

Production Practices and Quality Assessment of Food Crops

Volume 2

Plant Mineral Nutrition and Pesticide Management

Edited by

Ramdane Dris and S. Mohan Jain

Kluwer Academic Publishers

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PREFACE

Plants require nutrients in order to grow, develop and complete their life cycle. Mineral fertilizers, and hence the fertilizer industry, constitute one of the most important keys to the world food supplies. There is growing concern about the safety and quality of food. Carbon, hydrogen and oxygen, which, together with nitrogen, form the structural matter in plants, are freely available from air and water. Nitrogen, phosphorus and potassium, on the other hand, may not be present in quantities or forms sufficient to support plant growth. In this case, the absence of these nutrients constitutes a limiting factor. The supply of nutrients to the plants should be balanced in order to maximise the efficiency of the individual nutrients so that these meet the needs of the particular crop and soil type. For example, it should be noted that EU-wide regulations are not designed to govern the specific details of mineral fertilizer use. Although plants receive a natural supply of nitrogen, phosphorus and potassium from organic matter and soil minerals, this is not usually sufficient to satisfy the demands of crop plants. The supply of nutrients must therefore be supplemented with fertilizers, both to meet the requirements of crops during periods of plant growth and to replenish soil reserves after the crop has been harvested.

Pesticides are important in modern farming and will remain indispensable for the foreseeable future. Without them it would be practically impossible to produce the enormous quantities of food that are required to feed the world's growing population. Multi-residue analysis of pesticides is applied routinely in food control laboratories around the world, especially in the control of fruits, vegetables, and cereals, since they are generally produced using direct applications of pesticides. Technical aspects of the application of pesticides and other agricultural inputs are in many countries of the world neglected and on field level unknown. Studies have shown convincingly that most farmers in developing countries can not handle highly hazardous pesticides in an acceptable manner. European Proficiency Tests 1996/97 (incurred pepper and spiked apple), Swedish NFA Inter-calibration Test 1995 (incurred grapes), and Spanish MAFF Inter-laboratory Tests 1994/95/96 (spiked and incurred peppers, and incurred lettuces). Pesticides must be applied with utmost care in the most efficient manner to protect crops and farm animals, while leaving the lowest possible residues in food and the environment. The Joint FAO/WHO Meeting on Pesticide Residues (JMPR) has, since its inception in 1963, updated on a regular basis the scientific principles and methods by which it assesses pesticides. However, its operating procedures and resources have remained static despite the huge increase in work load associated with the evaluation of pesticides today compared to the time of its inception forty years ago.

Nine chapters are included in this book, which are: Environmental and Biological Monitoring of Exposure to Pesticides in occupationally Exposed Subjects; Crop Quality Under Adverse Conditions: Importance of determining the Nutritional Status; Phosphorus Management in French Bean (*Phaseolus vulgaris* L.); Nutrition and Calcium Fertilization of Apple Trees Diagnosis, Prediction and Control of Boron Deficiency in Olive Trees; Boron-Calcium Relationship in Biological Nitrogen

Fixation Under Physiological and Salt-Stressing Conditions; Lime-Induced Iron Chlorosis in Fruit Trees; Si in Horticultural Industry; Biological Monitoring of Exposure to pesticides in the General Population (Non-Occupationally Exposed to Pesticides).

In this book, we will cover various aspects on mineral nutrition, fertilizers and pesticide management to improve agricultural production, yield and to amelioration of soil fertility. The production of good quality food can not be achieved without the strict control of the quality and the use of pesticides. There is a need to increase research and development facilities to focus on new product development, seeking solutions to environmental problems and making more efficient use of applied nutrients and pesticides.

The editors wish to express their sincere gratitude to all authors for their valuable contributions. We are grateful to Kluwer Academic Publishers for giving us an opportunity to compile this book.

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ENVIRONMENTAL AND BIOLOGICAL MONITORING OF EXPOSURE TO PESTICIDES IN OCCUPATIONALLY EXPOSED SUBJECTS

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1. INTRODUCTION

Exposure to pesticides affects much of the population, including persons who are occupationally exposed as well as the general population, which may have contact with pesticides through domestic use, consumption of contaminated food and drink or by living in agricultural areas or areas treated for reasons of public health.

From the occupational viewpoint, exposure to pesticides regards the industrial, agricultural, public health (pest and rat control) and veterinary sectors (treatment of animals).

The major agricultural tasks carried out in the field or in greenhouses or tunnels, include mixing, loading, distribution, maintenance and repair of machinery and tools, and re-entry of treated areas. During loading and mixing, exposure depends on the type of formulation (solid, liquid), the size of solid particles, the size of the container, the number of operations carried out during the work shift, the quantity of formula and method of loading (use of soluble bags helps to reduce exposure levels). During distribution, exposure levels depend on the type of machines, the technique used, the size of aerosol particles and the quantity of pesticide distributed, which in turn depends on the size of the area to be treated and the time of application.

Re-entry tasks include all manual and mechanical operations carried out on plants previously treated with pesticides. They include harvest (fruit, vegetables and flowers), irrigation, thinning, staking, spacing, securing and so forth. In this case exposure depends on the quantity of pesticide applied and the interval elapsing since treatment. The term 're-entry period' (Goh et al., 1986) means the interval between distribution of pesticide and re-entry of the treated area necessary for safe manual operations without means of protection. Re-entry times have been established for various pesticides by monitoring decay of pesticide residues on leaves. Variables affecting pesticide break down include the physicochemical properties of the active ingredient, its capacity to be absorbed by plants, as well as microclimatic and environmental factors such as temperature and solar radiation (Brouwer et al., 1992a).

Activities and operations carried out in the chemical industry include synthesis and packaging of active ingredient, formulation, packaging of formula and maintenance and repair of machinery and tools. In such cases, workers are usually exposed to few active ingredients relatively constantly for long periods.

Agricultural activities in confined spaces and formulation of commercial products

(mixing of active ingredients with excipients) are intermediate in character between farming in the open field and industrial activity. The work is done in a controlled microclimate and there is contact with many different products formulated in cycles.

Knowledge of exposure levels is a first step in the risk evaluation process and measurement may be done in different ways (predictive models, existing measurements, measurement under experimental conditions, representative sampling).

Predictive models of exposure are used when direct measurements cannot be made or are difficult or costly. They consist of mathematical representation of pesticide dispersal in the environment, based on its physicochemical properties and partial measurements. If not carefully validated, models may be much less accurate than direct evaluation of exposure. Although they are widely used in epidemiology to estimate environmental exposure, they are rarely used to evaluate occupational risk.

The use of existing measurements has the advantage of exploiting direct measurements reported in the literature and obtained during evaluation of environmental or occupational exposure. This method is therefore less costly than studies carried out for the specific purpose. An important application is to predict exposure to compounds that are not determined but which are used in the tasks monitored. A condition of this technique is that exposure be determined more from the physical properties of the formula, and from methods and conditions of use, than from the chemical nature of the pesticide.

Use of measures obtained under experimental conditions may lead to large errors because of the difficulty of reproducing in the laboratory real multiple conditions of field exposure (weather, climate and process techniques).

Representative sampling is the best strategy for evaluating exposure, its main problem being cost and sometimes practical considerations.

2. RESPIRATORY EXPOSURE

For certain types of active ingredient, method of distribution, work environment, climate (or microclimate) and occupational task, pesticides may be dispersed in the air as aerosols and/or vapour.

Direct methods of evaluating respiratory exposure proposed by Durham and Wolfe in 1962 (Durham and Wolfe, 1962) employ a respirator interfaced with a pad which may be of various materials. Surgical gauze and alpha-cellulose have been used to sample substances in dry and liquid form, respectively. The pads intercept the total quantity of aerosol that would otherwise be inhaled by the worker. This quantity can be expressed as potential hourly dose by dividing by the time of exposure. The advantages of this technique are simplicity of use and the fact that the amount of aerosol trapped by the system depends on the real respiratory regime of the subject. Disadvantages are dampening of the pad by expired air which modifies capture efficiency and may lead to hydrolysis of the active ingredient. These limits and the difficulty of convincing workers to wear the respirator have meant that direct methods have largely been replaced by air sampling procedures.

2.1. Methods of air sampling

The strategy may involve personal and/or area air sampling, depending on whether the sampler is worn by the operator (near the mouth and nose) or whether it is installed in the work place. Personal air sampling is more suitable than area air sampling for evaluation of exposure of workers. Temperature and pressure of sampling must be recorded in order to correct and standardise the volumes of air sampled.

The duration of sampling is determined by changes in concentration that may occur in time, by sampling flow and by limits of detection (LOD) of analytical methods. Short sampling periods repeated during the work shift may provide a good approximation of real exposure conditions. For example, a worker may be engaged in various tasks during the work shift and each of these can be monitored. Mixing and loading are tasks which may only last a few minutes, but it may be useful to sample them separately as there may be large variations in exposure. If the sampling substrate is changed with each change of task (Brouwer et al., 1993)), daily exposure is represented by the time-weighted mean of pesticide concentrations detected in each period. In other cases (Aprea et al., 1994a; Aprea et al., 1995; Aprea et al., 1998; Aprea et al., 1999b; Aprea et al., 2001a; Aprea et al., 2002; Fenske and Elkner, 1990), sampling is made to cover the whole work shift or a shorter but representative interval of the working day.

During synthesis and packaging of active ingredient, work proceeds in a continuous manner with the same products. In this case evaluation of exposure should be directed at all active ingredients and excipients dealt with in each production cycle in a differentiated way and should be repeated at different times of year for the various substances.

Interpretation of exposure data obtained in the field (external air) is more difficult than interpretation of values measured in a confined environment because in the former case, the results are affected by variables such as wind (direction and speed), temperature and thermal inversions.

2.2. Sampling of pesticides dispersed as aerosol

Of the various techniques (van Dyk and Visweswariah, 1975) of sampling aerosols (filtration, bubbling, impact and granulometric separation, sedimentation, electrostatic precipitation, thermal precipitation, centrifuge methods), the most widely used is filtration with cellulose ester or nitrate membranes or fiberglass filters. Table 1 shows recent papers on capture of particulate by air filtration. The sampling substrates reported in the official methods of the U.S. National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) are also indicated.

2.3. Sampling of pesticides dispersed as vapour

The most widely used methods are adsorption on solid materials in vials and absorption in liquids by bubbling.

Table 1. Systems of air filtration sampling used in official and other methods.

Pesticide	Sampling substrate	Flow (l/min)	References
2,4-D	Glass fiber filter	4	Abbott et al., 1987
2,4-D	Glass fiber filter binding free	1-3	NIOSH, 1994a
2,4-D, MCPA	Glass fiber filter	2	Aprea et al., 1995
Acephate	Mixed cellulose ester filter	4	Maroni et al., 1990
Acephate, Benomyl, Carbaryl, Diazinone Chlorothalonil, Dicofol	Glass fiber filter	2	Leonard and Yeary, 1990
Alachlor	Solid phase extraction filter	1	NIOSH, 1998a
Captan	Glass fiber filter	2 ^d	de Cock et al., 1995
Carbaryl	Glass fiber filter binding free	1-3	NIOSH, 1994c
Chlorpyrifos	Glass fiber filter	2 ^e	Fenske and Elkner, 1990
Delthametrin, Fenvalerate	Mixed cellulose ester filter	2 ^f	Zhang et al., 1991
Ethylenethiourea	Glass fiber filter	2	OSHA, 1992
Ethylenethiourea	Polivinyllchloride filter	1-3	NIOSH, 1994e
Ethylenethiourea	Mixed cellulose ester filter	1-3	NIOSH, 1994e
Ethylenethiourea	Mixed cellulose ester filter	2-3	Kurttio and Savolainen, 1990; Kurttio et al., 1990
Ethylenethiourea, Mancozeb, Dimethoate	Glass fiber filter	2.8 ^a	Aprea et al., 1998
Fenvalerate, Delthametrin	Glass fiber filter	2-10	He et al., 1988
Fenvalerate, Delthametrin	Mixed cellulose ester filter	2-10	He et al., 1988
Fosetil-Al	Glass fiber filter	2	Fenske et al., 1987
Maneb	Mixed cellulose ester filter	2	OSHA, 1996
Metomyl, Pirazophos, Fenarimol, Captan, Endosulfan, Carbendazim	Glass fiber filter	14 ^c	Stevens and Davies, 1981
Metomyl, Captan, Endosulfan, Carbendazim, Pirazophos, Fenarimol	Mixed cellulose ester filter	3	Stephanou and Zourari, 1989
Picloram	Glass fiber filter	1	OSHA, 1990c
Piretro	Glass fiber filter	1-4	NIOSH, 1994d
Propetamphos	Glass fiber filter	1	OSHA, 1989c
Propoxur	Glass fiber filter	2 ^{b,c}	Brouwer et al., 1993
Temephos	Glass fiber filter	1	OSHA, 1990e
Thiophanate-methyl	Glass fiber filter	1	OSHA, 1989e
Thiram	Politetrafluoroethylene filter	1-4	NIOSH, 1994b
Thiram, Zineb, Thiophanate-methyl	Mixed cellulose ester filter	2 ^b	Brouwer et al., 1992b
Zineb	Mixed cellulose ester filter	2	OSHA, 1996

^a Inhalable fraction with 7 mm reduction cone.

^b Inhalable fraction with IOM sampler.

^c Two filters in series.

^d Inhalable fraction with 6 mm reduction cone.

^e Inhalable and respirable fractions (cyclone).

^f Granulometry was determined by impact at a flow of 20 l/min.

The main features of an adsorbent are low flow resistance, high adsorption capacity, inertness, resistance to fracture and easy release of the adsorbed substance for analysis (van Dyk and Visweswariah, 1975).

Liquids used to absorb pesticides must not foam or be inflammable, volatile or viscous. They should ensure ready solubilisation of the pesticide in the vapour phase and should be chemically stable and non corrosive (van Dyk and Visweswariah, 1975). Ethylene glycol has been used for lindane, dieldrin and DDT, and n-butanol, toluene, hexane and water for diclorvos (van Dyk and Visweswariah, 1975). Ethylene glycol has proved to be an excellent absorbent for most pesticides but its use is limited by the fact that it absorbs atmospheric humidity which may lead to hydrolysis of active principles.

Liquids that react with the substance to be sampled have also been used, for example monoethanolamine reacts with diclorvos to form a coloured compound that can be analysed by spectrophotometry (van Dyk and Visweswariah, 1975). Reactive liquids (2-methoxymethanol/NaOH, 1:1 v/v) have also been used for parathion and methylparathion (van Dyk and Visweswariah, 1975). Solutions of cholinesterase have been used as absorption liquid for parathion and demeton (van Dyk and Visweswariah, 1975).

The most recent systems for sampling pesticide vapours are shown in Table 2.

2.4. Combined sampling systems

A combined or two-stage system consists of two or more sampling units linked in series in order to sample various physical forms of airborne pesticide simultaneously present in a work environment or that may form by stripping in the first system as an effect of the air flow. Systems containing more than one unit of the same

Table 2. Sampling systems based on adsorption/absorption used in official and other methods.

Pesticide	Sampling substrate	Flow (l/min)	References
2,4-D, Diclorprop, Picloram	Florisil	0.2	Libich et al., 1984
2,4-D, MCPA, Diclorprop, Mecoprop	Water	1	Kolmodin-Hedman et al., 1983a; Kolmodin- Hedman et al., 1983b
Chlorpyrifos, Carbaryl, Permethrin	PUF**	2	Byers et al., 1992
Cipermethrin	ORBO 42	2	Wright et al., 1993
Deltamethrin, Dicofol	Hydrated Florisil		Mestres et al., 1985
Dimethoate	Amberlite	1	Apra et al., 1998
Fluvalinate, Dicofol, Chlorpyrifos, Etazol	PUF**	3	Stamper et al., 1989
Chlorinated and phosphoric ester insecticides	PUF**	1-5	EPA, 1987b
Mevinfos	XAD-4	0.2-1.5	Kangas et al., 1993
Pentachlorophenol	XAD-7*	0.2	OSHA, 1982

* The device consists of two vials containing XAD-7 disposed in series.

** Polyurethane foam, the substrate also samples particulate but its efficiency is not known.

type (two vials in series or two membranes in series) have also been used to collect all the compound, when low capture efficiency makes it impossible to collect it all with a single unit (Brouwer et al., 1993; OSHA, 1982; Stephanou and Zourari, 1989). Recently used combined systems are shown in Table 3.

When combined systems are used, exposure is obtained summing the concentrations detected in the various serial units.

2.5. Comparison with environmental limits

The American Conference of Governmental Industrial Hygienists (ACGIH, 2002) has published threshold limit values (TLVs) for various pesticides. Similarly OSHA, NIOSH and other government and non government bodies of different countries (Australia, Belgium, Denmark, France, Germany, Switzerland, UK, Finland, Japan etc.) have published various types of limits for respiratory exposure to pesticides, sometimes with the notation 'skin' to indicate the possibility of transcutaneous exposure.

In the case of industrial occupations, respiratory exposure can be compared with limit values. Farm work, on the other hand, has characteristics that make comparison with limit values, if they exist, almost impossible:

- pesticide use is concentrated in short periods repeated during the year (intermittent exposure);
- more than one substance having different toxicological properties may be used simultaneously;
- tasks vary and are sometimes associated with cutaneous rather than respiratory exposure, or vice versa;
- pesticide use is characterised by qualitative and quantitative variations that may depend on agricultural factors, weather, and so forth.

2.6. Respiratory dose

To estimate respiratory dose using air sampling, the concentration of pesticide detected in personal air samples (RE = respiratory exposure) expressed in units of mass per cubic metre, is corrected for the volume of air inhaled by the subject during the period of exposure (T). This volume depends on pulmonary ventilation (PV) expressed in l/min which is in turn determined by the physical exertion required by the task undertaken. Table 4 shows lung ventilation values used by various authors to calculate respiratory dose (RD) for various occupational tasks.

The general formula used to calculate respiratory dose is:

$$DR(\text{mass}) = \frac{ER (\text{mass}/\text{m}^3) \cdot PV(\text{l}/\text{min}) \cdot T(\text{min})}{1000}$$

To calculate absorbed dose, the numerator of the formula is multiplied by PR%.

If personal protection such as a mask is not worn and if no specific studies exist, various authors use a PR of 100% (Aprea et al., 1998; Fenske and Elkner,

Table 3. Two-stage sampling systems of official and other methods.

Pesticide	Sampling substrate	Flow (l/min)	References
Alachlor	OVS*	0.2-1	NIOSH, 1998b
Aldicarb	OVS-2	1	OSHA, 1988b
Atrazine	OVS*	0.2-1	NIOSH, 1998b
Bendiocarb	OVS-2	1	OSHA, 1989a
Carbaryl	OVS-2	1	OSHA, 1987a
Chlordane	OVS-2	1	OSHA, 1987b
Chlorpyrifos	OVS-2	1	OSHA, 1986
Clorothalonil	M FV ^c /XAD4	1	Spencer et al., 1991
Clorothalonil	M EMC ^a /XAD2	2 ^b	Brouwer et al., 1992b
Cyanazine	OVS*	0.2-1	NIOSH, 1998b
DDVP	OVS-2	1	OSHA, 1986
Demeton	EMC/XAD-2	0.2-1	NIOSH, 1994f
Diazinon	OVS-2	1	OSHA, 1986
Bendiocarb, Chlorpyrifos Diazinon	M FV ^c /chromosorb	1.7	Currie et al., 1990
Endosulfan	OVS-2	1	OSHA, 1988c
Fonophos	OVS-2	1	OSHA, 1989b
Phosphoric ester insecticides	OVS-2*	0.2-1	NIOSH, 1994g
Malathion	OVS-2	1	OSHA, 1986
Metolachlor	OVS*	0.2-1	NIOSH, 1998b
Metribuzin	OVS-2	1	OSHA, 1990a
Monocrotophos	OVS-2	1	OSHA, 1990b
Parathion	OVS-2	1	OSHA, 1986
Permethrin	M EMC ^a /tenax	0.5	Llewellyn et al., 1996
Dimethoate, Permethrin	M. EMC ^a /etanolo	0.3-0.5	Adamis et al., 1985
Pirimiphos-Methyl			
Propoxur	OVS-2	1	OSHA, 1987c
Pyrethrum	OVS-2	1	OSHA, 1988a
Resmethrin	OVS-2	1	OSHA, 1989d
Ronnel	OVS-2	1	OSHA, 1994
Simazine	OVS*	0.2-1	NIOSH, 1988b
Sulprofos	OVS-2	1	OSHA, 1990d
Azinphos-methyl, Chlorpyrifos, Diazinon, Dicrotophos, Disulfoton, Ethion, Ethoprop, Fenamiphos, Fonophos, Malation, Methamidophos, Parathion-methyl, Mevinphos, Monocrotophos, Parathion, Phorate, Ronnel, Sulprofos, Terbufos	OVS-2	1	Kennedy et al. 1994
Aldicarb, Benomyl, Captan, Carbaryl, Carbofuran, Chlorpropham, Diuron, Formetanate, Methiocarb, Metomyl, Oxamyl, Propham, Propoxur, Thiobencarb	OVS*	1	Kennedy et al. 1997
2,4-D	OVS*	0.2-1	NIOSH, 1998b
2,4-D 2-ethylhexyl estere	OVS*	0.2-1	NIOSH, 1998b
2,4-D 2-butoxyethyl estere	OVS*	0.2-1	NIOSH, 1998b
2,4-D Carbofuran, Trifluralin,	M PVC ^d /tenax	0.5	Guidotti et al., 1994

^a Mixed cellulose ester membrane; ^b inhalable fraction (IOM sampler); ^c fiberglass membrane; ^d PVC membrane.

EMC/XAD-2 is a device consisting of a mixed cellulose ester membrane and vials containing XAD-2; OVS-2 is a commercially available device consisting of a glass vial containing XAD-2 divided into two sections, 270 mg (front) and 140 mg (back), separated by polyurethane foam. The front section is held in place by a fiberglass filter fixed with a polytetrafluoroethylene ring.

* A device similar to that reported in OSHA method 62 except that the filter is not fiberglass but quartz fiber.

Table 4. Pulmonary ventilation (PV) values and pulmonary retention (PR) used in various studies to calculate respiratory dose.

Task	PV (l/min)	PR (%)	References
Spraying in greenhouse	14.2	100	Stephanou and Zourari, 1989
Pest control of buildings	29 ^a	100	Fenske and Elkner, 1990
Formulation, bottling and/or packaging	Males 28.6 ^b Females 16.3 ^b	100	Aprea et al., 1998
Harvesting flowers in greenhouse	20.8	40 ^c	Brouwer et al., 1993
Mixing, loading and distribution	20		Fenske et al., 1987
Distribution	25		Kurttio and Savolainen, 1990; Kurttio et al., 1990
Harvest of tomatoes in greenhouse	16.7		Adamis et al., 1985
Mixing and loading	29 ^a		Byers et al., 1992
Formulation	20.8		Maroni et al., 1990
Mechanical harvest of tomatoes	Females 16 ^d	100	Spencer et al., 1991

^a Reported by Durham and Wolfe (Durham and Wolfe, 1962) for light work; ^b reported by Taylor (Taylor, 1941) for light work; ^c value based on studies with volunteers (Machemer et al., 1982); ^d reported by EPA for light work (EPA, 1987a).

1990; Spencer et al., 1991; Stephanou and Zourari, 1989). Other authors (Brouwer et al., 1993) use PR values obtained in studies on volunteers (Machemer et al., 1982).

If respiratory protection is worn, personal sampling provides a measure of potential exposure. To estimate real exposure it is necessary to check whether respiratory protection is worn throughout the work shift and determine the protection it affords.

3. SKIN EXPOSURE

Skin contamination may occur as a result of immersion, deposition or surface contact. For example, immersion occurs when part of the skin is immersed in a container containing a mixture of pesticides to be dispersed on crops. In such cases, exposure depends on chemical concentration of pesticide, area of skin immersed and duration of exposure. It can be reduced if protective clothing is worn and is generally evaluated by biological monitoring or by means of models, rather than by direct measurement. A special situation arises when a worker wears garments, such as gloves, contaminated with pesticide on the inside.

Contamination by deposition may occur when workers are engaged in environments where pesticides are present as aerosols. Aerosols may form during treatment or other operations, such as manipulation of leaves or other material containing pesticide residues.

Skin contamination may also occur by contact with surfaces bearing pesticide residues. Transfer from surfaces to the skin is a complex process influenced by factors such as contact pressure, affinity of the substance for the skin surface, working methods and hygiene. Contact is the made source of exposure of farm workers re-entering a sprayed area.

Skin exposure may contribute to exposure by other routes. Residues on the

hands can be transferred to the eyes, nose and mouth and may contaminate food, cigarettes and drinks. Hand contact with other parts of the body may spread the contaminant to the genitals. Residues on skin and clothes may be a source of para-occupational exposure (other family members).

Evaluation of skin exposure, difficult to predict a priori, is crucial for identifying sources and mechanisms of contamination, as well as assessing the effectiveness of protective clothing. Since more than 50% of the dose of pesticide may be absorbed through the skin under normal working conditions, evaluation of respiratory exposure alone may not be exhaustive. It is advisable to measure skin exposure and perform environmental sampling and biological monitoring at the same time and evaluate the results as a whole to ensure accuracy in estimates of risk. Measurements of skin contamination are particularly appropriate because few biological indicators of exposure validated for humans are available.

The ideal method of evaluating skin exposure should:

- enable measurement of the quantity of substance available through skin penetration;
- enable an accurate estimate of contamination throughout exposure and sampling;
- enable repetitive sampling in time;
- be applicable to areas of the body regarded as at risk for skin absorption;
- simulate the various processes of skin contamination and removal.

The most widely used methods are discussed below.

3.1. Skin surrogates for evaluating skin exposure

These methods involve placing sampling substrates on the skin and later analysing them to determine pesticide content. The systems used tend to retain substances with low vapour pressure in solid particulate or mist form. The assumption is that the substrate has a similar behaviour to skin, though none of the systems proposed has actually been systematically tested to evaluate retention efficiency. This technique presumably gives overestimates of exposure because the substrates are selected on the basis of their absorbing properties.

3.1.1. Pads

Pads cover a small part of the skin area to sample and exposure is calculated by extrapolation of contaminant levels to the whole anatomical district represented. The validity of pads for monitoring exposure depends on various factors. In the case of uniform distribution of the active ingredient on the area of skin, pads provide representative data. Non uniform distribution has been documented in several studies (Fenske, 1990). In these cases pads may lead to over- or under-estimation of real skin exposure.

Although the pad technique is not always accurate for estimating cutaneous dose, it is widely used because it is cheap and easy to perform. Table 5 shows some of the studies reported in the literature in which skin exposure was evaluated by this method.