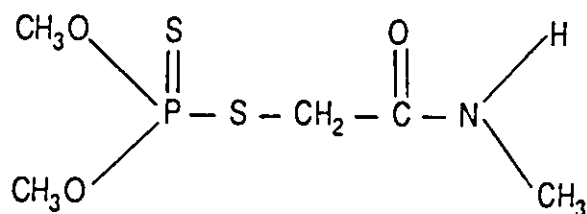
Dimethoate is the common technical name designated by the International Organization for Standardization (ISO) for O,O- dimethyl S-methyl- carbamoylmethyl phosphorodithioate.

5.1.1.2. Common name

Dimethoate

5.1.1.3. Trade names

Cygon ; Perfekthion ; Rogor ; Roxion; Dimethoate.

5.1.1.4. Empirical formula $C_5 H_{12} NO_3 PS_2$. formula weight 229.28.**5.1.1.5. Structural formula****5.1.2. Physical properties**

The pure substance is a colourless crystalline solid with an odour of mercaptan with the following physical properties (WHO, 1988) , the technical grade is a yellow-brown oil.

—	melting point (°C)	51 (pure)
		45.0- 52.5 (technical)
—	boiling point (°C)	107 at 0.05 mmHg

- vapour pressure (25°C) 8.6×10^{-6} mmHg
- water solubility (21°C) 25 g/liter (pure)
up to 39 g/liter (technical)
- highly soluble in chloroform, methylene chloride, benzene, and toluene.
- insoluble in aliphatic hydrocarbons like petroleum ether.

5.2. Formulations And Types of Actions :

Dimethoate is an OP insecticide, introduced commercially in 1965. It is formulated as 40% emulsifiable concentrate (EC), 25% wettable powder (WP) and as dust (D). There is also a formulation for ultra-low-volume (ULV) application (WHO, 1988). It has contact and systemic action that is used against a broad range of insects and mites in agriculture.

5.3. Toxicity

Dimethoate is an indirect acting OP insecticide. It is usually oxidized in the human body into the active metabolite dimethoxon which is about 10 times more toxic. Also dimethoate is hydrolyzed in the body to a less toxic metabolites O,O-dimethyl-dithiophosphoric acid, O,O-dimethyl-thiophosphoric acid, and O,O-dimethylphosphoric acid (De Bock, 1984).

The acute oral toxicity of dimethoate to female rats is moderate with LD₅₀ range of 150-400 mg/kg (WHO 1988). Acute dermal LD₅₀ to guinea pigs is > 1000 mg/kg (Farm Chemicals Handbook, 1986). The toxicity of this compound, however, is greatly dependent on storage conditions. It was reported that in the United Kingdom (U.K.), the LD₅₀ of dimethoate following 7

months of storage was 30-40 mg/kg. Under tropical conditions it was reported to 15 mg/kg following 9 months storage. The toxicity of dimethoate was found to increase by increasing storage temperature (Hays, 1982).

Dimethoate enters the body through ingestion, inhalation and skin. Toxic effects of acute dimethoate poisoning appears when erythrocyte AChE is reduced by 50% or more below the base line value (WHO, 1988).

5.4. Exposure Assessment

Human exposure to dimethoate as well as for other OP insecticides have been quantified in occupational exposure by direct or indirect measurement methods (Davis, 1980; Davies and levine, 1980).

The direct methods involve the use of some mechanism to trap the toxic material as it comes in contact with the workman during his exposure period. The direct methods are used to assess dermal and respiratory exposure (Durham and Wolfe, 1962).

The indirect methods involve the measurement of some effect of the toxicant upon the exposed individual e.g. measurement through biological indices. Cholinesterase activity determination provides satisfactory biological index for exposure (Durham and Wolfe, 1962).

The direct methods for measurement of dermal exposure to dimethoate involves attaching absorbent pads made of alpha-cellulose at different locations on the worker's skin or clothing (Durham and Wolfe, 1962; WHO, 1975). Copplestone *et al.* (1976) used pads made of alpha-cellulose to measure dermal exposure of spraymen to dimethoate in the Sudan. Gauze sponges were used to indicate dermal exposure potential for spraymen applying dimethoate

on citrus trees in the United States of America (Carman *et al.*, 1982).

Respiratory exposure has been estimated most commonly by measuring concentration of dimethoate from air. Cartridge-type- respirators were worn by sprayers applying dimethoate in the Sudan (Coppelstone *et al.*, 1976). Midget impinger has been used for air sampling during application of dimethoate (Hill and Arnold, 1979). Greenburg-Smith impinger filled with ethylene glycol was utilized to trap dimethoate in the U.S.A. (Carman *et al.*, 1982). Direct measurement of respiratory exposure to dimethoate utilizes respiratory pads made of alpha-cellulose for trapping liquid spray (Durham and Wolfe, 1962; WHO,1975). For above mentioned methods, analysis for dimethoate residue in dermal and respiratory exposure samples was determined by using the gas chromatographic methods.

Many methods are available for determining the activity of ChE's (Augustinsson, 1963; WHO, 1975; Vandekar, 1980). All are applicable to ChE's when measured under laboratory conditions. Only a few of these methods are suitable under true field conditions. The spectrophotometric method of Ellman *et al.* (1961) has been found adequate for determining whole blood, erythrocyte, and plasma cholinesterase activity. The filter-paper method of Augustinsson and Holmstedt (1965) was adopted to tropical conditions. The difficulty of extracting erythrocyte AChE from dried blood spot on filter paper limits this method to plasma ChE only. Ecobichon and Crocker (1978) used the method of Ellman *et al.* (1961), to measure plasma ChE activity. De Bock *et al.* (1984) used titration method to determine plasma ChE. The WHO Expert Committee On Insecticide (WHO, 1975) suggested that the spectrophotometric method of Ellman *et al.* (1961) would be suitable as a field and laboratory

method for determining erythrocyte AChE and plasma ChE. In this method, the time of assay is considered short (1-2 min.), simple to perform, reliable, and it is considered as a reference method. This modified method was recommended by WHO (Vandekar, 1980). The various methods used for the determination of dermal, respiratory exposure and ChE's are summarized in Table (2).

Table 2 : Analytical methods used for dimethoate determination and cholinesterases activity in human blood.

Sample	Detection and quantitation	Reference
<u>Dermal exposure</u>		
exposure pads (alpha-collulose)	-gas chromatograph (GC) with phosphorus-sensitive flame photometric detector (FPD)	Cocplestone <i>et al.</i> (1976)
gauze sponges	-GC	Carman <i>et al.</i> (1982)
<u>Respiratory exposure</u>		
Cartridge-type respirator	-GC with FPD detector	Cocplestone <i>et al.</i> (1976)
midget impinger	-GC with FPD detector	Hill and Arnold (1979)
Greenburg-Smith impinger	-GC	Carman <i>et al.</i> (1982)
respiratory pads (alpha-collulose)	-GC	Durham and Wolfe (1962), WHO (1975).
<u>ChE's activity</u>		
Whole blood, erythrocyte, plasma	-spectrophotometry	Elman <i>et al.</i> (1961)
Plasma	-manometer	Augustinsson and Holmstedt (1965).
Plasma	-spectrophotometry	Eccbichon and Crocker (1978)
Plasma	-titrimetric	De Bock <i>et al.</i> (1984)

III MATERIALS AND METHODOLOGY

1. PREPARATION FOR THE FIELD STUDY

1.1. Selection Of Operational Site

This study was conducted under plastic houses at the University-Experimental-Farm in the Central Jordan Valley (CJV) during the growing season of 1988-1989.

Six plastic houses already planted with tomato for production were used. The plants were in the fruiting stage. Each plastic house was arc shaped, north-south direction, 19 meter long, 9 meters wide and 3.2 meters height, covered with 180 μ polyethylene trans- parent plastic sheet.

Five rows, along each plastic house, 90 cm wide, 75 cm apart were levelled. Drip irrigation line covered with black mulch was installed in the middle of each row. Holes, 10 cm in diameter, 40 cm apart, were cut in the plastic mulch, alternately, to form 2 planting rows. One tomato seedling, of the variety " Carmello", was planted in each hole on Nov. 17, 1988. Weeds were kept under control by hand weeding.

1.2. Study Subjects

A spraying team consisted of 6 volunteers, were chosen to assess dermal and respiratory exposure, and to measure plasma ChE activity.

These volunteers aged between 21 and 26 years (mean age 22.3 years). At the time of this study they were clinically healthy, according to medical examination carried out by occupational health specialists.

A preexposure " baseline" value of plasma ChE for each person was determined at a time where the worker has not been exposed directly to OP for 36 days.

The typical clothing worn consisted of a trouser, a short-sleeved open neck shirt, and tennis shoes. Gloves, hats, and masks were not worn.

2. FIELD OPERATIONS

2.1. Dermal Exposure (Carman *et al.* (1982) method)

2.1.1. Apparatus

- a. Gauze sponges 12 ply, 10x10 cm (China Syrgica, China).
- b. Ice box.
- c. Cardboard (11 x 11 cm). aluminum foil , staples, Scotch filament tape, freezer bags with twist and ties.

2.1.2. Chemicals

- a. Acetone A.R. (May and Backer Ltd, England).
- b. Ethylene glycol (Gaurantee Analysis, Riedel-de Haen, W. Germany).

Gauze sponges, precleaned by Soxhlet-extraction with acetone, were immersed for 10 min. in 10% ethylene glycol in acetone and air dried for 10 min. under fume hood. Each sponge was wrapped with aluminum foil and stabled at the four corners onto flexible cardboard to which taps (made of Scotch filament) has been attached. Each assembly was placed in a freezeer bag which is tightly closed by twist and tie for brief storage and transport to the field.

Just prior to starting the test, individual assemblies were placed on the following sites :

1. Chest near the throat.
2. Back near the nape of the neck .
3. Top of each shoulder .
4. Upper arm near the shoulder (right and left).
5. Dorsal side of lower arm near the wrist (right and left).
6. Upper leg just above the knee (right and left).

The total number of gauze sponges per person was ten (Fig.2).

Immediately at the end of the test, each sponge with only its foil packing was returned to a freezer bag, closed tightly by twist and tie, then placed in ice box for transport to the laboratory. Samples were stored at -25°C until analysis was carried out. Sampling was repeated 2 times for each sprayer at 15 days intervals. The grand total number of gauze sponges was $2 \times 6 \times 10$ sponges = 120 samples.

2.2. Respiratory Exposure (Carman *et al.* (1982) method)

2.2.1. Apparatus

- a. Greenburg- Smith impingers (Casella, England).
- b. Mine Safety Appliance Co. pumps (Casella, England).
- c. Ice box.

2.2.2. Chemicals

- a. Ethylene glycol (Guarantee Analysis, Riedel-de Haën, W. Germany).

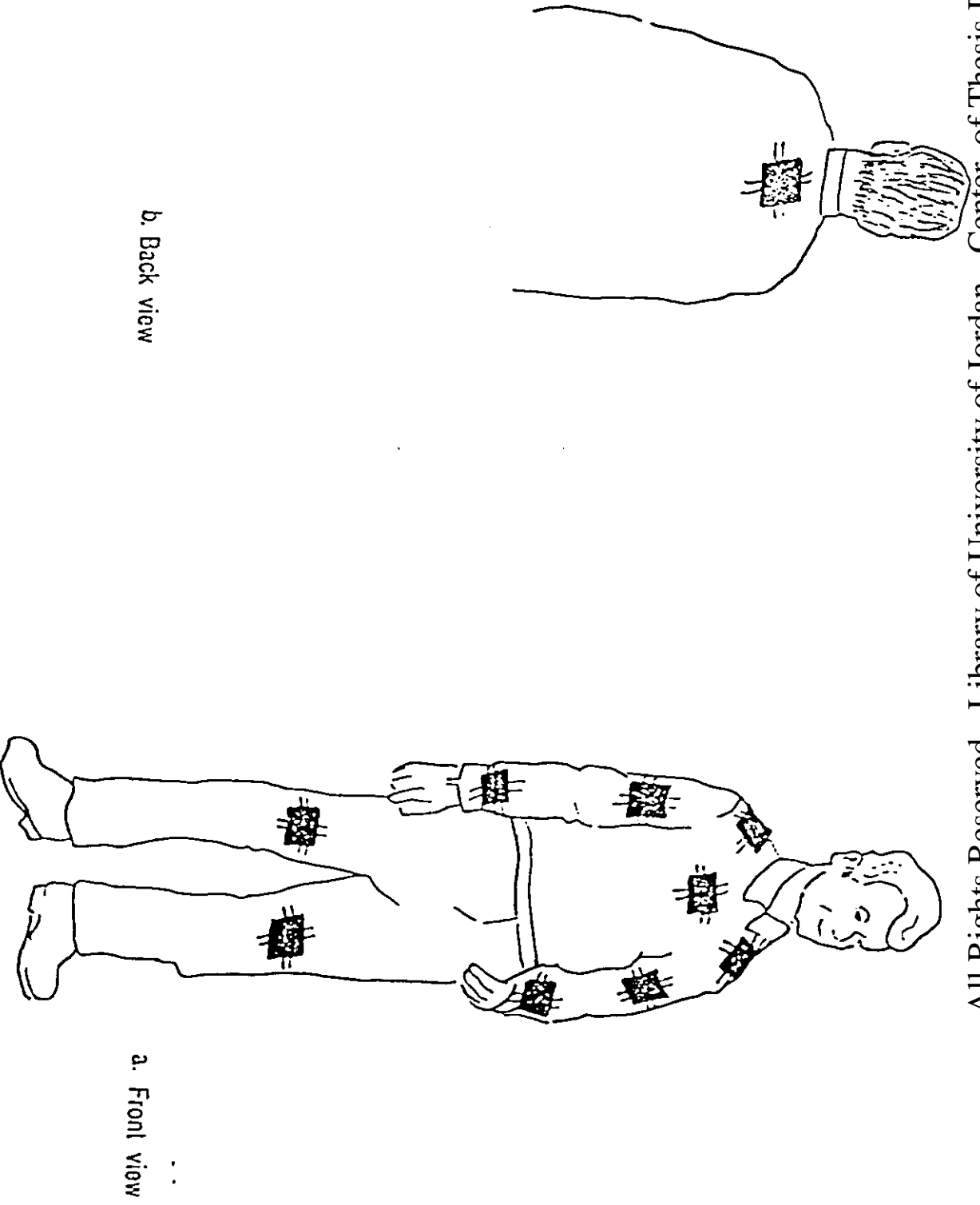


Fig . 2 : Site of gauze sponges on individual spraymen body .

A Greenburg- Smith impinger containing 15 ml of ethylene glycol was placed on each sprayman's chest by using Scotch filament tape just prior to the start of the test. A Mine safety Appliance Co. pump was used at a flow rate of 1.2 L/min. (Fig. 3). Immediately after the end of the test, samples were placed in ice box for transport to the laboratory . Samples were stored at -20°C until analysis was carried out. Sampling was repeated 2 times for each sprayer at 15 days intervals. The total number of respiratory exposure samples was $2 \times 6 \times 1 = 12$ samples.

2.3. Blood Samples

2.3.1. Apparatus

- a. Micro-Haematocrit centrifuge (Hawksley, England).
- b. Haematocrit- capillaries (75 mm/75 μ l, i.d. 1.5-1.6 mm, W. Germany).
- c. Sterilized disposable blood lancets.
- d. Ice box.

Two capillary puncture blood samples were collected from each sprayman on each field test at time zero (immediately before application), 1/2 and 24 hr later. the finger from which the blood will be drawn was warmed by rubbing it back and forth several times, then sterilized using sterile cotton wetted with 70% alcohol. The finger tip was punctured using sterile lancet. The first drop of the squeezed finger blood was wiped off with a piece of sterile cotton. For each blood sample, 2 haematocrit-capillaries were filled with about 150 μ l blood and immediately centrifuged at 10,000 rpm for 7

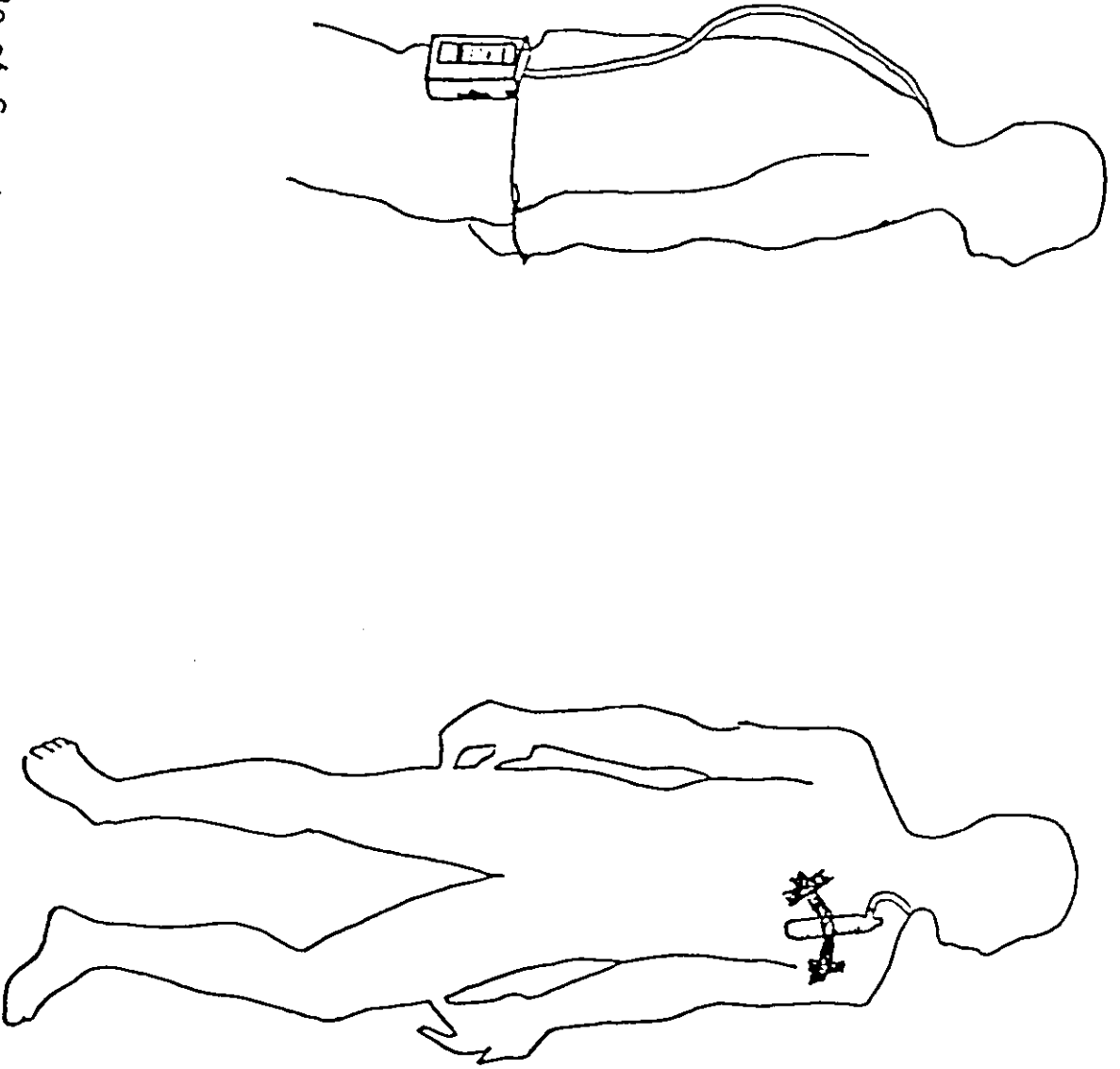


Fig . 3 : Site of Greenburg Smith impinger and Mine Safety Appliance Co. pump on the individual spraymen body.

minutes. The erythrocyte pellet was removed and the plasma was stored in ice box for transport to the laboratory. Plasma was kept in the refrigerator at +4°C until analysis was carried out . Plasma ChE activity was determined within 24 hrs of sample collection. Sampling was repeated 2 times for each sprayer at 15 days intervals. The number of samples was $2 \times 6 \times 3 = 36$ samples.

2.4. Dimethoate Spraying

The spraying programme for each sprayman consisted of two sprays, 15 days apart. Dimethoate was applied by each person to tomato plants under the assigned plastic house. All sprayers used " Lurmark-PTP 20" Knapsack sprayer * which gives a working pressure of around 40 psi, and has a liquid capacity of 20 liters. A hollow cone spray nozzle was used for applying dimethoate. Approximately 25 ml of emulsifiable concentrate containing 40% active ingredient were diluted to make 20 liters. The spraying solution was applied to tomato plants under the plastic house by each sprayman on each field test.

2.5. Field Data Collection

The data that was collected for each sprayman on each field test are :

1. Test number, and date of test.
2. Starting and finishing time .
3. Weather data- temperature and relative humidity under plastic houses at the starting and finishing time.

* (Lurmark Ltd, England)

4. Volume sprayed.
5. Direction of sprayman's travel between rows while spraying.

3. LABORATORY ANALYSIS

3.1. Apparatus And Equipment

1. Gas-liquid Chromatograph (GLC), Model 304 (Pye Unicam, England),
equipped with :
 - a. Flame photometric detector (FPD).
 - b. Recorder PM 8251 (Pye Unicam, England).
2. Analytical electronic balance AE 100 (Mettler, Switzerland).
3. Rotary vacuum evaporator with thermostatic water bath (Buchi, Switzerland).
4. 1 μ l standard microliter syringe with cemented needles (Hamilton-Bonaduz, Switzerland).
5. Other basic laboratory equipment.

3.2. Reagents And Chemicals

1. Acetone A.R. (May and Baker Ltd, England).
2. Dichloromethane (CBH Lab Chemicals, England).
3. Sodium sulfate (Fluka, AG, Switzerland).
4. Dimethoate standard with 99.5% purity (Dr. S. Ehrenstorfer, W. Germany).

3.3. Extraction

3.3.1. Dermal exposure samples

Each sponge was separated from the foil and placed in a 250 ml

separatory funnel. It was extracted 3 times with 50 ml of dichloromethane, using hand shaking each time for 2 minutes. The 3 portions of dichloromethane were combined together, then concentrated up to 1 ml using a rotary vacuum evaporator at 38°C. The concentrate was quantitatively transferred and adjusted to 5ml with acetone, the residue is ready for injection into GLC.

3.3.2. Respiratory exposure samples

Each 15 ml ethylene glycol sample was diluted with 100 ml of 2% aqueous sodium sulfate solution, then placed in a 250 ml separatory funnel. Twenty ml of dichloromethane was added, the mixture was vigorously shaken for 1 min. and left for separation. After separating the lower layer of dichloromethane, the upper layer was reextracted with another 20 ml dichloromethane as described above. The 2 dichloromethane extracts were combined together and successively passed through sodium sulfate which later was rinsed with 10 ml of dichloromethane. The extract was concentrated, transferred, adjusted, and prepared for injection into GLC as described for dermal exposure samples in part 3.3.1.

3.4. Recovery Tests

The efficiency of instrumentation and operator to perform the analysis was examined by recovery tests.

Recovery test for both dermal and respiratory exposure samples were done by adding the appropriate volume from the stock solution of 10^3 ppm dimethoate in acetone to a non treated sample and within the linear range

(75 μ l of 1000 ppm which is equal to 750 ng/cm² of a gauze sponge and 5000 ng/ml of ethylene glycol). Thereafter, extraction procedure was carried out as described in parts 3.3.1. and 3.3.2. , respectively. Recovery percentage was calculated according to the following equation :

$$\text{Recovery percentage (\%)} = \frac{\mu\text{g dimethoate found}}{\mu\text{g dimethoate added}} \times 100$$

3.5. Calibration Curve

The stock standard solution was prepared by accurately weighing 25.13 mg dimethoate standard, corrected for 100% purity into a preweighed 25 ml volumetric flask and diluted to the mark with acetone. The concentration of this stock solution is 10³ ppm.

From this stock solution, different concentrations of 5.0, 7.5, 10.0, 12.5, and 15.0 ppm were prepared by taking appropriate volumes and diluting it with acetone. The standard solutions were kept tightly sealed in the refrigerator.

Calibration curve for dimethoate was established by injecting 2-3 times of a constant volume of 1 μ l from each of the above mentioned different concentrations. The average height of the closest 2 injections was calculated. Calibration curve was constructed by plotting peak heights versus dimethoate mass. The correlation coefficient, the intercept, the slope and the equation of regression line were calculated.

3.6. Gas-Liquid Chromatographic Conditions

The following GLC conditions were used throughout the study.

- a. Column : 1.5 m length, 2 mm internal diameter, glass column packed with 4% SE 30+ 6% OV 210 on Gaschrom Q 100-120 mesh.
- b. Detector : Flame photometric detector (FPD).
- c. Temperature ($^{\circ}\text{C}$):
 - i. Column : 200
 - ii. Injector : 220
 - iii. Detector : 220
- d. Flow rate (ml/min.) :
 - i. Carrier gas (N_2) 30
 - ii. Hydrogen (H_2) 18
 - iii. Air 17
- e. Amplifier :
 - i. Attenuation. 64
 - ii. Back off. 2
 - iii. Range. 10
- f. Recorder : Chart speed = 0.5 cm/min.

3.7. Injection

One μl of the residue was injected into the GLC. On the average 2-3 injections for each sample were carried out. Samples were diluted when necessary to give peak heights within the linear range.

3.8. Calculations

3.8.1. Dermal exposure

1. Hourly exposure /unit area of gauze sponges ($\mu\text{g dimethoate}/\text{cm}^2/\text{hr}$) =

$$(\mu\text{g dimethoate in the sample}) \times \frac{1}{A} \times \frac{60 \text{ min.}}{L}$$

A= area of gauze sponge (100 cm^2).

L= length of time applicator exposed (min.).

2. Daily exposure for any exposed body part (mg/day) as calculated by Davis (1980) =

$$(\text{mg dimethoate } \text{cm}^{-2} \cdot \text{hr}^{-1}) \times S \times T \times \frac{1}{10^3}$$

S= surface area of body part (cm^2) (Table 3).

T= working day, it is equal to 4 hours working ⁽¹⁾.

10^3 = to change from μg to mg .

3.8.2. Respiratory exposure

1. Concentration of dimethoate in air ($\text{mg}/\text{m}^3/\text{hr}$) was calculated according to the following equation :

$$(\text{mg dimethoate in the sample}) \times \frac{10^3}{V} \times \frac{60 \text{ min.}}{T}$$

(1) : Copplestone *et al.* (1976).

Table 3 : Dermal exposure pad location used for calculation of exposure body parts and surface areas of these parts⁽²⁾.

Body parts	Exposure pad used to represent body part	Surface area of body part (cm ²)
Face	Shoulder pads	650
Back of neck	Back pad	110
Front of neck	Front pad	150
Back	Back pad	3350
Chest and stomach	Front pad	3350
Upper arms	Upper arm pads	1320
Forearms	Forearm pads	1210
Upper legs	Upper leg pads	2250

(2) : Calculated from data of Berkew Body Surface Area Table. Durham and Wolfe (1962), Davis (1980).

V = volume of air sampled (Liter).

$10^3 =$ to change from liter to m^3 .

T = exposure time (min.).

2. Daily respiratory exposure (mg/day) was calculated according to the following equation as calculated by Davis (1980):

$$(\text{mg dimethoate in the sample}) \times \frac{1740}{V} \times T$$

V = volume of air sampled (Liter).

T = working day, it is equal to 4 hours working.

1740 = average hourly ventilation rate of a man doing light work (L/hr)*.

3.9. Plasma Cholinesterase Activity Determination

3.9.1. Apparatus and equipment

- a. Spectrophotometer, Model 690 (Sequoia-Tuner).
- b. Constant temperature, stainless-steel tank water bath.

3.9.2. Chemicals and reagents

- a. Normal saline solution (sodium chloride 0.9%).
- b. Menagent cholinestrace U.V. (Division Diagnostic, Italy), consists of :
 1. Buffer solution of pH 7.6-8.0.
 2. Substrate (enzymatic reagent), P-hydroxybenzoylcholine.

*: Durham and Wolfe (1962).

The method of Ellmam *et al.* (1961) was followed :

1. A working reagent prepared by reconstituting a vial of enzymatic reagent using 16 ml of the buffer.
2. The solution was shaken gently until it is completely dissolved, and kept at 37°C during working.
3. Exactly 1.5 ml of sodium chloride 0.9%, 1.5 ml of working reagent, and 0.025 ml of plasma were pipetted into a cuvette.
4. The mixture was shaken gently and kept for 1 min. in the water bath at 37°C.
5. The absorbance was read each 60 sec. for 3 min. at 340 nm.
6. The average value of the absorbance difference ($\Delta A/60$ sec.) was established and used for calculation.
7. The blank for such a run consisted only of 1.5 ml sodium chloride 0.9% and 1.5 ml working reagent. The same procedure described above was followed for the blank.

3.9.3. Calculation

Plasma ChE activity is proportional to the absorbance decrease when measured at 340 nm. One international unit (I.U.) corresponds to that enzymatic activity which transforms one μ mole of substrate per minute.

Values were obtained by using the following equation :

$$\text{I.U./L} = \Delta A/60 \text{ sec.} \times 9807 \times D$$

$$\Delta A/60 \text{ sec.} = \Delta A/60 \text{ sec.}_{\text{plasma}} - \Delta A/60 \text{ sec.}_{\text{blank}}$$

$$D = \text{dilution factor} = 2$$

1. % inhibition of plasma ChE =

$$\frac{\text{Activity before work} - \text{Activity after work}}{\text{Activity before work}} \times 100$$

2. The remaining activity of plasma ChE = 100 – % inhibition

1. CALIBRATION CURVE AND RECOVERY

The calibration curve gave straight line in the range between 5 to 15 ng/ μ l (5-15 ppm) of standard dimethoate (Fig.4). The data of standard dimethoate concentrations and peak height response to GLC is presented in Appendix (1).

The calculated regression line equation was derived from the straight line equation:

$$Y = a + b X$$

where Y= peak height (cm), a = regression line intercept with Y axis, b= slope, and X = dimethoate mass injected in ng. After substituting the values of a and b, the equation becomes

$$Y = 0.02 + 1.038 X$$

$$r = 0.9939 \text{ (correlation coefficient)}$$

Average recovery was 83.6% (627 ng/cm² found /750ng/cm² added) and 68.8% (3440 ng/ml found / 5000 ng/ml added) for dermal and respiratory exposure samples, respectively. For the exact calculation of the recovery percent see Appindex (9).

2. DIMETHOATE RESIDUES

Dimethoate application made in field test I took place on March 11, 1989. The average prevailing temperature in the six plastic houses was 28.9 ± 2.4 °C; and the relative humidity was $76.7 \pm 2.2\%$. The second field test took place on March 25,1989. The average prevailing temperature was 25.7 ± 3.5 °C; and the relative humidity was $78.3 \pm 3.5\%$. Tomato plants were in the fruiting

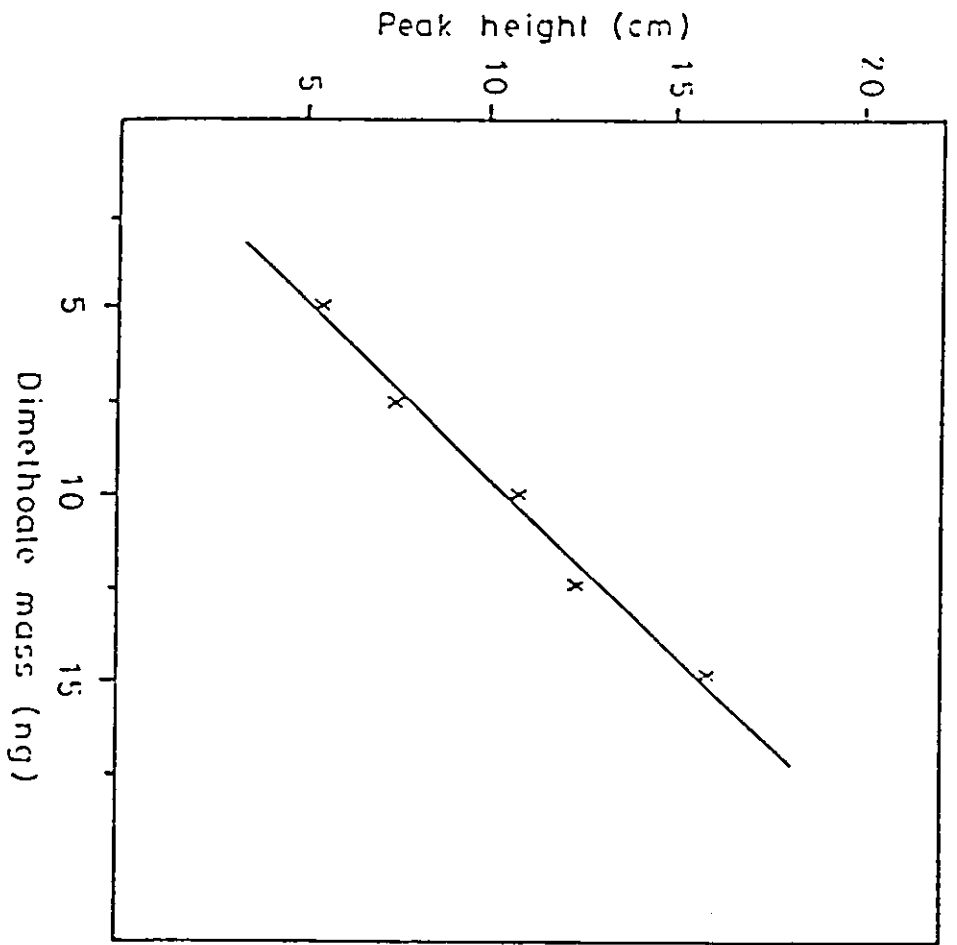


Fig. 4 : Dimethoate calibration curve

$$(Y = -0.02 + 1.038 X)$$

($r = 0.9939$: correlation coefficient)

stage and the average height of the plants was 210cm.

2.1. Dermal Exposure

2.1.1. Dermal external exposure

The amounts of diemthoate recovered from gauze sponges placed on different sites of the individual sprayers body in both field tests, are presented in Table (4) and Appendices 2,3. The results in this table and all other result tables are calculated for the recovery factors. The mean total external exposure for all sprayers in the two field tests was 215.52 $\mu\text{g}/\text{cm}^2/\text{hr}$. This varied with individual sprayers and ranged from 177.17 $\mu\text{g}/\text{cm}^2/\text{hr}$ -248.19 $\mu\text{g}/\text{cm}^2/\text{hr}$ (Table 4). There were no significant differences between sprayers with respect to total external exposure in each field test when data was analyzed using the Randomized Complete Block Design (RCBD) at the 5 percent level. Data in Table (4) shows results obtained from all exposure gauze sponges according to site. The highest levels of exposure were to the lower right arm sponges (53.08 $\mu\text{g}/\text{cm}^2/\text{hr}$), while the lowest levels of exposure were to the back sponges (0.61 $\mu\text{g}/\text{cm}^2/\text{hr}$).

Table (5) represents the ranking of gauze sponges according to external exposure and their ratio in relation to the least exposed sponge which is the back. This ratio ranged between 87.0 to 2.0 times greater than that of the back, for the lower right arm and the front sponges, respectively.

It was obvious that the right side of sprayers body obtained the greatest dosage (122.79 $\mu\text{g}/\text{cm}^2/\text{hr}$), than the left side (90.90 $\mu\text{g}/\text{cm}^2/\text{hr}$).

Table 4: Average external exposure to dimethoate for individual spraymen.

Sprayman No.	dimethoate ⁽¹⁾ recovered from gauze sponges (ug/cm ² /hr). placed on											Total ⁽²⁾
	Front	Back	Right shoulder	Left shoulder	Upper right arm	Upper left arm	Lower right arm	Lower left arm	Upper right leg	Upper left leg		
1	0.87	0.69	11.00	7.52	4.32	6.51	78.01	43.95	50.88	39.17		242.82
2	1.89	0.68	9.42	10.28	19.85	48.78	44.07	30.54	39.70	34.82		240.03
3	1.63	0.58	3.05	5.21	12.75	30.95	50.56	20.00	54.32	27.58		206.63
4	0.69	0.59	15.00	2.72	20.51	32.33	67.93	30.34	55.85	22.23		206.63
5	1.26	0.43	14.49	10.33	12.46	12.86	35.24	12.03	35.06	44.13		248.19
6	1.07	0.70	10.16	4.94	12.99	15.93	42.68	19.22	36.47	33.01		178.29
Mean ⁽³⁾	1.23	0.61	10.52	6.83	13.81	24.56	53.08	26.01	45.36	33.49		215.52

(1) : Average of two gauze sponges on each site for each individual spraymen.
 (2) : Average of 2 field tests.
 (3) : Average of 12 gauze sponges.

Table 5 : Ranking of gauze sponges sites according to external exposure to dimethoate.

Site	Mean dimethoate residue ⁽¹⁾ (ug/cm ² / hr)	Ratio ⁽²⁾
Back	0.61	1.0
Front	1.23	2.0
Left shoulder	6.83	11.2
Right shoulder	10.52	17.2
Upper right arm	13.81	22.6
Upper left arm	24.56	40.3
Lower left arm	26.01	42.6
Upper left leg	33.49	54.9
Upper right leg	45.36	74.4
Lower right arm	53.08	87.0

(1) : Mean of 12 gauze sponges.

Dimethoate residue at any site

(2) : Ratio =

Dimethoate residue at the least exposed site (back)

Statistical analysis indicated that there was significant differences in the external exposure between the two body sides for all spraymen (Table 6).

Differences between dimethoate recovery mean for all sponges according to their site on spraymen body parts are presented in Appendix (4). There were significant differences in dimethoate residues for each of the highly contaminated sponges (lower right arm, upper right leg, upper left leg, lower left arm, and the upper left arm, respectively) and each of the less contaminated sponges (upper right arm, right shoulder, left shoulder, front, and the back, respectively).

2.1.2.Total dermal exposure

The total dermal exposure of each body part for individual spraymen was calculated according to the equation (2) in part 3.8.1. Table (7). and Appendices 5,6. Mean total dermal exposure in the two field test was in the range of 584.29-802.57 mg/day (mean value : 701.70 mg/day) (Table 7), no significant differences were observed between spraymen according to total dermal exposure in each field test when data was analyzed using the RCBD at the 5 percent level.

Ranking of body parts according to dermal exposure and ratio correlated to the least exposed body part, the back of neck are given in Table (8). The ratio ranges between 1330.8 and 2.7 times greater than that of the back of neck for the upper legs and the front of the neck, respectively.

There was significant differences in the mean of total dermal exposure for each of the highly exposed body parts (the upper legs, forearms, and the upper arms respectively) and each of the less exposed body parts (face, chest,

Table 6 : Dimethoate external exposure of individual spraymen body sides.⁽¹⁾

Sprayer No.	Dimethoate external exposure (ug/cm ² /hr) ⁽²⁾	
	right side ⁽³⁾	left side ⁽⁴⁾
1	144.22	97.13
2	113.01	124.42
3	120.68	83.75
4	159.29	87.62
5	97.25	79.35
6	102.3.	73.10
Mean	122.79	90.90

(1) :Front and back sponges were excluded.

(2) :Average of 2 field tests.

(3) :Total of 4 sites (RSH, URA, LRA, URL).

(4) :Total of 4 sites (LSH, ULA, LLA, ULL).

Table 7: Dermal exposure of individual sprayers to dimethoate (mg/day)*.

Sprayerman No.	Face	Back of neck	Front of neck	Back	Chest and stomach	Upper arms	Forearms	Upper legs	Total dermal exposure (mg/day)
1	24.04	0.31	0.52	9.80	12.29	28.59	295.15	431.87	802.57
2	25.61	0.30	1.13	9.59	26.84	181.18	180.22	335.30	760.18
3	10.69	0.26	0.98	8.24	23.15	115.36	170.77	368.51	697.96
4	23.01	0.26	0.41	8.38	9.80	139.49	237.80	351.34	770.49
5	32.26	0.19	0.76	6.04	17.90	66.87	114.37	356.32	594.71
6	19.63	0.31	0.64	9.87	15.20	76.34	149.68	312.62	584.29
Mean									701.70

* : Average of 2 field test.

Table 8 : Ranking of body parts according to dermal exposure.

Body part	Mean ⁽¹⁾ dermal exposure (mg/day)	Ratio ⁽²⁾
Back of neck	0.27	1.0
Front of neck	0.74	2.7
Back	8.65	32.0
Chest and stomach	17.53	64.9
Face	22.55	83.5
Upper arms	101.30	375.2
Forearms	191.38	708.8
Upper legs	359.32	1330.8

(1) :Mean of 12 body parts.

Dimethoate residue at any body part

(2) : Ratio = $\frac{\text{Dimethoate residue at the least exposed body part (back of neck)}}{\text{Dimethoate residue at the least exposed body part (back of neck)}}$

back, front of neck, and the back of neck, respectively) Appendix (7). High significant difference was observed in the mean dermal exposure of the upper legs than the forearms. No significant differences were observed between any of the less exposed body parts (face, back, front of neck, and the back of neck).

2.2. Respiratory Exposure

Dimethoate concentrations in air are presented in Table (9). Dimethoate concentrations in air ranged from 2.18-6.97 mg/m³ with mean value of 4.09 mg/m³. Table (10) shows the ratio of dimethoate for individual spraymen compared to data by WHO (1988) in Europe. The established ceiling exposure limit value is 0.5 mg/m³ of dimethoate in air in the work-place. This ratio ranged from 5.8-12.3 times with an average of 8.3 times greater than the WHO ceiling value.

Total respiratory exposure levels were calculated according to the equation (2) in part 3.8.2. Data is presented in Table (11) Exposure was in the range of 8.86-14.58 mg/day with a mean value of 11.61 mg/day.

Table (12) and Fig.(5) represent the total respiratory exposure and total dermal exposure. Also, they show the percentage of respiratory to dermal exposure for individual spraymen. The mean percentage was 1.67%.

When exposure was expressed as percent toxic dose received per 4-hour working day, results of this study, were well above the level of 1% with a mean value of 1.67% day⁻¹ (Table 13). This 1% exposure level was used by Copplestone *et al.* (1976). The formula used to calculate the percentage toxic dose was established by Durham and Wolfe (1962).

Table 9: Concentrations of dimethoate in the breathing zone of workers during spraying under plastic houses (mg/m³).

sprayman No.	Field test		Average
	I	II	
1	5.09	3.58	4.34
2	3.72	6.46	5.09
3	6.97	5.37	6.17
4	2.96	3.34	3.15
5	2.18	4.30	3.24
6	2.80	2.96	2.88
Mean			4.09 + 1.6 mg/m ³

Table 10: Ratio of dimethoate concentration in air for individual spraymen in relation to WHO ceiling value (0.5 mg/m³)

Sprayman No.	Average diemthoate in air (mg/m ³)	Ratio
1	4.34	8.7
2	5.09	10.2
3	6.17	12.3
4	3.15	6.3
5	3.24	6.5
6	2.88	5.8
Mean		8.3

Table 11 : Respiratory exposure to dimethoate (mg/day) for individual sprayers.

Sprayman No.	Field test		Average
	I	II	
1	13.60	10.34	11.79
2	10.76	12.71	11.74
3	14.58	12.47	13.53
4	10.33	11.61	10.97
5	8.86	11.99	10.43
6	11.08	11.02	11.05
Mean	11.61 + 1.5 mg/day		

Table 12 : Total respiratory and dermal exposure to dimethoate for individual spraymen.

Sprayman No.	Total respiratory exposure (mg/day) ⁽¹⁾	Total dermal exposure (mg/day) ⁽²⁾	percentage ⁽³⁾ (%)
1	11.79	802.57	1.47
2	11.72	760.18	1.54
3	13.53	697.96	1.94
4	10.97	770.49	1.43
5	10.43	594.71	1.75
6	11.05	584.29	1.89
Mean			1.67

(1),(2): Data are average of two field tests.

$$(3) : \text{Percentage (\%)} = \frac{\text{Total respiratory exposure (mg/day)}}{\text{Total dermal exposure (mg/day)}} \times 100$$

Table 13 : Results of dermal and respiratory exposure , together with calculation of percentage of toxic dose received per day for individual spraymen.

Sprayman No.	Dermal exposure (mg/day)	Respiratory exposure (mg/day)	Percentage toxic dose/day*
1	802.57	11.79	1.88
2	760.18	11.72	1.79
3	697.96	13.53	1.70
4	770.49	10.97	1.80
5	594.71	10.43	1.43
6	584.29	11.05	1.42
Mean			1.67

$$* : \text{Percentage toxic dose} = \frac{\text{Dermal exposure (mg/day)} + [\text{Respiratory exposure (mg/day)} \times 10]}{\text{Dermal LD}_{50} \text{ mg/kg (rat)} \times 70} \times 100$$

dermal LD₅₀ (rat) ~ 700mg/kg

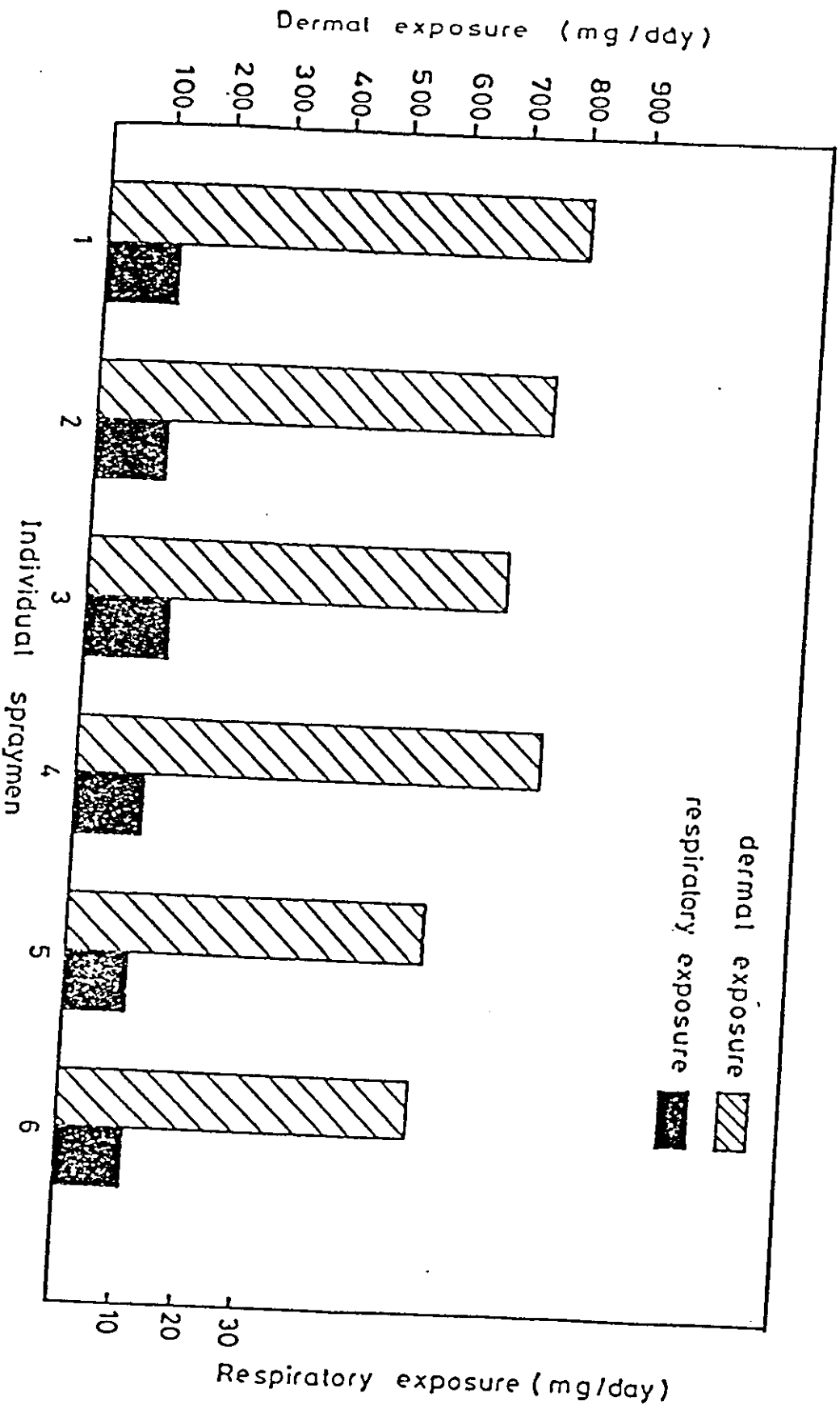


Fig. 5 : Total dermal and respiratory exposure to dimelthoate for individual spraymen.

2.3. Plasma ChE Activity

The average of plasma ChE activity in the individual spraymen before and after spraying operation are presented in Table (14) . This table shows that the average enzyme activity for all spraymen 30 min. after spraying operation was 71.9% of the preexposure activity level of 98.9%. The mean depression of plasma ChE activity ranged from 19.1-36.7% with an average of 27.0%. This is close to the range of exposure index to dimethoate (20-25%) established by WHO (1988). After 24 hrs, the enzyme recovered and the activity was 96.2% of the preexposure level (Table 14). This means that in all test group, recovery of plasma ChE was almost complete with 24 hrs after the spraying operation. During working hours exposure to dimethoate was high and reduced the plasma ChE activity to values of exposure index sufficient to warrant necessity of protective measures during pesticides application under plastic houses.

(11)

Table 1⁴ : Plasma cholinesterase activity percent in spraymen exposed to diemthoate.

Sprayer No.	Plasma CHE Activity (%) ⁽²⁾			differences (%)	
	-5min. (1)	+30min. (2)	+ 24 hrs (3)	(1)-(2)	(1)-(3)
1	100.0	77.5	94.6	22.5	5.4
2	100.0	80.9	95.3	19.1	4.7
3	100.0	67.1	89.0	32.9	11.0
4	96.0	64.1	100.0	31.9	-4.0
5	100.0	80.8	97.3	19.2	2.7
6	97.7	61.0	101.1	36.7	-3.4
Mean	98.9	71.9	96.2	27.0	2.7

(1):The measurement were done before (-) and after (+) the spray operation .

(2):Average of 2 tests.

1. SAMPLING

1.1. Dermal And Respiratory Exposure

Two types of dermal exposure pads have been found to be most useful to measure dermal exposure potential. Gauze sponges, and alpha-cellulose, 10cm², packed with aluminum foil or glazed weighing paper were used. This wrapping is taken to avoid any contamination by pesticides. Also, the pads are previously extracted by solvent to remove materials that interfere with analysis. These specifications were approved and used by Durham and Wolfe (1962); WHO (1975); Carman *et al.* (1982)

Gauze sponges were used in this study because they are easy to prepare and to use. Ethylene glycol was used to serve as solvent and keeper for dimethoate impinging on sponges (Carman *et al.*, 1982). The sites and number of gauze sponges for each sprayman were used and recommended by several researchers (Durham and Wolfe 1962; Simpson and Beck 1965; Engelhard *et al.* 1979; Davis 1980; Carman *et al.* 1982). Also, this protocol suggested a total of 10 gauze sponges for the routine test.

For respiratory exposure assessment, Greenburg-Smith impinger filled with ethylene glycol was used to trap dimethoate from air. This procedure was preferred over other methods due to its advantage of sampling a large volume of air in a given time. Also, it has better trapping efficiency when duration of a particular exposure is brief (Durham and Wolfe, 1962; Davis 1980). Samples of dermal and respiratory exposure were stored at -20°C till the time of extraction. This type of storage minimizes chemical decomposition and volatilization losses.

2. DIMETHOATE EXPOSURE

The mean total external exposure for the ten pads to dimethoate was $21.55 \mu\text{g}/\text{cm}^2/\text{hr}$. This is in close agreement with the finding of Leavitt *et al.* (1982). They reported that the mean external exposure of professional pesticides applicators applying carbaryl on trees in the U.S.A. was $15 \mu\text{g}/\text{cm}^2/\text{hr}$.

The lower right arm sponges obtained the highest levels of dimethoate ($53.08 \mu\text{g}/\text{cm}^2/\text{hr}$), while the back sponges obtained the lowest levels of dimethoate ($0.61 \mu\text{g}/\text{cm}^2/\text{hr}$). All spraymen were right-handed carrying the sprayer hose with their right hand. Consequently, the lower right arm sponges collected the highest level through high spray drift falling on that part (Table 5). Back sponges located on the back of spraymen bodies are away from direct spray drift or contact with wet plants. This leads to less chances of contamination with the insecticide, consequently, they received the lowest amounts of dimethoate residues.

The right side of the spraymen which includes the right shoulder, upper right arm, lower right arm and the upper right leg received an average of $122.79 \mu\text{g}/\text{cm}^2/\text{hr}$. Meanwhile the left side of spraymen which includes the left shoulder, upper left arm, lower left arm and the upper left leg received an average of $90.90 \mu\text{g}/\text{cm}^2/\text{hr}$ (Table 6). This is consistent with the fact that in this case the sprayman entered the plastic house from the left side, start spraying the right side of the row, then he turns to the right when the row was sprayed. Carman *et al.* (1982) reported similar results, where spraymen

received higher pesticide residue on the side close to the sprayed plants.

The pumping handle was mounted on the left side of the sprayers, and the Knapsack was operated by the left hand while spraying. Therefore, it is not surprising to find out that the upper left arm sponges contaminated with significant amounts of dimethoate ($24.56 \mu\text{g}/\text{cm}^2/\text{hr}$) higher than the upper right arm sponges ($13.18 \mu\text{g}/\text{cm}^2/\text{hr}$) through direct contact with wet branches and leaves as results of continuous movement.

The mean total dermal exposure to dimethoate was 701.70 mg/4hr day (Table 7). This was calculated from Table (3) according to the equation (2) in part 3.8.1. It was found that the mean dermal exposure to parathion while spraying tomato bushes in open fields with a Knapsack Mister in Australia is 72.8 mg/8 hr day (Simpson and Beck 1965). In Ivory Coast it was found that the mean dermal exposure of sprayers applying a pyrethroid insecticide on cotton in open fields is 14.8 mg/hr (Prinsen and Sittert, 1980). Leavitt *et al.* (1982) found that the mean dermal exposure of sprayers to carbaryl in open fields was 128.4 mg/hr. Amounts of total dermal exposure reported in this work are higher than those reported above because of the nature of spraying conditions. All above reports were conducted in open fields. In our work under plastic houses, the number of plants per unit area was double the number of plants in the open fields. Also, the nature of vertical training of plants under plastic houses is different than the prostrate training in the open fields. Consequently, the chances of sprayers exposure to drift and contact with sprayed plants is higher inside the plastic houses than in open fields. Similar results of differences in exposure to insecticides during indoor and outdoor application was reported by Wolfe *et al.* (1959). They found that the dermal

exposure to DDT was 1755 mg/hr and 243 mg/hr during indoor and outdoor house spraying. It is obvious that the dermal exposure during indoor spraying was about 7.2 times greater than the outdoor spraying.

In this study it was found that the highest level of total dermal exposure was to the upper legs 359.30 mg/day followed by the arms (upper arms and forearms) 292.68 mg/day (Tables 3 & 9). Results and explanations of total dermal exposure agreed with amounts of dimethoate recovered from sponges used to represent body parts. About 93% of the total dermal exposure to dimethoate was to upper legs and arms Appendix (8). These results are in agreement with Prinsen and Sittert (1980) reports that the most exposure was to the arms when the spraymen applied a pyrethroid insecticide on cotton. Also, Copplestone *et al.* (1976) found that the legs exposed to the highest amount of dimethoate when it was sprayed on vegetables in the open fields. Similar results were obtained by leavitt *et al.* (1982). He found that 87% of the total dermal exposure was to the hands and forearms, when the spraymen applied carbaryl to trees in the U.S.A.

When measuring the amounts of dimethoate concentrations in air in the spraying area under plastic houses it was 4.09 mg/m³ (Tables 9 & 10). These concentrations are 8.2 times greater than the ceiling value of 0.5 mg/m³ set by WHO (1988). Researchers reported much lower values of pesticides in the air while spraying in the open fields. Hedman *et al.* (1980) found that the mean concentration of 2,4-D and 2,4,5-T in the breathing zone of spraymen in forestries in Sweden was 0.1-0.2 mg/m³. Also, it was found that the concentration of maneb in the breathing zone of spraymen applying this

pesticide in cotton fields was below 0.1 mg/m^3 Kangas *et al.* (1980). Similar results were obtained by Batchelor and Walker (1954). The average concentration of parathion in air during orchard spraying was less than 0.1 mg/m^3 . The high dimethoate values observed may be due to the concentration effect of the indoor atmosphere under plastic houses, and the dilution effect in open fields.

The mean total respiratory exposure of spraymen under the plastic houses was 11.61 mg/4hr day , calculated according to equation (2) in part 3.8.2. (Table 11). These results are higher than those measured by Simpson and Beck (1965). They found that the mean respiratory exposure of spraymen applying parathion to tomato bushes in Australia was 2.32 mg/8hr day . Also, Leavitt *et al.* (1982) found values of 0.1 mg/hr for spraymen applying carbaryl to trees. However, Copplestone *et al.* (1976) reported very low respiratory exposure ($19.9 \text{ } \mu\text{g/4hr day}$) while spraying dimethoate to vegetables in open field in Sudan.

Our results are in more harmony with the finding of Wolfe *et al.* (1959). They reported that the mean respiratory of spraymen applying DDT during indoor spraying was 64.5 times higher than outdoor spraying with the same compound.

The mean percentage of respiratory exposure of dimethoate to dermal exposure ranged from 1.43-1.94% calculated according to the formula in Table (12) with an average of 1.67% (Table 12 & Fig 5). This value is in good agreement with studies of Copplestone *et al.* (1976); Prinsen and Sittert (1980) who reported that the ratio ranges from about 0.1-3.0%.

When exposure was expressed as percent toxic dose received per 4-

hours day according to the formula in Table (13), results of our study were above the 1% level. Values ranged between 1.42-1.88% with an average of 1.76% (Table 13). This value is 31.5 times higher than the maximum value for spraymen applying dimethoate in open fields in Sudan. Similar results were obtained by Wolfe *et al.* (1959) who found that the indoor house spraying with DDT is 7 times as hazardous as outdoor spraying. The percentage toxic dose for indoor and outdoor house spraying was 1.02 and 0.14, respectively. WHO (1971) pointed out that the percent toxic dose higher than 1% is considered hazardous to spraymen.

Results of this study showed that the range of plasma ChE depression was 19.1-36.7% with a mean of 27%. These results are in good general agreement with the finding of several researchers reported here. This depression is considered as diagnostic of exposure to the insecticide according to exposure index set by WHO (1988). Ngatia and Megni (1980) reported significant reduction in plasma ChE levels in subject working in the Agricultural Entomology Sections at the Tropical Pesticides Research Institute (TPRI) in Tanzania. This reduction reached 50% of the preexposure level as a result of continuous exposure to OP insecticides. Loosli (1980) recorded the activity of plasma ChE in field workers during a study for monitoring program to assess human safety in operations involving OP insecticides. Results indicated that reductions in the activity of plasma ChE ranged between 11 and 40%. Depression of 50% in plasma ChE activity was observed among workers during production and formulation of OP pesticides in the U.K. (Burgess and Roberts, 1980). Rhyänen *et al.* (1984) measured the activity of ChE's in 7 garden workers in a greenhouse exposed to OP pesticides.

Workers showed erythrocyte AChE inhibition ranged from 21-40% of the normal. Also, they showed 25% of plasma ChE inhibition as a result of exposure. Nazer *et al.* (1985) reported reduction of whole blood ChE in agricultural workers ranged from 26.16-36.66%. Also, they reported that the enzyme activity became normal two months after the end of the agricultural season.

VI CONCLUSIONS

From the results of this study we could draw the following conclusions:

1. Dimethoate concentrations in air under plastic houses while spraying are 8.2 times higher than the ceiling value of dimethoate in air in the work-place set by WHO (1988).
2. Total dermal exposure 701.70 mg/day was significantly higher than the total respiratory exposure 11.61 mg/day under the conditions of this study.
3. About ninety three percent (93%) of the total dermal exposure was on the upper legs and arms.
4. Depression of 27.0% in plasma cholinesterase activity was observed among applicators. This is considered as indicator of exposure to pesticides according to exposure index set by WHO (1988).
5. The percentage toxic dose received per day was 1.76% which is above the level of 1% set by WHO (1971).
6. Based on the monitoring of dermal, respiratory exposure and plasma ChE activity after exposure to moderately toxic insecticide, dimethoate, it could be stated that:
 - a. Under spraying condition, where no protective measures were taken, the risk of exposure to pesticides application is high.
Consequently, more precautions should be taken when highly toxic compounds are sprayed.
 - b. Protective clothing e.g. overall, gloves and masks should be worn while spraying insecticides under plastic houses in order to reduce the excessive exposure to these pesticides.

SUMMARY

To obtain relative exposure data for the spraymen applying an organophosphorus insecticide under plastic houses in the Jordan Valley, dermal and respiratory exposure, and plasma cholinesterase (ChE) activity were monitored on a group of six volunteers. The spraymen applied dimethoate 40% EC to tomato plants using Knapsack sprayers during the agricultural season of 1988/1989.

Gauze sponges (12 ply, 10x10 cm) pinned on ten different body parts were used to indicate dermal exposure potential. Ethylene glycol-containing impinger type air samplers with pumps at a flow rate of 1.2L/min. were used to monitor respiratory exposure potential. Finger prick blood samples were taken from each participant to measure the plasma ChE activity.

The dermal and respiratory exposure samples were analyzed for dimethoate using gas-Liquid chromatograph (GLC) equipped with flame photometric detector. Plasma ChE activity was measured by using Ellman spectrophotometric method.

The mean total external exposure on the ten pads was 215.52 $\mu\text{g}/\text{cm}^2/\text{hr}$. Total dermal exposure averaged 701.70 mg dimethoate day^{-1} and was much higher than the total respiratory exposure of 11.61 mg day^{-1} .

It was estimated that 93% of the total dermal exposure was to the upper legs and arms. The mean percent toxic dose received by applicators was 1.67% which is above the 1% level set by WHO (1971).

Results, showed reduction in plasma ChE activity among applicators after spraying dimethoate. The mean difference percent was 27.0% less than

the preexposure values, which is considered diagnostic of exposure based on limits set by WHO (1988). Results of this study revealed that spraymen under plastic houses must pay more attention to the importance of protective measures which are necessary to avoid excessive exposure, especially to highly toxic pesticides, above the recommended health-based limits.

تقييم تعرض عمال الرش لمبيد الـايمثويت تحت البيوت البلاستيكية في غور الأردن

ملخص

لتقييم تعرض عمال الرش لأحد المبيدات الفسفورية العضوية عند استخدامها تحت البيوت البلاستيكية في غور الأردن ، تم رصد التعرض الجلدي والإستنشاقى ومراقبة نشاط خميرة كولين استراز في بلازما الدم على مجموعة من عمال الرش مكونة من ست متطوعين. قام هؤلاء برش مبيد الـايمثويت على هيئة مركز قابل للإستحلاب بنسبة ٤٠٪ على نباتات البندورة باستعمال مضخة رش محمولة على الظهر في الموسم الزراعي ١٩٨٨/١٩٨٩ .

استخدمت وسائل التعرض (١٢ طية ، ١٠.٨١٠ سم) لتقدير التعرض الجلدي ، ولتقييم التعرض الإستنشاقى استخدم أنبوب يحتوي على ايثيلين جلايكول ، ويتصل الأنبوب بجهاز الجمع بالتصادم بطاقة (١٢) لتر هواء/دقيقة وذلك لجمع الهواء الذي يحمل المبيد . لقياس نشاط خميرة كولين استراز في بلازما الدم تم أخذ عينات دم بطريقة وخز الأصبع بواسطة ابرة حادة ومعقمه.

حددت تراكيز مبيد الـايمثويت في كل من عينات التعرض الجلدي والإستنشاقى على جهاز التحليل الكروماتوغرافى الغازى المزود بالكاشف اللهبى الطيفى ،أما نشاط خميرة كولين استراز في الدم فقد حده باستخدام طريقة ايللمان الضوئية الطيفية .

كان معدل مجموع تراكيز مبيد الـايمثويت في وسائل التعرض ٢١٥ر٥٢ ملغرام/سم^٢/ساعة . أما معدل التعرض الجلدي فكان ٧٠.١٧٠ ملغرام/ يوم وهو أعلى بكثير من التعرض الإستنشاقى والذي بلغ ١١ر١٦ ملغرام/يوم .

وجد أن الفخذين واليدين كانا أكثر أعضاء الجسم تعرضاً للمبيد حيث بلغت نسبة تعرضهما ٩٢٪ من مجموع التعرض الجلدي . أما النسبة المحسوبة للجرعة السامة المستقبلية لكل يوم عمل فكانت ١٦٧ر١٪ وهي أعلى من النسبة ٨٪ والمحددة من قبل منظمة الصحة العالمية (١٩٧١) .

وافق هذا التعرض انخفاض ملحوظ في مستوى نشاط خميرة كولين استراز في بلازما دم عمال الرش ، حيث وصل الكبت في نشاط الخميرة إلى ٢٧٪ من مستوى نشاط

الخبيرة قبل الرش ويعتبر هذا الإنخفاض كدليل للتعرض للمبيدات المبيدات على الحدود الموصى بها من قبل منظمة الصحة العالمية (١٩٨٨) .

من نتائج هذه الدراسة يتضح أن تعرض القائمين بعملية رش المبيدات تحت البيوت البلاستيكية لكميات من المبيدات تعتبر أكبر من الحدود المسموح بها وفق توصيات منظمة الصحة العالمية وخاصة عند رش مبيدات عالية السمية توجب عليهم أخذ المزيد من الإهتمام لدور الملابس الواقية خلال عملية الرش لما لها من ضرورة لتجنب التعرض الزائد - خاصة للمبيدات عالية السمية - عن الحدود الموصى بها والمبنية على أساس صحي .

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Appendix 1 : Response of Gas-Liquid chromatograph to standard dimethylate.

Mass injected (ng)	Peack height (cm)		
	First injection	Second injection	Average
5.0	5.3	5.5	5.4
7.5	7.4	7.3	7.4
10.0	10.8	10.8	10.8
12.5	12.4	12.4	12.4
15.0	15.8	15.9	15.9

Appendix 2 : Analysis of gauze sponges for individual spraymen in field test 1

Sprayman No.	Front	Back	dimethoate recovered from gauze sponges (ug/cm ² /hr), placed on							
			Right shoulder	Left shoulder	Upper right arm	Upper left arm	Lower right arm	Lower left arm	Upper right leg	Upper left leg
1	0.83	0.70	17.0	10.78	4.51	9.08	80.97	44.70	48.36	38.78
2	0.64	0.47	9.92	6.89	19.92	49.60	37.97	29.35	28.36	34.40
3	1.45	0.41	3.65	6.81	14.03	31.73	62.99	18.25	77.31	32.05
4	0.59	0.70	16.68	3.96	18.37	34.74	70.70	29.08	75.08	24.67
5	0.64	0.64	17.07	9.48	12.29	10.46	30.14	10.46	30.53	39.68
6	1.29	0.85	7.81	3.79	10.14	11.02	29.33	26.26	41.08	30.76

Appendix 3: Analysis of gauze sponges for individual spraymen in field test II

Spray man No.	Front	Back	dimethoate recovered from gauze sponges ($\mu\text{g}/\text{cm}^2/\text{hr}$), placed on							
			Right shoulder	Left shoulder	Upper right arm	Upper left arm	Lower right arm	Lower left arm	Upper right leg	Upper left leg
1	0.90	0.68	5.00	4.21	4.13	3.94	75.05	43.20	53.24	39.56
2	3.14	0.88	8.92	13.67	19.78	47.96	50.16	31.72	50.76	35.23
3	1.81	0.75	2.44	3.61	11.47	30.16	38.13	21.76	31.32	23.10
4	0.79	0.48	13.29	1.47	22.65	29.91	65.15	30.88	36.61	19.79
5	1.88	0.21	11.91	11.17	12.62	15.26	40.33	13.59	39.58	48.57
6	0.85	0.54	12.51	6.09	15.84	20.83	56.03	12.18	31.85	35.25

Appendix 4 : Difference between dimethoate recovery means ($\mu\text{g cm}^2/\text{hr}$), for all sponges according to site.

	Back	Front	Left shoulder	Right shoulder	Upper right arm	Upper left arm	Lower left arm	Upper left leg	Upper right leg	Lower right arm
	0.61 (1)	1.23(2)	6.83(3)	10.52(4)	13.81(5)	24.56(6)	26.01(7)	33.49(8)	45.36(9)	53.08(10)
	(10)	(9)	(8)	(7)	(6)	(5)	(4)	(3)	(2)	
(1)	52.47*	44.75*	32.88*	25.4*	23.95*	13.20*	9.91	6.22	0.62	
(2)	51.85*	44.13*	32.26*	24.78*	23.33*	12.58*	9.29	5.60		
(3)	46.25*	38.53*	26.66*	19.18*	17.73*	6.98	3.69			
(4)	42.56*	34.84*	22.97*	15.49*	14.04*	3.29				
(5)	39.27*	31.55*	19.68*	12.20*	10.75*					
(6)	28.52*	20.80*	8.93	1.45						
(7)	27.07*	19.35*	7.48							
(8)	19.59*	11.87*								
(9)	7.72									

* : Means are significantly different, using Least Significant Difference(LSD) at 0.05 level of propability.

Appendix 5 : Dermal exposure of different body parts to dimethoate (mg/day) of individual sprayers in field test I

Sprayerman No.	Face	Back of neck	Front of neck	Back	Chest and stomach	Upper arms	Forearms	Upper legs
1	36.11	0.31	0.50	9.94	11.79	35.88	304.12	392.13
2	21.85	0.21	0.38	6.67	9.09	183.53	162.91	283.64
3	13.60	0.18	0.87	5.82	20.59	120.81	196.60	492.12
4	26.83	0.31	0.35	9.94	8.38	140.21	243.21	448.88
5	34.52	0.28	0.38	9.09	9.09	60.06	98.25	315.95
6	15.08	0.37	0.77	12.07	18.32	55.86	134.29	323.28

Appendix 6 : Dermal exposure of different body parts to dimethoate (mg/day) of individual sprayers in field test II

Sprayerman No.	Face	Back of neck	Front of neck	Back	Chest and stomach	Upper arms	Forearms	Upper legs
1	11.97	0.30	0.54	9.66	12.78	21.30	286.17	471.60
2	29.37	0.39	1.88	12.50	44.59	178.83	198.15	386.96
3	7.87	0.33	1.09	10.65	25.70	109.90	144.93	244.89
4	19.19	0.21	0.47	6.82	11.22	138.76	232.39	253.80
5	30.00	0.09	1.13	2.98	26.70	73.68	130.49	396.68
6	24.18	0.24	0.51	7.67	12.07	96.81	165.07	301.95

Appendix 7 : Total dermal exposure (mg/day), of different body parts.

	Back of neck	Front of neck	Back	Chest and stomach	Face	Upper arms	Forearms	Upper legs
	0.27 (1)	0.74 (2)	8.65 (3)	17.53 (4)	22.55 (5)	101.30 (6)	191.30 (7)	359.32 (8)
	(8)	(7)	(6)	(5)	(4)	(3)	(2)	
(1)	359.05*	191.11*	101.03*	22.28	17.26	8.38	0.47	
(2)	358.58*	190.64*	100.56*	21.81	16.79	7.91		
(3)	350.67*	182.73*	92.65*	13.90	8.88			
(4)	341.79*	173.85*	83.77*	5.02				
(5)	336.77*	168.83*	78.75*					
(6)	258.02*	90.08*						
(7)	167.94*							

* : Means are significantly different, using Least Significant Difference(LSD) at 0.05 level of probability.

Appendix 8 : Percentage * of mean dermal exposure of each body part to mean total dermal exposure.

Body part	Percentage (%)
Back of neck	0.04%
Front of neck	0.11%
Back	1.23%
Chest and stomach	2.50%
Face	3.21%
Upper arms	14.44%
Forearms	27.27%
Upper legs	51.21%

$$\therefore \text{Percentage} = \frac{\text{Mean dermal exposure of each body part (mg/day)}}{\text{Mean total dermal exposure (701.7 mg/day)}} \times 100$$

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Appendix 9 : Calculations of the recovery percent for dermal and respiratory exposure samples.

1. Dermal exposure samples:

a. Dimethoate stock solution is 1000 ppm, each 1 μ l contains 1000 ng.

b. 75 μ l of the stock solution were spread on a 100 cm² gauze sponge.

This gave a concentration of 750 ng/cm² of the gauze sponge.

c. Extraction was carried out and the end volume was adjusted to 5 ml with acetone. This should gave 15 ng/ μ l.

d. 1 μ l of the standard dimethoate (15 ppm) was injected, then 1 μ l of the residue was injected.

e. Results revealed that the 1 μ l of the residue gave 12.54 ng which gave
 $12.54 \times (5000 \mu\text{l} = \text{end volume}) / 100 \text{ cm}^2 = 627 \text{ ng/cm}^2$.

Recovery = $627/750 \times 100 = 83.6\%$.

2. Respiratory exposure samples:

a. Dimethoate stock solution is 1000 ppm, each 1 μ l contains 1000 ng.

b. 75 μ l of the stock solution were added to 15 ml ethylene glycol. This gave a concentration of 5000 ng/ml of the ethylene glycol .

c. Extraction was carried out and the end volume was adjusted to 5 ml with acetone. This should gave 15 ng/ μ l.

d. 1 μ l of the standard dimethoate (15 ppm) was injected, then 1 μ l of the residue was injected.

e. Results revealed that the 1 μ l of the residue gave 10.32 ng which gave

$$10.32 \times (5000 \mu\text{l} = \text{end volume}) / 15 \text{ ml} = 3440 \text{ ng/ml.}$$

$$\text{Recovery} = 3440 / 5000 \times 100 = 68.8\%.$$