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Exposure to pesticides

Part III. Application to chrysanthemums in greenhouses

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Part III. Application to chrysanthemums in greenhouses

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SUMMARY

During twenty applications with a spray pistol of methomyl to chrysanthemums, inhalation exposure as well as potential and actual dermal exposure were monitored.
Inhalation exposure to methomyl was measured with an IOM personal sampler with extended housing containing a cartridge with the adsorbent XAD. Dermal exposure was measured with a "whole body"-method, using a cotton overall for potential exposure, and cotton gloves, a long sleeved T-shirt, long-legged undertrousers and socks for actual exposure. The clothing was analysed in parts to study the distribution of the contamination over the body parts. Exposure of the hands was monitored separately during mixing and loading, and application.
Inhalation exposure during mixing, loading and application averaged 5.1 µg/hour (GM, active ingredient, GSD 5.0). Dermal exposure of the hands during mixing and loading, and application was 13.1 mg/hour (GSD 7.1) and 0.8 mg/hour (GSD 4.9) respectively. The potential exposure of the remaining parts of the body was 1710 µg/hour (GSD 3.1) showing exposure mainly of the front torso (23%) and the legs (57%). The actual dermal exposure (excluding the hands) was 40 µg/hour (GSD 4.4). Penetration of the pesticide through the overall was less than 5% on average. On the basis of the exposure data in terms of exposure to the liquid formulation and the spray liquid, the possible health risk for methomyl and thirteen other pesticides, frequently used in ornamentals, was indicatively assessed. From the No-Observed-Adverse-Effect-Level (NOAEL) in animal experiments an Indicative Limit Value (ILV) was derived. The ILV is considered as being indicative of the the level of daily exposure for a worker which probably gives no rise to adverse health effects[1]. Assuming that exposure is independent of the pesticide, using a suitable format, the actual exposure can be compared with the ILV. Calculations showed that the ILV for inhalation exposure was exceeded once, and the ILV for dermal exposure was exceeded by twelve pesticides for which the calculations were made. For reduction of the dermal exposure levels below the ILV the exposure of the hands has to be reduced e.g. by using impermeable gloves. If the used work clothing is in addition less permeable for pesticides than 5%, the ILV of only three pesticides is exceeded.

[1] This value is a rough approximation since the database for a proper assessment of such a value is generally incomplete. Furthermore, a concept for assessing a limit value for skin exposure has not yet been fully developed.

1 INTRODUCTION

On request of the Directorate-General of Labour from the Ministry of Social Affairs and Employment, TNO conducts pesticide exposure studies in ornamentals to gather information on possible health effects and on exposure-determining variables. Previous studies were carried out in the cultivation of carnations and roses (Brouwer et al. 1991, Brouwer et al. 1992a, 1992b) mainly aimed at assessing exposure during crop activities after re-entry. A study in the second largest culture of ornamentals, the chrysanthemum, is now in progress; the present report focuses on exposure of applicators.

Chrysanthemums are cultivated in greenhouses on some 800 farms with a total acreage of 625 ha using 223 kg/ha of pesticides yearly (LNV 1990).

Exposure to pesticides mainly occurs during mixing, loading and application and during crop activities, such as harvesting. Mixing and loading is generally done in an open tank with a content of 500-1000 l. Pesticides are added by weighing or measuring an amount in a graduated beaker. When a high-volume technique is used, the spray liquid is transported from the tank to the greenhouse by pumping under pressure (20-30 bar) through a fixed system. The application is done with a flexible hose, taking liquid from the piping system using quick-fit couplings. High-volume spraying with a spray pistol is the most frequently used method.

In handling pesticides, the dermal route of exposure is considered very important (Wolfe et al. 1967). Several methods are used for monitoring dermal exposure, such as washing or wiping, pseudo-skin methods, biological monitoring and video-imaging (Fenske 1993). Dermal exposure of the hands can be assessed by washing the hands with an organic solvent/water mixture, or ordinary water and soap. A disadvantage of the method is that only the non-resorbed fraction of the pesticide is washed off and that the use of organic solvents may disrupt the skin barrier function. The efficiency of removing pesticides from the hands has to be established in laboratory experiments. Biological monitoring can give the absorbed dose directly (Van Hemmen and Brouwer, 1989). The route of exposure, however, remains unknown and a suitable metabolite as well as toxicokinetic data have to be known, preferably studied in volunteers. The use of a tracer technique (Fenske et al. 1985; Bierman et al. 1992) is a method in which a fluorescent compound is added to the spray solution. Exposure can be made visible with the use of ultraviolet light. Quantitative exposure can be assessed with the use of a camcorder and digitizing the images. Other

methods of monitoring dermal exposure make use of a "pseudo"-skin (Van Hemmen and Brouwer 1989, Davies 1982). The most widespread method in the past was the use of patches made of surgical gauze or other textiles (Durham and Wolfe 1967, Wolfe et al. 1972). Use of these methods are described in EPA and WHO protocols (EPA 1986, WHO 1982). A disadvantage in the use of patches is the relative small fraction of the surface (generally less than 10%) that is measured. The emergence of video-imaging techniques have shown an irregular distribution over the parts of the body, thus introducing relatively large margins of uncertainty in calculating the total amount of exposure (Fenske 1990). To avoid this disadvantage, the use of clothing itself as a monitor (called the "whole body"-technique) is considered to give a better estimate of potential exposure (Chester 1993).
The "whole body"-technique is a method to determine the potential as well as the actual exposure by analysis of the active ingredient in the clothing, preferably work clothing and underclothing as well as inhalation monitoring and biological monitoring. Part of the exposure of the hands is assessed by washing with soap and water. The clothing may be analysed in parts to give details of the distribution of the contamination over the body. In the present study this method was applied with the difference that the exposure of the hands was monitored with cotton gloves and no biological monitoring was done.
The aim of the study was to estimate the exposure to pesticides during high-volume application in greenhouses for chrysanthemum culture with particular interest in the assessment of potential and actual dermal exposure and the distribution of the pesticide over the body. Data were also gathered for risk assessment purposes and should be usable for generic data bases (Van Hemmen 1992).
The following questions had to be answered:

- what are the levels of potential and actual dermal exposure and how is the contamination distributed over the body?
- what are the levels of inhalation exposure during application?
- are health risks to be expected at the observed exposure levels?

2 MATERIALS AND METHODS

2.1 Methomyl

Criteria for the selection of a suitable pesticide for this study were the availability of a validated analytical method (annex 1) in our laboratory and a widespread use of the pesticide in the growth of chrysanthemums in greenhouses. Methomyl was one of the pesticides that met these criteria. The pesticide is mainly used in the period from April to October as an insecticide and acaracide (annex 2). Moreover it is one of the few pesticides readily dissolvable in water, which facilitated enormously the procedure preparing the clothing samples for chemical analysis.

2.2 Selection of farms

A questionnaire was sent in November 1991 to 411 farms with an acreage of more than 0.25 ha to gather data on the use of pesticides, the seasonal variation in use, the techniques of application, the techniques used in harvesting, and to obtain consent to participate in the survey. Of these questionnaires 239 were returned (58 %). On 181 farms the only culture was chrysanthemums. Of these farmers 99 (55 %) were willing to participate in the survey.

The main results, regarding the use of pesticides and application techniques, of these questionnaires are presented in Tables 1 and 2. Application using a spray pistol (one nozzle) is so widespread that a comparison of exposure using various methods of application was not considered feasible.

In the fall of 1992 the farmers who had indicated not to use methomyl were sent a second questionnaire to see if the use of pesticides had changed. Of these 71 questionnaires 56 were returned (79%) adding 17 farms where methomyl was used. In total 52 farmers using methomyl with a single nozzle (spray pistol) application method were asked to participate in the study, of which 20 (37%) consented. In Table 3 an overview is given of the approached farmers and reasons for non-participation.

Table 1 The use of pesticides (1991)

Active ingredient	Pesticide (trade names)	Number of farms (percentage)
abamectin	Vertimec	177 (98%)
triforin	Funginex	124 (69%)
methomyl	Lannate	175 (41%)
dichlorvos	various formulations	62 (34%)
heptenofos	Hostaquick	61 (34%)
methiocarb	Mesurol	54 (30%)
bitertanol	Baycor	l53 (29%)
pyrazofos	Curamil	51 (28%)
oxamyl	Vydate	49 (27%)
pirimicarb	Pirimor	38 (21%)
deltamethrin	Decis	38 (21%)

Table 2 Application techniques and the use of methomyl (1991)

Technique	Number of farms	Number of farms using methomyl
High-volume techniques		
single nozzle	178	35
multi nozzle	33	6
Low-volume technique		
Colfog	7	1
Ultra-low-volume technique		
Swingfog/Dynafog	27	2
LVM	25	2
Other techniques	19	6
Sum	295*	54

* More than one method for application may be used

Table 3 Participation in the survey

	Number of applicators
Participation in survey	20
Use of methomyl later in the year	7
Methomyl replaced by other pesticides	9
Different technique	6
Refused participation without further indication	4
No response by telephone/ change of culture/ no longer farmer	6
Total	52

2.3 Study design

On twenty farms a study was undertaken to assess the inhalation exposure as well as the potential and actual dermal exposure during application of methomyl with a high-volume spray method using a spray pistol. Farmers participating in the survey were informed about the purpose and scope of the survey and were asked to apply pesticides as usual. Clothing and personal sampler for the exposure assessment were worn throughout the procedures of mixing, loading and application. In view of the short time necessary for mixing and loading only the exposure of the hands was assessed separately. Mixing and loading covered the procedure of filling the tank with water, measuring the amount or weight of the pesticides and adding these to the tank. Application included the procedure of fixing the flexible hose to the piping system, the actual application and deconnecting the flexible hose.

For each application, data were recorded including time and length of mixing, loading and application, amount of active ingredient applied, usual work clothing and additional observations.

2.4 Inhalation exposure

When applied under pressure, part of the spray is in the form of an aerosol, which may evaporate rapidly, therewith posing a problem for sampling. To collect aerosol particles as well as the vapour, an IOM personal air sampler with extended housing was used, containing a XAD-cartridge as an adsorbent (Brouwer et al. 1993). This method meets the requirements for sampling the inspirable fraction of the aerosol in combination with a suitable adsorbent for volatile compounds. The flow rate was calibrated at 2.0 l/min per minute. The pump, a Dupont P 2500, was worn on a belt underneath the overall.

2.5 Dermal exposure

The dermal exposure of the hands was monitored using cotton gloves. Separate samples were taken during mixing and loading, and application. When repair of the spray equipment was necessary, separate gloves were handed out. The potential dermal exposure was

monitored using a khaki coloured cotton overall that fitted as well as possible to the workers' size. The actual exposure was measured with a T-shirt with long sleeves, long-trousered cotton underpants and socks, worn underneath the overall. The T-shirt was worn over the underpants.
After application the clothing was divided into separate pieces as shown in Table 4.

Table 4 Dissection of clothing for distribution over body parts

Body part	Overall	T-shirt	Underpants
Torso, frontside	X	X	
Torso, backside	X	X	
Left lower arm	X	X	
Left upper arm	X	X	
Right lower arm	X	X	
Right upper arm	X	X	
Left upper leg	X		X
Left lower leg	X		X
Right upper leg	X		X
Right lower leg	X		X

2.6 Additional observations and quality control

Temperature and relative humidity were measured continuously during the application. Data on mixing and loading, area of application, protective garment usually worn and a description of the working method were recorded. A sample of the spray liquid was taken. The use of other pesticides was noted. Each sample was given an unique code before transportation.
For quality assurance (annex 1) a blank of each textile was taken before each application. Also one of the textiles, or a XAD-cartridge was spiked with standard solution or spray liquid. Some of the spiked samples were stored immediately to detect loss of methomyl during transportation, other spiked samples were exposed to light, humidity and temperature to mimic the "real" field samples.
A protocol to conduct the survey was written. Standard operating procedures were drafted for field blancs and spikes, and for monitoring inhalation and dermal exposure.

3 RESULTS

The survey was carried out on twenty farms; the workers all applied methomyl with a high-volume technique. Conditions under which pesticides were applied were usual operating procedure for the workers, the only difference being the prescribed clothing. In general this was no objection since most of the workers do not wear special clothing during application. Respiratory protection equipment did not interfere with the protocol. Clothing and protective equipment usually worn during application are given in annex 3. Only in three cases where a worker was used to wear a rainsuit the time of the experiment was abbreviated to 45 minutes to avoid clear breakthrough of the overall. On eighteen of the farms the owner usually applied pesticides; on two farms one of the employees applied pesticides. On one farm not a spray pistol was used, but a spray equipment with more than one nozzle; for this reason the worker was excluded from the data base. One of the applicators used a deviating work method compared to the others, resulting in complete soaking of the overall. This farmer was also excluded, because measuring potential and actual exposure with overall and underwear was not possible anymore; leaving eighteen applications to be used for analyses.
Usually one tank load with a mixture of two or more pesticides was applied; during seven applications more tank loads were made, and mixing and loading took place two or three times, due to the fact that different stages of growth require different mixtures of pesticides. Measurements were only carried out when methomyl was part of the mixture. Pesticides were mixed according to the instructions on the label. Methomyl was applied as a liquid formulation eighteen times and twice as a wettable powder. It should be noted that application times were generally less than two hours.
Statistical analyses (SOLO, BMDP statistical software) showed that the raw data per matrix (expressed as exposure/sample) followed a lognormal distribution. A graphical presentation of the exposure values is presented in Figure 1. The data are presented as hourly values to compensate for differences in time. The inhalation concentrations, expressed in $\mu g/m^3$, were multiplied by an assumed pulmonary ventilation of 1.25 m^3/hour. The mean exposures and standard deviations are presented in Table 5. Some details of the applications regarding spray concentration, area treated etc. are presented in annex 4. In annex 5 exposures are also expressed in μl/hour annd in μg/kg applied active ingredient. In Table 6 the distribution of the potential dermal exposure over the body is presented.

Figure 1 **Exposure on various body parts during application**

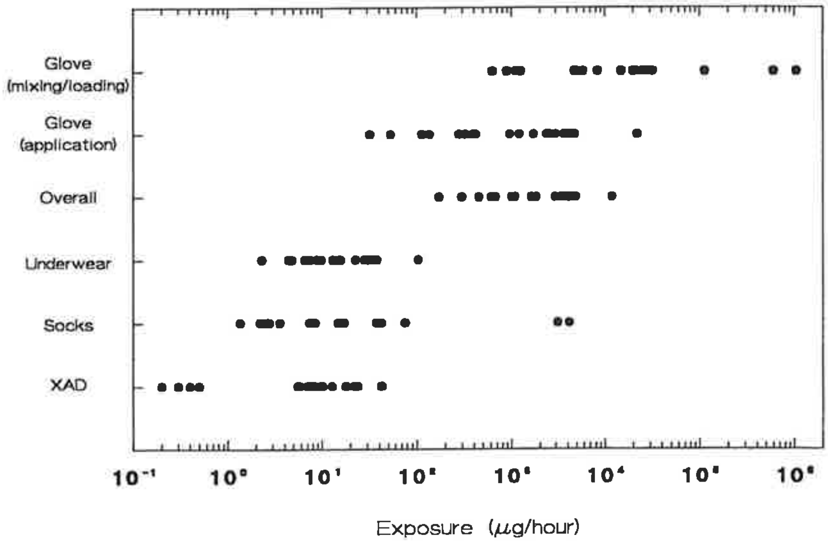


Table 5 **Mean exposures and standard deviations**

	AM (µg/hour)	STD (µg/hour)	GM (µg/hour)	GSD
Inhalation exposure	11.6	12.2	5.1	5.0
Hands (mixing and loading)	103530	258570	13110	7.1
Hands (m/l, per application; µg)	15900	41400	1810	7.0
Hands (application)	1860	1960	760	5.9
Potential dermal (excl. hands)	3180	4270	1710	3.1
Actual dermal (excl. hands)	330	1210	40	4.4

The methods used for the assessment of potential and actual dermal exposure imply that each part of the body was measured with the overall as well as the underclothing. On ten parts of the body there are corresponding samples for dermal and actual exposure. From these data the penetration of the overall was calculated. All together 180 samples were available. The mean penetration through the overall was on average less than 5% (annex 6).

Table 6 **Distribution of potential dermal exposure over the body during application**

	Exposure (AM)		
	(µg/hour)	(%)	(% excluding hands)
Hands	1860	37	
Torso front	740	15	23
Torso back	220	4	7
Upper arms	80	2	3
Lower arms	310	6	10
Upper legs	1090	22	34
Lower legs	720	14	23

4 DISCUSSION AND CONCLUSIONS

4.1 General aspects

The assessment of dermal exposure using the "whole body"-technique not only offers theoretical advantages, but also proved to be a "workable" method in practice. For the farmers the method is not very time consuming and the usual work habits do not have to be changed. Samples taken for quality assurance proved that there was no contamination or loss of sample during handling, transport and storage of the field samples.
Exposure of the hands (Table 5) is (very) high, especially during mixing and loading. Data in Table 5 are in μg/hour and the mixing and loading takes a relative short time (average 9 min) compared to application (average 81 min). But also absolute values of exposure of the hands during mixing and loading are high, and often in a milligram range. Visual observation showed that mixing and loading is often done in a hurry, no time is taken for a hygienic work procedure. The monitoring method for hand exposure (cotton gloves), may give an unknown overestimation of the dermal exposure when liquids are handled, as presently is the case. The highest observed level of exposure for a pair of gloves during mixing and loading is 175 mg, which indicates almost 1 ml formulation, which is a relatively high amount. Materials in use, such as bottles of pesticides or measuring beakers often are not cleaned after use. Incidental exposure during application may occur when the flexible hose is connected to and removed from the fixed piping system, which is done about three times per application.
Distribution of contamination over the body parts shows that the legs and front torso have the highest exposure (table 6). Spraying of the flowers is done in a slightly downward direction, moving the pistol from left to right. This may account for exposure of the legs. The short distance between spray pistol and the body may account for the relative high exposure of the front torso.
Penetration of the overall is on average less than 5%, but can incidentally exceed 30%. There is no specific body part with high penetration through the clothing, but it may be noted that high penetration on the left arm is more frequent than the right arm, probably because the flexible hose is generally moved with the left arm.

4.2 Protective clothing

When protective equipment is used, inhalation protection appears to be more popular than dermal protection (annex 3). In table 7 a summary of the used personal protection is presented.

Table 7 Use of personal protection

Protective equipment	Number of farmers
Mask with filter	9
Mask with fresh air supply	8
Gloves during mixing and loading	0
Gloves during application	9
Coverall	4
Rainsuit (trousers only)	3
Rubber boots	4
No protection at all	3
Normal work clothing	13

In three cases no protection was used at all. In fact not more than one of the farmers actually knew that in handling pesticides dermal exposure generally exceeds inhalation exposure. The most frequently used combination was inhalation protection (a mask with carbon filters or battery powered fresh air supply) in combination with usual work clothing, trousers and long sleeved shirt. Neither was the work clothing changed after application, nor was it washed. The same clothing is used days after application without washing. Mixing and loading was usually done without protective gloves because the packages (mostly one or five litre bottles) were said to be difficult to handle or to open. Between mixing and loading, and application hands were not washed. Filters in masks are not often changed: only once or twice a year when used once or twice per week. Protective clothing, i.e. coveralls, rain clothing, rubber boots are generally in good condition (not torn) but not cleaned after use, which may result in extra exposure the next time used.
In the actual spraying, the applicator generally avoids to walk through already treated crop. The spraying is done sidewards when walking ahead, and left and right when walking backwards. One of the applicators did not walk backwards, but straight ahead through the spray, resulting in complete soaking of the overall and underwear. Dermal exposure was 90 mg/hour on the overall and also 90 mg/hour on the underwear. For this way of application the presently used monitoring of dermal exposure obviously failed. For one application the exposure underneath a Tyvek overall was monitored. The actual exposure was 500 μg/hour, showing actual dermal exposure does occur underneath protective clothing.

4.3 Risk identification

Health effects of pesticides depend on the toxic properties of the pesticide ("hazard") and on the levels of exposure. The hazard evaluation is based on animal and human experiments in which acute, subacute, semi-chronic and chronic effects are determined, together with skin effects (irritation and sensitization), teratogenic and carcinogenic properties and effects on reproduction. From these data a No-Observed-Adverse-Effect-Level (NOAEL) can generally be derived, forming the basis for the establishment of an Indicative Limit Value (ILV) for a worker handling pesticides. Extrapolation and uncertainty factors are introduced, accounting for differences between animal and man, differences between experimental and occupational exposure conditions and the adverse character of the effect. The ILV should protect the worker against adverse health effects even after chronic exposure during a whole work-life (40 years). Because toxicity studies are generally performed by oral administration and an ILV has to be derived for the inhalation and dermal route, corrections have to be made for differences between oral, inhalation and dermal absorption. The NOAEL-values used in this report are derived from data in the open literature (JMPR 1986, 1989). It should be emphasized that the toxicological data on which they are based are not critically reviewed, with the exception of abamectin. Standard values of 50% oral, 100% inhalation and 30% dermal absorption were assumed. The ILV-dermal for abamectin is calculated assuming 1% dermal absorption. The value for dermal absorption is for the present goal assumed to be independent of degree and location of the contamination on the body. The ILV's are therefore only to be used as indicators[2]. Tentative comparisons of a ILV for a pesticide with the level of exposure, both expressed in mg/day, gives an indication for a possible health risk. The exposure level to be used is the sum of the exposures for each task performed that day. The assumption is made that the total time for the application is one quarter of an hour for mixing and loading and two hours for the actual application. The exposure level is expressed as the mean (AM) of the measured values or as the 90-percentile, the last value presenting the "reasonable worst case" of exposure. It is assumed that during mixing and loading or during application no gloves are used, which may be incorrect, but appears to be frequently occurring in actual practice. This means that potential and actual dermal exposure for the hands are taken the same. For the exposure of the body the actual exposure was used. In Table 8 the

[2] The calculated values are rough approximations since the database for a proper assessment of such a value is generally incomplete. Furthermore, a concept for assessing a limit value for skin exposure has not yet been fully developed.

calculated values for the $ILV_{inhalation}$ (assuming 1,25 m^3/hour pulmonary ventilation) and the ILV_{dermal} and the exposure levels per task are presented for methomyl.

Tabel 8 Tentative comparison of the ILV of methomyl to exposure levels

	Actual exposure per task** (mg/day)		ILV* (inhalation or dermal) (mg/day)	Ratio (exposure/ILV)	
	AM	90 %		AM	90 %
Inhalation	0.03	0.07	10	0.003	0.007
Actual dermal exposure:					
Hands (mixing/loading)	26	88	25	1.0	3.5
Hands (application)	4	12	25	0.2	0.5
Rest of the body (ex. hands)	0.6	0.8	25	0.02	0.03
Sum dermal exposure	31	101	25	1.2	4.0

* Indicative limit values are rough estimates only to be used for comparisons

** Task time 15 min for mixing and loading and two hours for application. Worker wearing overall, but no protective gloves.

It may be concluded that the inhalation exposure to methomyl is quite acceptable but the ILV_{dermal} for methomyl is exceeded and there may be an elevated health risk. Reducing the potential exposure levels of the hands during mixing, loading and application by appropiate gloves will probably reduce the actual exposure level to well below the ILV_{dermal}.

In the present applications always a mixture of pesticides is used. According to the information from the survey and the questionnaires some 24 pesticides are used frequently. For 13 pesticides with a liquid formulation tentative ILV's could be roughly estimated from data in the literature. Also for these pesticides a risk assessment can be made both for inhalation and dermal exposure with the likely assumption that inhalation and dermal exposure is independent of the pesticide used, when similar formulation types and application techniques are used (Van Hemmen 1992).

The exposure of the hands during mixing and loading was recalculated using concentrations in the liquid formulation of the pesticide. Concentration of the pesticides in the spray solution were calculated from label prescriptions. The exposure can then be expressed in μl/hour.

Table 9 Indicative risk identification for 14 frequently used pesticides

Pesticide	$ILV^{*}_{inhalation}$ (mg/day)	$Exposure_{inhalation}$ AM	90 %	ILV^{*}_{dermal} (mg/day)	$Exposure_{dermal}$ AM	90 %
abamectin	0.01	0.01**	0.01**	1	5	10
triforin	1	0.03	0.08	10	30	100
chlorothalonil	1	0.16	0.42	5	90	300
tolylfluanide	50	0.13	0.35	150	50	150
mancozeb	5	0.26	0.7	10	105	325
oxamyl	1	0.05	0.14	1	40	135
vinchlozolin	5	0.03	0.07	10	70	235
deltamethrin	1	0.01**	0.01**	5	5	10
permethrin	150	0.01**	0.01	500	35	115
dichlorvos	0.5	0.06	0.15	1	80	275
mevinphos	0.01	0.02	0.06	0.1	25	75
carbofuran	5	0.10	0.28	10	45	140
parathion-methyl	0.5	0.03	0.08	1	40	125

* Data based on JMPR. Indicative limit values are rough estimates only to be used for comparisons. Task time 15 min for mixing and loading and two hours for application. Worker wearing overall, but no protective gloves.
** Rounded to two decimals.

Penetration through the clothing may well depend on the pesticide used, resulting in a different actual exposure with a given potential exposure. The actual exposure for the present analysis is assumed to be 5% of the potential exposure as observed with the monitoring overall. In table 9 ILV's and computed exposure levels are presented, both for the mean value as well as the 90-percentile. It can be concluded that exposure by inhalation generally does not result in a health risk, with the possible exception of mevinphos, but the level of dermal exposure for all but one of the pesticides appears to exceed the ILV.

An alternative method of extrapolating the observed data for methomyl to obtain exposure to other pesticides is using the format µg/kg applied active ingredient rather than exposure in µl/hour. If calculations are repeated using this format the results of exposure levels are roughly the same.

For safe work conditions the dermal exposure has to be reduced below the indicative limit values. Apart from a change to better work methods and application techniques, better dermal protection, mainly of the hands, is a first step in reducing the exposure levels. If impermeable gloves are used during mixing, loading and application and for this scenario it is assumed that if 30% of the potential exposure of the rest of the body penetrates through the work clothing, than the indicative limit values for eight pesticides appears to be exceeded. Further reduction of the actual exposure of the rest of the body may be achieved by using less permeable work clothing. If work clothing, like the cotton overall used in this survey is permeable less than 5% for pesticides the indicative limit values of only three pesticides (chlorothalonil, dichlorvos and mevinphos) appear to be exceeded. When the application is finished the used work clothing is generally not changed or washed. Absorption of pesticides by the clothing may thus continue for some time after the exposure. If protective clothing like rubber gloves, rainsuits, boots or coverall are used, they are seldom cleaned after use, which may lead to enhanced exposure during the next application. A more hygienic work method can be achieved by paying more attention to incidental exposure, by taking more time for careful mixing and loading. During application changing of the flexible hose should be done with care, avoiding contact with the spray liquid. During the actual spraying, contact with already treated crop should be avoided. Walking backwards when spraying is the best method. The used nozzle of the spray pistol and the applied pressure should be chosen carefully, avoiding a too far "reach" of the spray liquid and subsequent contact of the body with the crop.

6 REFERENCES

Bierman, E.P.B., Brouwer, D.H., Hemmen, J.J. van (1992). Quantification of dermal exposure with an image analysis system: instrumental design in Book of abstracts, Workshops. First International Scientific Conference of the International Occupational Hygiene Association, Brussels, Belgium.

Brouwer, R., Brouwer, D.H., Tijssen, S.C.H.A., Hemmen, J.J. van (1991). Pesticides in the cultivation of carnations in glasshouses. Part II Relationship between foliar residue and exposure. Am. Ind. Hyg. Assoc. J. 53:582-587; Brouwer, R., Brouwer, D.H., De Mik, G, Hemmen, J.J. van (1991). Exposure to pesticides. Part I. The cultivation of carnations in greenhouses. S-reeks 131-1, Ministerie van SZW, Den Haag.

Brouwer, D.H., Brouwer, R., Mik, G. de, Maas, C.L., Hemmen, J.J. van (1992a). Pesticides in the culture of carnations in glasshouses. Part I Exposure and concomitant health risk. Am. Ind. Hyg. Assoc. J. 53:575-581.

Brouwer, R., Marquart, J., De Mik, G., Van Hemmen, J.J. (1992b). Dermal exposure to pesticides and related health risk for greenhouse workers after re-entry. Arch. Environ. Contam. Toxicol. 23:273-280; Brouwer, R., Marquart, J., De Mik, G., Van Hemmen, J.J. (1990). Exposure to pesticides. Part II The cultivation of roses in greenhouses. S-reeks 141-2, Ministerie van SZW, Den Haag.

Brouwer, D.H., Ravensberg, J.C., De Kort, W.L.A.M., Van Hemmen, J.J. (1994). A personal sampler for inhalable mixed-phase aerosols; Modification to an existing sampler and validation test with three pesticides. Chemosphere 28:1135-1146; Brouwer, D.H., Ravensberg, J.C., Feron, J.H. (1993). Development and validation tests with pesticides for a personal inspirable aerosol sampler. MBL 1993-20.

Chester, G. (1993). Evaluation of Worker Exposure to, and Absorption of, Pesticides during occupational use and crop re-entry. Ann. Occup. Hyg. 37:509-524.

Davies, J.E. et al. (1982). Reduction of pesticide exposure with protective clothing for applicators and mixers. J. of Occup Med. 24:464-468.

Durham, W.F. and Wolfe, H.T. (1967). Measurement of the Exposure of Workers to Pesticides. Bull. WHO. 26:75-91.

Environmental Protection Agency (1986). Pesticide Assessment Guidelines, Subdivision U, Applicator Exposure Monitoring. US EPA/540/9-87/127 Washington, DC.

Fenske, R.A., Leffingwell, J.T, Spear, R.C. (1985) Evaluation of Fluorescent Tracer Methodology for Dermal Exposure Assessment. In: Dermal Exposure Related to Pesticide Use. (Eds. R.C. Honeycutt, G. Zweig en N.N. Ragsdale). ACS Symposium Series 273:377-393.

Fenske, R.A. (1990). Non-uniform Dermal Deposition Patterns During Occupational Exposure to Pesticides. Arch. Environ. Contam. Toxicol. 19:332-337.

Fenske, R.A. (1993). Dermal exposure assessment techniques. Ann. Occup. Hyg. 37:687-706.

Hemmen, J.J. van (1992). Agricultural Pesticide Exposure Data Bases for Risk Assessment. Rev. Environ. Contam. Toxicol. 126:1-85; Hemmen, J.J. van (1992). Assessment of Occupational Exposure to Pesticides in Agriculture. Part I General Aspects. Part II Mixing and loading. Part III Application. S 143 1-3, SZW, Den Haag.

Hemmen, J.J. van, Brouwer, D.H. (1989). Meetstrategieën voor huidexpositie onder arbeidsomstandigheden in Huidtoxicologie in het beroep (P.A. Lavrijsen e.a. ed.) Boerhaave commissie voor Postacademisch onderwijs in de Geneeskunde, Leiden, p. 37-55.

JMPR. (1986,1989). Report of the Joint Meeting of the FAO Panel of experts on Pesticide Residues in Food and the Environment and the WHO Expert Group on Pesticide Residues. Evaluations-Part II, Toxicology. FAO plant production and protection papers 78/2 and 100/2.

LNV (1990). Rapportage Werkgroep Bloemisterij. Achtergronddocument Meerjarenplan Gewasbescherming. Ministerie van Landbouw, Natuurbeheer en Visserij, Den Haag.

Wolfe, H.R., Durham, W.F., Armstrong, J.F. (1967). Exposure of workers to pesticides. Arch. Environ. Hlth. 14:622-633.

Wolfe, H.R., Armstrong, J.F., Durham, W.F. (1972). Exposure of Spraymen to Pesticides. Arch. Environ. Hlth. 25:29-31.

World Health Organisation (1982). Field Surveys of Exposure to Pesticides. Standard Protocol. VBC/82.1. WHO, Geneva, Switzerland.

ANNEX 1 Analytical methods and quality control

Chemical analysis

Clothing samples were collected in 1 and 5 litre polypropene containers and after transport stored at -5 °C. Methomyl was extracted from the samples with water and analysed using HPLC-UV detection. Each sample was given an unique code.

During each application field blancs and field spikes were taken to establish contamination and loss of sample under influence of light, temperature and moisture. Samples of the spray solution were taken and analysed.

Respiratory samples were stored at -20 °C and extracted within 24 hours with ethanol, separating front and back section of the XAD-cartridge. Analysis of the extract was also done with HPLC-UV detection.

The lower limit of detection for parts of the overall was 10 µg/sample. For the underclothing the limit of detection after pre-concentration was 1 µg/sample.

HPLC data:

Column	Spherisorb-ODS 2 (10 cm; ID 4.6 mm; df 3 µm)
Mobile phase	Methanol/water (30:70 v/v + 5 g/l ammonium acetate)
Pump	Waters M-45
Pressure	8 atm
Flow	0.8 ml/min
Detector	Perkin-Elmer LC-95 UV-VIS spectrophotometer
Wavelength	238 nm
Injection volume	20 µl

The matrices used were validated for background signal, stability and recovery. The coefficient for variation for analysis and sampling was ca. 4%.

ANNEX 1 Analytical methods and quality control

Quality control

In the survey, control samples were taken (field samples and field spikes) to assess possible contamination and stability of the samples under influence of light, relative humidity, temperature and storage.

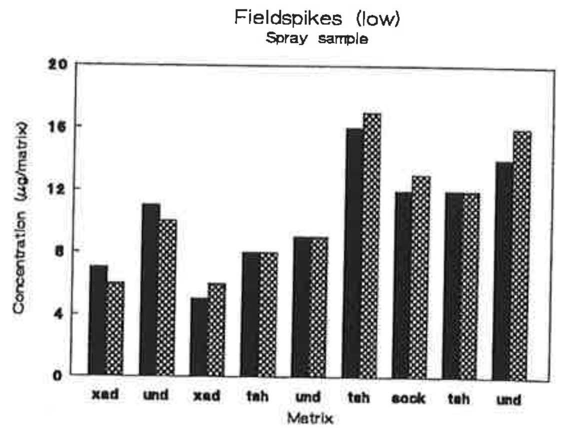
Samples were spiked in the same concentration range as the field samples. With every application a sample of the spray solution was taken and analysed.

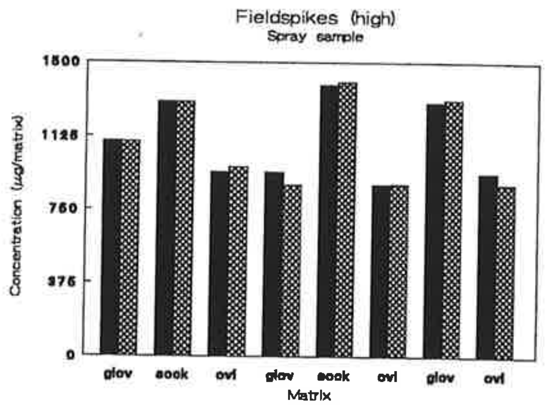
Contamination of the samples was determined by exposing a blank the same way as a field sample with the difference that there was no direct contact with the active ingredient. For instance, to assess inhalation exposure blanks ambient air was sampled on a XAD-cartridge for the same period of time as the personal XAD air sampling. Both of the samples were transported, stored and analysed in the same way.

Stability during transport and storage was assessed by spiking one of the matrices with a known amount of the spray solution and storing this matrix right away. Stability under field conditions was assessed by spiking one of the matrices and expose it to the same conditions of light, relative humidity and temperature as the field samples.

Results None of the field blancs exceeded the limit of detection, so no contamination of the samples took place. The recovery of the field spikes was on average more than 90%: see figures on the next page.

ANNEX 1 Analytical methods and quality control





The black bars represent the spiked amount on the samples; the striped bars the recovered amount. Undergarment (und), T-shirt (tsh) and XAD were spiked with low concentrations, gloves (glov), socks (sock) and overall (ovl) with high concentrations.

Average recovery low concentrations: AM = 92.1% (STD = 7.2)

Average recovery high concentrations: AM = 97.7% (STD = 2.6).

ANNEX 2 Toxicological data of methomyl

Methomyl [S-methyl N-(methylcarbamoyloxy)thioacetimidate] is a carbamate used as insecticide and acaracide. It is a systemic working agent based on cholinesterase inhibition. In chrysanthemum culture it is used from April to October against Lepidoptera, Thysanoptera and Aphidoidea. It is available as wettable powder (25%), soluble concentrate (200 g/l) and water soluble powder. Label instruction: soluble concentrate: 100-150 ml/ 100 l water, wettable powder: 80-120 g/ 100 l water.

Toxic properties (JMPR 1986, 1989).
LD_{50} (acute oral) rat (male) 17 mg/kg, (female) 24 mg/kg
LD_{50} (acute dermal) rabbit 5000 mg/kg
LC_{50} (acute inhalation, 4 hours) rat 0.3 mg/l
Irritation to eye (rabbit) and irritation to skin (hamster)
NOEL chronic oral toxicity: mouse 8.7; rat 2.5; dog 3.1 mg/kg b.w./day
Methomyl is absorbed from the gastro-intestinal tract rapidly and penetrates through the skin. No evidence for oncogenicity or teratogenicity is available, and only slight effects on reproduction were observed.

Physical properties
Molecular weight 162.2
Vapour pressure: 6.65 mPa at 25 °C
Solubility: water 58 g/l; methanol 1000 g/l; acetone 730 g/l; moderately soluble in hydrocarbons

ANNEX 3 Protective equipment

Farm number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Mask and filter	x	x		x	x	x	x			x						x				x
Mask and fresh air			x						x		x		x	x			x	x	x	
Rubber gloves	x		x			x			x		x		x	x			x			x
Coverall									x				x	x						x
Rainsuit (trousers)				x							x		x							
Rubber boots											x		x	x					x	x
Work clothing	x	x	x		x	x	x	x		x		x			x	x		x	x	

During mixing and loading in general no protective clothing nor inhalation protection is used; above-mentioned protective equipment is only used during application. Work clothing is usually a long legged cotton pair of trousers (type blue jeans) in combination with a long sleeved cotton shirt.

ANNEX 4 Data of the applications

No	Area (m²)	Litres appl. (l)	Time appl. (min)	Conc. theor. (mg/l)	Conc. anal. (mg/l)	Gram a.i. (g)	T °C	RH %
1	13500	1150	135	200	228	262	19.0	80
2	6500	600	78	200	184	110	n.a.	n.a.
3	5500	600	45	250	217	130	19.4	76
4	4000	400	41	200	260	104	17.2	75
5	5000	500	50	200	212	106	n.a.	n.a.
6	10000	800	105	250	230	184	n.a.	n.a.
7	5000	350	66	200	209	73	20.0	84
8	7000	700	86	200	232	162	23.9	72
9	11500	730	115	200	167	122	31.8	51
10	8500	680	115	200	187	127	23.7	75
11	8500	850	64	200	188	160	19.0	93
12	7200	750	64	200	171	128	30.6	57
13	8000	500	56	313	277	139	27.2	57
14	3000	300	56	200	176	53	19.3	77
15	5500	600	68	300	324	194	22.8	65
16	6000	250	69	240	241	60	24.3	60
17	8000	525	79	258	242	127	n.a.	n.a.
18	10500	1900	164	250	276	524	23.6	82
19	7200	700	116	200	259	181	22.8	75
20	5200	500	51	200	187	94	19.5	88

n.a. = not available

In the colums from left to right are: the number of the farm, the area of application, litres spray liquid used, time of application, the concentration the worker planned to make, the actual concentration in the spray liquid, the amount of active ingredient in the spray solution, temperature and relative humidity in the glasshouse during application.

	Farm	1	2	3	4	5	6	7
	Exposure (μg/sample)							
Inhalation	XAD*	4.64	8.11	0.43	17.43	10.26	5.93	0.36
Gloves	Mixing and loading	80040	147	174500	4875	967	148	698
	Application	6710	6235	714	15155	272	3002	2656
Overall	Left lower leg	544	1005	363	17800	1261	292	343
	Right lower leg	620	915	306	11700	1408	629	131
	Left upper leg	263	521	782	16100	311	171	173
	Right upper leg	334	460	908	16700	330	277	73
	Left lower arm	278	565	36	965	137	57	115
	Right lower arm	203	931	45	809	101	179	23
	Left upper arm	13	19	27	151	31	16	24
	Right upper arm	19	19	27	361	41	30	26
	Torso front	3104	508	432	19600	268	1046	34
	Torso left	1250	200	466	6936	170	154	34
T-shirt	Left lower arm	12.0	0.5	3.0	503.0	9.0	1.0	2.0
	Right lower arm	8.0	0.5	3.0	31.0	3.0	2.0	3.0
	Left upper arm	0.5	0.5	0.5	21.0	0.5	0.5	0.5
	Right upper arm	0.5	0.5	2.0	50.0	2.0	1.0	0.5
	Torso front	0.5	0.5	14.0	682.0	5.0	8.0	14.0
	Torso left	0.5	0.5	6.0	66.0	5.0	0.5	8.0
Underpant	Left lower leg	0.5	5.0	5.0	13700.0	1.0	0.5	0.5
	Right lower leg	2.0	8.0	10.0	10900.0	0.5	0.5	0.5
	Left upper leg	2.0	2.0	11.0	10900.0	0.5	0.5	4.0
	Right upper leg	6.0	2.0	8.0	11500.0	0.5	0.5	0.5
Socks		6.0	54.0	11.0	40000.0	2.5	7.0	2.5

* μg/m3

N.a. = not available. Non detectables are denotated as half of the limit of detection, which for XAD equals 0.2 μg for T-shirt, underpants and socks 0.5 μg and for gloves and overall 3 μg.
Farmer 4 is excluded from calculations because of soaking of the clothing.
Farmer 7 used a spray wand and is also excluded fot calculations.

	Farm	8	9	10	11	12	13	14
	Exposure (µg/sample)							
Inhalation	XAD*	0.26	0.20	4.47	34.40	6.00	33.57	0.36
Gloves	Mixing and loading	1743	n.a.	2005	396	2590	20628	2882
	Application	6480	4562	805	7328	3924	2409	30
Overall	Left lower leg	313	275	488	813	124	33	17
	Right lower leg	334	132	365	2636	106	123	10
	Left upper leg	176	115	361	5942	254	18	11
	Right upper leg	177	64	232	6696	644	16	14
	Left lower arm	15	28	77	146	116	1285	8
	Right lower arm	29	26	43	200	83	823	8
	Left upper arm	20	16	31	84	9	306	3
	Right upper arm	38	16	49	121	10	184	3
	Torso front	5296	105	202	3096	2216	364	10
	Torso left	34	86	66	1128	80	408	76
T-shirt	Left lower arm	1.0	0.5	9.0	2.0	0.5	16.0	2.0
	Right lower arm	3.0	0.5	4.0	3.0	0.5	74.0	0.5
	Left upper arm	1.0	0.5	0.5	1.0	3.0	0.5	0.5
	Right upper arm	0.5	1.0	0.5	1.0	0.5	0.5	0.5
	Torso front	14.0	3.0	10.0	0.5	24.0	0.5	0.5
	Torso left	3.0	3.0	1.0	0.5	5.0	5.0	0.5
Underpant	Left lower leg	93.0	21.0	0.5	127.0	0.5	0.5	0.5
	Right lower leg	61.0	21.0	0.5	246.0	0.5	2.0	0.5
	Left upper leg	18.0	0.5	0.5	2340.0	0.5	0.5	0.5
	Right upper leg	17.0	0.5	1.0	2971.0	27.0	0.5	0.5
Socks		108.0	15.0	2.5	13.0	9.0	35.0	2.5

* µg/m3

N.a. = not available. Non detectables are denotated as half of the limit of detection, which for XAD equals 0.2 µg for T-shirt, underpants and socks 0.5 µg and for gloves and overall 3 µg.
Farmer 4 is excluded from calculations because of soaking of the clothing.
Farmer 7 used a spray wand and is also excluded fot calculations.

	Farm	15	16	17	18	19	20
	Exposure (µg/sample)						
Inhalation	XAD*	6.47	5.63	7.73	6.57	14.33	19.17
Gloves	Mixing and loading	780	110	293	1074	2349	5891
	Application	315	157	70	311	2327	336
Overall	Left lower leg	174	43	34	467	135	47
	Right lower leg	857	67	36	537	118	18
	Left upper leg	292	49	43	664	713	85
	Right upper leg	155	58	57	573	652	47
	Left lower arm	21	114	56	70	288	25
	Right lower arm	145	159	22	37	276	44
	Left upper arm	101	10	12	16	301	19
	Right upper arm	21	11	19	25	89	22
	Torso front	222	114	64	240	450	192
	Torso left	88	74	50	332	512	74
T-shirt	Left lower arm	10.0	3.0	3.0	4.0	17.0	0.5
	Right lower arm	1.0	7.0	0.5	4.0	14.0	0.5
	Left upper arm	0.5	0.5	2.0	0.5	2.0	0.5
	Right upper arm	0.5	0.5	0.5	0.5	0.5	0.5
	Torso front	13.0	29.0	10.0	6.0	14.0	5.0
	Torso left	0.5	0.5	4.0	3.0	7.0	0.5
Underpant	Left lower leg	2.0	4.0	0.5	5.0	4.0	0.5
	Right lower leg	3.0	1.0	1.0	4.0	0.5	0.5
	Left upper leg	2.0	1.0	2.0	4.0	7.0	2.0
	Right upper leg	2.0	4.0	0.5	3.0	4.0	1.0
Socks		48.0	3.0	3.0	6.0	33.0	3.0

* µg/m3

N.a. = not available. Non detectables are denotated as half of the limit of detection, which for XAD equals 0.2 µg for T-shirt, underpants and socks 0.5 µg and for gloves and overall 3 µg.
Farmer 4 is excluded from calculations because of soaking of the clothing.
Farmer 7 used a spray wand and is also excluded fot calculations.

ANNEX 6 **Amounts in μg active ingredient/hour, μl spray liquid/hour and μg/g applied active ingredient**

Summary

	μg/hour GM (GSD)	μl/hour GM (GSD)	μg/kg applied a.i. GM (GSD)
Inhalation	5.1 (5.0)	25 (4.7)	60(5.1)
loves (mixing/loading)	13110 (7.1)	65 (7.1)*	13610 (6.9)
Gloves (application)	760 (4.9)	3500 (5.2)	7210 (4.7)
Overall	1710 (3.1)	7850 (3.1)	16170 (2.6)
Underwear	40 (4.4)	165 (4.4)	340 (3.9)
Socks	7.5 (3.3)	35 (3.4)	70 (3.1)

* Expressed as μl liquid formulation

ANNEX 7 Penetration through the overall

Summary

Percentage Penetration (Cumulative)	No samples	Cumulative (percentage)
1	60	33.3
2	94	52.2
5	141	78.3
10	165	91.7
20	174	96.7
30	178	98.9
40	180	100.0

Of 180 matching samples of overall and underwear the penetration was calculated by:
Penetration (%) = (exposure underwear) * 100/(exposure overall + underwear)

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