SVERIGES
LANTBRUKSUNIVERSITET

Chemical Health Risks after Pesticide Spraying in Greenhouses

Ulla Nilsson

Institutionen för lantbruksteknik
Avd för park- och trädgårdsteknik

Rapport 199
Report

Swedish University of Agricultural Sciences
Department of Agricultural Engineering

Alnarp 1995

ISSN 00283-0086
ISRN SLU-LT-R-199-SE

Printed at Repro, Alnarp 1995

ABSTRACT

There are no re-entry regulations for workers performing different tasks soon after pesticide applications in Sweden. In practice, work is not performed the same day as spraying because of the inhalation risk for air concentration of the pesticide, the risk for dermal exposure is not considered. The more widespread use of pesticides in greenhouses and more frequently harvested crops made a study on working environment after application of fungicides in such a cultivation particularly motivated.

The objectives were to investigate the concentrations and declination rates of fungicides in greenhouse conditions and to examine the relationship between concentrations on the crop and the exposure on worker´s clothes to be able to estimate the health risks when working in a greenhouse after application.

The fungicides used in the study were vinclozolin, active ingredient (500 g/L) in the formulation Ronilan FL and triadimefon, active ingredient (50 g/kg) in Bayleton Special. To sample the concentrations of these fungicides new methods for sampling and analyszng were developed.

The results showed that the applied dose of triadimefon gave low concentrations both in air and on surfaces in the greenhouse both with the low volume and the high volume sprayers.

Vinclozolin sprayed gave considerably higher concentrations and declined slowly; on day one after application the concentration on leaves was in average 0.74 $\mu g/cm^2$, on day four about 80% of that remained and after one week about 50% remained. The declination after low volume spraying seem to go faster than after high volume spraying.

In the exposure studies the estimation made was that if workers do not protect themselves during the first harvest day with gloves and long sleeved shirts or other protective garments covering these parts of the body, they risk exposure for amounts close to the acceptable daily intake (ADI) setup for foodstuffs by the World Health Organization (WHO).

LIST OF INCLUDED PAPERS

This thesis for the degree of *Agronomie Licentiat* consists of a summary and of the three papers listed below. In the text, these papers are referred to by their Roman numerals.

I. Papantoni, M.; Mathiasson, L.; Nilsson, U. Long-Term Studies of Fungicide Concentrations in Greenhouses. 1. Technique for Determining Surficial Foliar Residues of Fungicides with Vinclozolin and Triadimefon as Model Compounds. J. Agric. Food Chem. 1995, 43, 157-164

II. Nilsson, U.; Nybrant, T.; Papantoni, M.; Mathiasson, L. Long-term studies of fungicide concentrations in greenhouses. 2. Fungicide concentrations in air and on leaves after different exposure times and in different climate conditions. Manuscript submitted to Journal of Agricultural Food and Chemistry

III. Nilsson, U.; Papantoni, M. Long-term Studies of Fungicide Concentrations in Greenhouses. 3. Exposure Risks after Spraying in Greenhouses. Manuscript submitted to Journal of Agricultural Food and Chemistry

Reprint from Paper I is published with permission of The Journal of Agricultural Food and Chemistry. Paper II and Paper III might be subjected to changes to fulfill the requirements of the journals in which they will be published.

INTRODUCTION

Chemical application is frequently used in greenhouse cultivation. Due to the warm and humid climate pests are more frequent than in field cultivation. In vegetable cultivation where the workers have to harvest soon after the application has been made, the most common type of pesticides used are fungicides. Chemical application in other cultivation types is also frequent but in, for example, ornamental production, personnel are not forced by harvesting to go inside treated houses soon after application, with the exception of roses and other cut flowers that have to be harvested every day.

Exposure risks after insecticide application have been studied in many investigations, organophosphorous compounds especially. On fungicide exposure Liesivuori et al. (1988) have performed one study of benomyl concentrations in rose cultivations in greenhouses. In field crop production studies of exposure to fungicides have been performed; for example, residues of and exposure to carbaryl (Zweig et al, 1984), captan and benomyl (Zweig et al, 1983) and captan (Winterlin et al., 1984). In the preliminary report of a study made in Sweden (Kolmodin-Hedman et al., 1992) exposure to propikonazol in grain was studied. Liesivuori et al. (1988) studied the dissipation of dimethoate and benomyl in rose greenhouses. In a closed room, such as a greenhouse, the air concentrations are of greater interest than in an outdoor environment. Air concentrations of for example thiophanate-methyl have been studied by Brouwer et al. (1992). In Sweden the Labor Inspection in Härnösand has made an exposure study on work in forestry nurseries and plantations (Persson & Palmqvist, 1992). No exposure study until now has been performed on residues of vinclozolin and triadimefon sprayed in greenhouse cultivations.

BACKGROUND

There are several health risks in agriculture and horticulture. Among them are near-accidents like falls, ergonomic, physical and chemical health risks and also psychosocial health risks.

In greenhouse work the most frequent injuries are to back, neck and fingers. Psychological stress such as time pressure with deliveries, bad relations with works managers, worries about losing jobs and financial problems were common among greenhouse workers and owners. In a Swedish investigation more than 50% mentioned stresses such as these (Lundqvist, 1985, Lundqvist, 1982a). Climate stress from working in a warm and humid environment (16-40°C and relative humidity 50-99%) is common. Noise from sprayers and rotary cultivators is also a common inconvenience (Lundqvist, 1982a).

According to Lundqvist (1985) who had interviewed a number of safety representatives problems with the back (91%), skin eczema (68%) and allergies (60%) were the most common inconvenient complaint that workers in greenhouses suffer from. Contact with chemical substances was mentioned by both safety representatives and the owner of a business as the most common factor for the occurrence of accidents and near-accidents at the workplace (Lundqvist, 1985). In an inquiry performed in connection with this study, the workers mentioned irritating complaints and general complaints such as headaches, weariness, smarting pain in the face and trouble with hands and arms. The symptoms might be explained by the lack of caution in the handling of chemicals and the long working week for many of the workers in the investigation; some workers had to put in 70 hours a week.

In a cohort study Littorin found that horticulturists were in general healthier than the rest of the population but for tumor illness in the brain, gliom and meningiom the frequency was higher than for the rest of the population. There is, however, a correlation between pesticide occurrence, especially fungicides, and long-term effects. (Littorin, pers. mess.)

Workers think that safety devices such as protective gloves, respiratory masks and eye-shields should be used to protect them from chemicals (Lundqvist, 1982a). The respiratory masks were experienced as troublesome to use. Protective gloves are the most common safety device in Swedish greenhouse cultivations and are used in many different working situations (Lundqvist, 1982b).

To decrease the health risks and worries among workers it is necessary to study the relationship between the concentrations occurring in the environment and the exposure on humans. In this way the health risk can be estimated and adequate safety measures can be established. At the present there are no concentration limits, hygienic values, for chemical substances applied in cultivations in Sweden.

OBJECTIVES OF THE STUDY

The objectives were to study the working environment after chemical application in greenhouses, and to investigate the declination rate of model fungicides under different climatic conditions. With a better knowledge about these matters it should be possible to improve the situation for workers in treated greenhouses.

Work in the house, especially in vegetable cultivations, is often done shortly after the chemical application. The frequently used fungicides vinclozolin and triadimefon have been used in this study as model substances. Vinclozolin is used as the active ingredient (a.i.) in Ronilan FL mainly against *Botrytis cinerea* and triadimefon is the active ingredient in Bayleton Special used against different fungal infections affecting horticultural and agricultural crops. One important reason for the choice of these two fungicides was that no study of these compounds had previously been performed in greenhouses.

Studies of the declination of the substance concentration after spraying in the greenhouse enable us to assess health hazards. By examining the relationship between residues on plants and clothes it should be possible to estimate the exposure on clothes by knowing the concentration on the leaves. From the uptake on the clothes it should be possible to estimate the dermal exposure and from that the health risks related to working in fungicide treated greenhouses.

Air concentrations after spraying were studied to estimate health risks through breathing contaminated air. The concentrations in air were suspected to vary between the two spraying techniques. For example, smaller droplets could be expected to give a higher air concentration than droplets of a larger diameter because they are suspended longer in the air.

The efficiency of the sprayers in general influence the dosage/m^2 of the pesticide. This means that knowledge of the efficiency of different spraying techniques provides a basis for improving the working environment.

LITERATURE STUDY

SURFACE SAMPLING

Several sampling techniques have been proposed in the literature for sampling pesticide concentrations from leaf areas.

The most commonly used technique is the dislodgable foliar residues (DFR) technique in which leaves are punched and then washed, using water with or without surfactant as extraction liquid (Gunther et al., 1971, Iwata et al., 1977). The assumption is that workers only come into contact with the substance bound to the dust. This method has also been used by for example Liesivuori (1988) when investigating benomyl concentrations on leaves and by Zweig et al. (1985), when collecting DFR of vinclozolin on strawberry leaves in field production.

Other methods used are mechanical brushing (Giles, 1992) and vacuuming of leaves (Popendorf, 1975). The idea behind the brushing techniques is that the brushing should imitate the workers contact with the treated foliage so that the same amount that reaches the workers´ skin gets brushed up. In the vacuuming procedure whole leaves are collected and sampled and vacuumed on both sides with a specially designed vacuum assembly.

Giles compares the water washing method (Gunther et al., 1971, Iwata et al., 1977) with mechanical brushing after application of permethrin (dosage 1.15 kg a.i./ha) in *Chrysanthemum*. The ratio between the two techniques depends on the application technique. For air-assisted electrostatic reduced-volume spraying (46 L/ha) the ratio brushing/washing was 0.135, and for conventional high volume application (2300 L/ha) it was 0.303. In a later experiment the ratio was 0.126 and 0.148. The difference was smaller in these later experiments, but the low-volume sprayer gave a smaller ratio brushing/washing in these experiments, too. (Giles, 1993).

Popendorf et al. (1975) found that the vacuuming procedure correlated better to the levels of airborne residues detected compared to the washing DFR-technique in his experiments, 0.985 versus 0.687 in correlation coefficient .

For all the methods described it is not possible to obtain information about the recovery of the applied substance. This important problem has not been addressed in any of the methodologies presented above.

AIR SAMPLING METHODS

Air sampling of pesticides, including triadimefon glassfibre filter or impinger technique with N,N- dimethyl as sorption liquids, have been studied by Garå (1984). He found that the glassfibre filter was most efficient when sampling the dust particles in the air dust particles from the filling of the sprayer. Garå (1984) suggests a glassfibre filter in series with another adsorbent or impinger to increase the efficiency of the air sampling during spraying procedures, to catch both the particles and the gaseous substances. Impinger technique is efficient when sampling gaseous substances, more efficient than chemosorption through solid adsorbents or adsorption tubes with reagents in an absorption solution (Andersson et al. 1983). The combination of filter and impinger seems to offer the most efficient air sampling.

ANALYSIS METHODS

In the literature no methods for determining concentrations of triadimefon, triadimenol and para-chlorphenol at the same time have been recognized. Triadimefon and both the diasteromeres of triadimenol were detected through gas chromatography by Garcia (1991) on packed column and by Nickless et al. (1991) on capillary column. The selectivity of the system was amplified by a selective detector, for example an electron capture detector (Newsome & Collins, 1989), using a nitrogen sensitive detector in the workup (Garcia, 1991). A silica-based normal phase system (10 µm, 25 cm x 4.6 mm in diameter) was used by Slahck (1985) for the analyze of triadimefon and parachlorphenol, with 1-chlorbutane as mobile phase.

Several multiresidue methods have been used for determination of the fungicides vinclozolin and triadimefon, e.g. Nickless et al. (1981). High performance liquid chromatography (HPLC) is suitable for investigations when only a few components are to be determined and have the advantage of simpler preparation compared to the gas chromatographic (GC) methods, which demand several work-up steps to make the sample suitable for injection (Garcia, 1991).

RESIDUE AND EXPOSURE STUDIES

Methods for Exposure Studies

In WHO:s standard protocol (1982) on "Field surveys of exposure to pesticides" two methods for assessing dermal exposure are presented. One method is the use of overalls and gauntlets and the other method is use of exposure pads. Using the pad method the pad area has to be translated to whole body exposure and this is achieved by using a standard body area for the different body parts. Exposure is expressed as mg/cm^2 body area and then related to time in mg/hour. Respiratory exposure (expressed as mg/day or mg/hour) does not usually exceed 1% of the dermal exposure (WHO, 1982).

Hand dipping in solution, e. g. in ethanol, is another method used to evaluate pesticide exposure on the skin. Another method is rubbing the skin with cotton wool moistened with ethanol (Kolmodin et al., 1991).

Correlation Studies between Residue and Exposure

The DFR varies between days after application and between substances (Zweig et al., 1985). Zweig et al. (1985) studied the correlation between dermal exposure and DFR of captan in field-grown strawberry cultivations. Dermal exposure (mg/hour) was estimated by determining the amount of captan on pads placed on the workers body (head, chest, back, upper arms, lower arms and lower legs) and on gloves. The DFR amounts of captan/hour (mg/hour) were 16.37 day 3, 6.50 day 13 and 5.88 day 48. The ratio DFR/dermal exposure was 5.97, 2.75 and 3.42 respectively. Compared to the ratios for vinclozolin (Zweig et al., 1985) the ratios for captan were smaller than for vinclozolin, Table 1.

Table 1.

Correlation between DFR and dermal rate for vinclozolin in the experiments of Zweig et al. (1985)

Day after application	*DFR ($\mu g/cm^2$)*	*Dermal dose rate (mg/hour)*	*Ratio DFR/dermal Rate 10^{-3} ($hour/cm^2$)*
31	0.09	0.27	30.6
32	0.01	0.33	61.27
33	0.01	0.23	44.27

Zweig et al., (1984) found that the declination rate of carbaryl is fast; from a DFR of 8.08 $\mu g/cm^2$ carbaryl on day one the DFR was 1.32 $\mu g/cm^2$ on day 7. After 14 days only 0.54 $\mu g/cm^2$ was left.

Pesticide Absorption through Human Skin

The degree of absorption through human skin varies over the body (Maibach et al., 1971). Ratios for uptake of the fungicide captan through human skin are presented in Table 2.

Table 2.

Uptake ratio for captan on different parts of the body from Maibach et al. (1971). Forearm is used as reference for the ratio. Urinary ^{14}C excretion of parathion expressed as % of applied dose is used as measurement of absorption.

Part of body	*Ratio*
Forearm	1
Palm	1.3
Foot, ball	1.6
Abdomen	2.1
Hand dorsum	2.4
Fossa cubitalis	3.3
Scalp	3.7
Jaw angle	3.9
Postauricular	3.9
Forehead	4.2
Ear canal	5.4
Axilla	7.4
Scrotum	11.8

The absorption on the forearm, that is used as ratio 1, was 8.6% of the dose applied. The dose applied was 4 $\mu g/cm^2$ and there were six subjects (persons) in each experiment.

TOXICITY

The degree of toxicity of a substance depends on its ability to disturb functions in the body. The harm caused by the substance is affected for example by its volatility, solubility and ability to penetrate the surface of skin.

Triadimefon, the active ingredient in the formulation Bayleton Special (CAS number 43121-43-3) has the chemical name 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-buthane-2-one. The Food and Agriculture Organization´s (FAO) limit for acceptable daily intake (ADI) is for triadimefon is 0.01 mg//kg body weight (FAO, 1983). LD_{50}-value (oral) for triadimefon 0.7-1.2 g/kg body weight and dermal 5.0 g/kg body weight (Pesticides, 1983).

The metabolite triadimenol, formed by hydrolysis, is very persistent in the environment and disturbance in reproduction in birds and fish have been reported (Autio, 1991). Further hydrolysis gives para-chlorphenol.

The chemical name of vinclozolin, active ingredient in Ronilan FL, is 3-(3,5-dichlorfenyl)- 5-methyle-5-vinyloxazolodine-2,4-dion. ADI-value for vinclozolin is 0.07 mg/kg body weight (WHO, 1991).

Vinclozolin uptake in stomach and intestine is secreted relatively fast. The metabolite is N-(3,5-dichlorfenyl)-methyl-2,3,4-trihydrozybutyramide which is secreted through urine and gall as glucoronid conjugat. In the intestine a deconjugation is made. Acute toxicity is low, LD_{50}-value (oral) for vinclozolin is 10 g/kg body weight for rat. Symptoms of poisoning are shivering, apathy and respiratory problems. The toxicity of Ronilan FL, a formulation that contains 500 g vinclozolin/L, is for oral or dermal uptake 4 g/kg body weight and for inhalation LC_{50} = 3 mg/L air on 7 hour exposure (Fransson, 1990). Vinclozolin gives sensitivity and is mildly irritating to the skin (Bergkvist et al., 1991). High doses (50 mg/kg body and day) given to rats caused feminisation of male foetus and even higher doses (200 mg/kg body weight and day) delayed ossifiation of the thoratic vertebrae and gave weak kidney function. No study on humans has been performed (Fransson, 1990).

Long-term effects of vinclozolin are not known today. Allergic problems are connected both with the overall environment situation and the working environment. To keep down the number of persons who suffers from allergic problems it is important to improve the working environment.

APPLICATION TECHNIQUES

Air concentrations of the sprayed pesticide depend on the spraying technique and air movements in the house. For sprayers, which give small droplets, sufficient air movements are necessary to obtain even distribution of the pesticide spray over the house. The combination of small droplets and air movements cause the droplets to stay longer in the greenhouse air, increasing the health risks related to inhalation.

Pesticide sprayers have poor efficiency, only 5-20% reaches the target. Greenhouses are not very air-tight with a relatively high rate of change of air. Between 25-50 % of the pesticide is ventilated out of the greenhouse after low-volume spraying (van Os, 1993). The percentage ventilated depending on the volatility of the substance.

The application technique used has a great influence on the placement of the deposit and the penetration of the spraying liquid. The distribution of the spray liquid is often uneven, for example only a small portion reaches the underside of the leaves and penetration into the plant canopy is poor. Many pests live on the underside of the leaves or in the plant canopy, so a great part of the sprayed pesticide does not reach the target. As a consequence larger amounts of pesticide have to be used with unnecessary environment pollution and a higher exposure to pesticide for the workers as a result.

In a study performed by Jarrett & Burges (1979) more than 99% of the pesticide distributed from a thermal fogger reached the upperside of the leaves. When Nielsen & Kirknel (1990) sprayed in pot plants with a low pressure sprayer (nozzle diameter 0.8 mm) the distribution between under- and upperside of leaves showed that 5 % was distributed on the underside and 95 % on the upperside in the top of the plants (*Chrysanthemum*). The distribution on vertical and horizontal surfaces was 57% and 43% respectively.

Electrostatic charging of droplets gave a more even distribution between upper and underside of the leaves in a study presented by Adams & Palmer (1986). Especially even was the result with an air-assisted fan that increase the penetration of the plant canopy (Adams & Palmer, 1986, Adams et al., 1986). Adams & Lindquist (1991) found that charged spray controlled glasshouse whitefly nymphs more effectively than uncharged or hydraulic sprays. In Sweden spraying with electrostatic sprayers are not used in plant protection but in USA and developing countries, for example, these types of sprayers are used.

SAFETY MEASURES

Working Methods

Using a period between the application and the earliest time it is possible to work in the house, a re-entry period, is a common way to avoid exposure. Such precautions are generally used after spraying with organophosphorous compounds to await the disappearance of the pesticide to a nontoxic level, before working in the cultivation. It is then possible to work with sprayed plants without risking the health without any special safety equipment. The length of the re-entry period is based on studies of declination.

Protective Garments

Exposure depends on dosage, concentration in the environment, the time period during which the person is exposed and personal protective equipment.

By wearing protective gloves a considerable proportion of the exposure can be avoided. Workers used to spray pesticides are more aware of the health risks, than those working afterwards with the crop, and almost always wear protective garments when spraying. The workers who feel illness or some kind of discomfort due to exposure are more willing to use protective garments (Ramaswamy & Boyd, 1991). Information is one important way of decreasing exposure. Another way is to find comfortable and less expensive protective garments. In a study presented by Waldron (1985) harvesters, although knowing about the risks, preferred to work with jeans and chambray shirts instead of protective garments such as Tyvek, Neoprene and Gore-Tex even though they knew they chose comfort and price before safety. The same attitude has been experienced by others (Chester et al., 1990, Ramaswamy & Boyd, 1991). In greenhouses special consideration must be paid to thermal comfort (Waldron, 1985).

The workers attitude to protective measures have the greatest effect on the extension of the exposure that reach their body (Waldron, 1985). Field studies in tropical climates (Chester et al., 1990) showed that cotton garments were comfortable and that they did not become more impaired than the Kleenguard garments tested in the same study. Kleenguards´ comfort was preferred to the Tyvek overall. Cotton garments are cheaper which is also a reason for their popularity. In a study by Branson & Sweeney (1991) Gore-Tex demonstrated the same thermal comfort as cotton, but at a much higher price. The authors do not think the thin cotton garment used in their study is sufficient for applicators to use as protective garment. Denim and twill fabrics give better protection.

Often the safety of a protective garment is canceled out by the comfort and the price for it. If they are uncomfortable and/or expensive people may not use them at all.

Hygiene

An important safety measure is a good personal hygiene. The exposure time can be decreased by washing off the substance that lies on the skin after working with treated plants and other material. Washing of hands after contact with treated material is an important measure to avoid uptake of substances on the skin (Eriksson et al., 1988).

MATERIAL AND METHODS

The concentration and declination of the two model substances, the fungicides vinclozolin and triadimefon, was studied in greenhouses after spraying, and the influence of important climate factors was separately studied in climate chambers. Exposure studies on greenhouse workers were performed in connection with the residue studies in greenhouses.

EXPERIMENTS

The following experiments have been performed:

A: Experiments made in 1991: spraying of Ronilan FL (500 g vinclozolin/L) and Bayleton Special (50 g triadimefon/kg) was performed with high and low volume sprayer in both tomato and cucumber cultivation with sampling made during the first week after application

B: Experiments made in 1992: spraying of Ronilan FL with high and low volume sprayer in cucumber cultivation with sampling during the first four weeks after application

C: Experiments made in 1993: spraying of Ronilan FL with high and low volume sprayer in cucumber cultivation with sampling during the first four weeks after application

D. Experiment made in 1994: spraying of Ronilan FL with low volume sprayer and sampling day 1 after application on upper and underside of cucumber leaves.

P1, P2, P3, P4 and P5: experiments performed in climate chambers to study climate effect on declination of a fungicide (vinclozolin in Ronilan FL)

Exposure study: In connection with experiments C and D exposure to vinclozolin on harvesters clothes was studied.

EQUIPMENT AND METHODS

Sprayers

Two sprayers, common in Sweden, were used in the experiments: one automatically operated *low-volume sprayer* cold-fogging machine and one manually operated *high-volume* high pressure sprayer (both manufactured in Sweden by Wanjet AB, Staffanstorp).

The *low-volume sprayer* (cold-fogger) was equipped with an air-jet nozzle. The air-jet principle is that the liquid from a nozzle is turned into small droplets with the help of a turbulent air stream flowing around the nozzle. The droplets are carried away with the help of an air stream created by a fan placed behind the nozzle. The sprayer applies 4 or 6 litres per hour depending on the nozzle used. In the experiments 0.007-0.011 L spray liquid/m^2 was applied. The sprayer works without manual assistance once it has been started and is switched off automatically by a timer. The spray mist is spread in the house with the help of the fan, which is started one or two hours before application, to increase the air movements in the house.

The *high volume sprayer* generates the droplets in traditional hydraulic nozzles. The working pressure in our trials was 80 bar (8 MPa) and the volume per m^2 was 0.365-0.416 L. The liquid is spread through four nozzles placed at the end of a tube and the operator walks up and down the aisles to perform the application. For the high volume sprayer the VMD (volume median diameter) was 43 μm (47 % RH, 23.2 °C temperature in air) and for the low volume sprayer the VMD was 26 μm (45% RH, 22.6 °C temperature in air) when measured in the laboratory. Droplet sizes of the sprayers were measured with a Malvern laser instrument.

Surface Sampling, Sample Workup and Analysis Equipment

The idea behind the methodology developed is that the solvent used (ethanol) should come into contact with the substance on the leaves but not with the tissue inside the leaves. In the DFR washing technique described earlier the extraction liquid can also reach and extract the substance inside the leaves from the wounded tissue. With the methodology used in our study, this extraction is avoided by not exposing wounded tissue to the extraction liquid. The surface is only exposed to the extraction liquid 20-30 seconds which prevents the ethanol from penetrating the leaf wax and extracting pesticide inside the leaf. By using this procedure, all of the pesticide on the leaf surface accessible to skin contact is supposed to be extracted, but not the pesticide inside the leaf. Too long contact time may cause transport of fungicide from inside the leaf or external fungicide from the surface into the leaf. With the time used we think that the fungicide in the deep pores remains there while the fungicide on the surface, accessible for dermal contact, is extracted, hence giving a good picture of the amount that workers become exposed to when working with treated plants.

With this methodology it may also be possible to estimate the *recovery* of the analysis procedure (see Paper I). The recovery study gives information about the proportion of the applied substance that is obtained in the final analysis, and how great the losses are in the different workup steps of the sampling and analysis procedure. In Paper I, a detailed description is found concerning surface sampling, sample workup methods and equipment. In the greenhouse experiment we took samples in the environment, on leaves at a height of 1.5 m, on plastic sheets placed on the floor (polythene) and on the walls (acrylate). In the climate chamber experiments, the application was performed with a pipette on to areas marked in advance. The area to be sampled was marked with a color pen. Sampling was thereafter randomly performed on these marked leaves. The procedure for leaf sampling is illustrated in Figure 1.

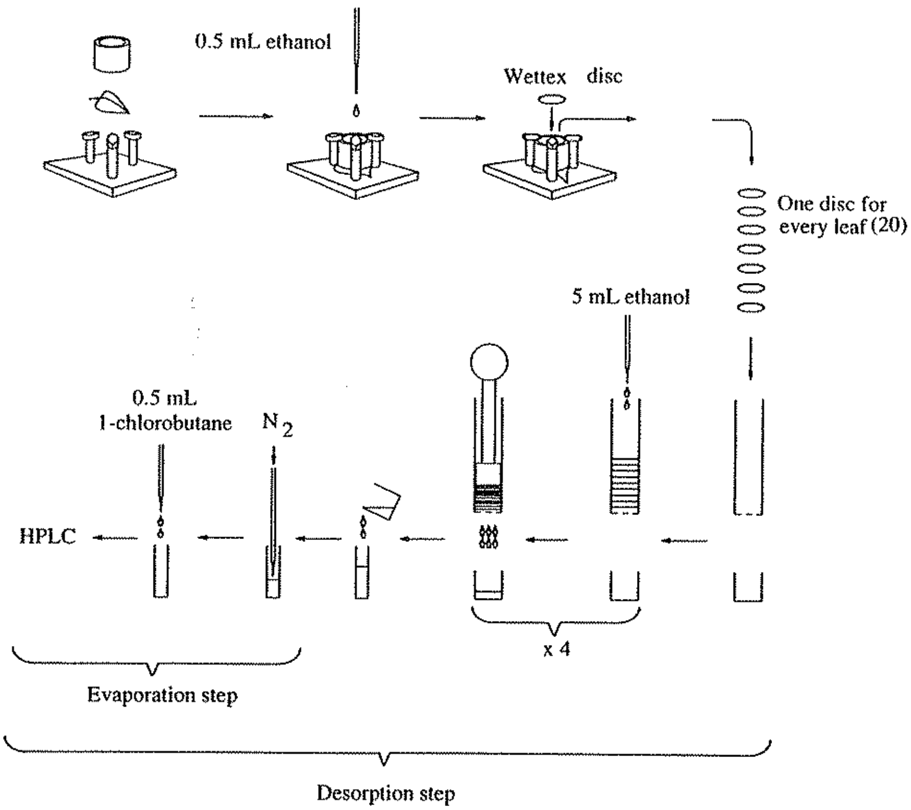


Figure 1. Leaf sampling equipment and sampling procedure.

A leaf cut at 1.5 m above the ground was placed on the plastic plate (a) and over it the plastic cylinder (b) was held to the plate by spring-loaded holders (c). An o-ring prevents leakage in the bottom of the cylinder. Ethanol was put on the leaf inside the metal cylinder and is collected with a circular cellulose cloth (Wettex) after 20-30 seconds. The collected cloths, 20-40 cloths, were extracted with ethanol four times and the extracted solution was collected in a glass tube. Before final analysis (after storage at 8°C) the sample is evaporated and 1-chlorobutane (0.5mL) was added.

Samples from plastic surfaces were collected in the same way with similar equipment. A circular metallic cylinder with an o-ring was placed on the surface to be sampled. The weight from the metallic cylinder helped to keep it on the sampled surface.

Air Sampling Equipment and Procedure

Air sampling was performed in experiment A and B with a combination of impinger and Teflon filter (0.8 µm) in series connected to a pump (see Figure 1 in Paper II).

The impinger solution was ethanol. The pumps used were Gilair S-C (Bicapa AB, Kungälv, Sweden) which worked with an air flow of 1.5 L/min in the first experiments and with 3.0 L/min in the later experiments. The sampling equipment was placed at 1.5 m height, approximately in the breathing zone. Sampling time was 120 or 180 minutes. In the first experiment, A, we sampled air with a combination of impinger and filter (Teflon, 0.8 µm pore size, Millipore) to be sure of avoiding losses caused by volatility of the substance. When analyzing the results no substance was detected in the impinger and therefore in the following experiments only filters were used in air sampling.

The concentrations presented in the results are the ones obtained after extraction from the filters and evaporation of the extracts as well as the impinger solutions evaporation to dryness. After this procedure 0.5 mL chlorobutane was added before the final analysis by high performance liquid chromatography (HPLC).

Clothes Sampling Procedure

The harvesting persons wore cotton overalls and cotton gloves when harvesting cucumbers in experiment C and detachable cotton sleeves and cotton gloves in experiment D. The sleeves were attached to the arms by safety pins. In experiment D two pairs of gloves, one inner and one outer, were worn by each harvester and thereby two outer and two inner gloves were analyzed for each person and occasion. After finished harvest the garments were turned inside out and put in plastic bags. They were stored cold (8°C) and dark until final analysis was carried out. Before final analysis the overalls were cut in pieces according to Figure 2.

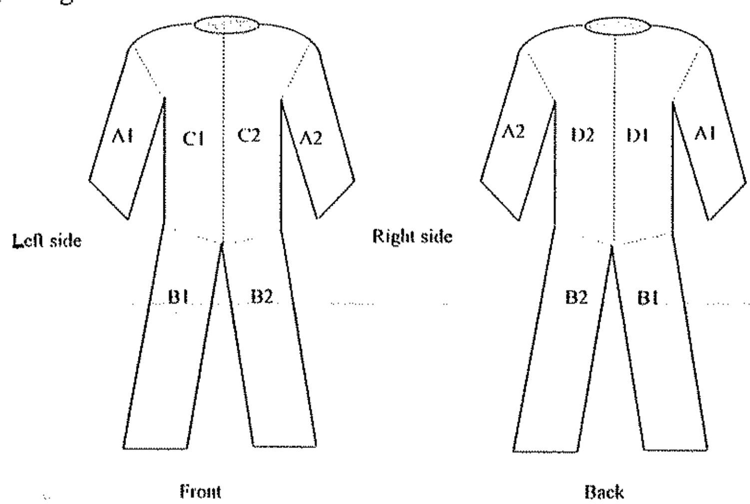


Figure 2. Overall sections that were cut before analysis

The cut pieces were placed in glass jars and covered with 1-chlorobutane and ultrasonicated for two hours. The chlorobutane was then evaporated to 10 mL. The same procedure with ultrasonicating and evaporation was used for the gloves and the sleeves. HPLC analysis was performed on the work-up samples as described in Paper I.

Fungicides used in Experiments

In the pilot study, experiment A, two fungicides were used. One was triadimefon (Bayer, Monheim, Germany) with active ingredient (50 g/kg) in Bayleton Special and the other one was vinclozolin (BASF, Limburgerhof, Germany) with active ingredient (500g/L) in Ronilan FL. Due to low concentration of triadimefon after application in experiment A we decided to concentrate our investigation on vinclozolin in the subsequent experiments.

The acute toxicity for both formulations is low, see Literature study.

The vapor pressure of vinclozolin is 0.13 mPa and water solvability is only 0.0026 g/L (Fransson, 1990). In water with pH 1 - 7 no hydrolysis occurs within 24 hours but at pH 13, about 50 % is hydrolyzed within 3.8 hours.

Triadimefon (CAS number 43121-43-3) has a vapor pressure < 10 mPa, the water solubility is 60-70 mg/L and it is hydrolysis stable at pH 4, 7 and 9 (Lundbergh, 1991)

Final analysis procedure

Previously developed methods for analysis of vinclozolin and triadimefon require a highly efficient separation step. High-resolution gas chromatography was used for the final analysis step combined with time consuming work-up steps prior to the injection. We developed a methodology based on high performance liquid chromatography (HPLC). This is a suitable technique for this kind of study, when the number of components to be analyzed are limited.

The recovery of the whole sampling procedure for vinclozolin is 90% on hard polymer (acrylate) , 5.2% on soft polymer (polythene) and 74% on leaves. The losses in the evaporation and desorption steps are 2% and 7% respectively, which leaves losses depending on inaccessible fungicide in pores at ca. 1% for hard polymers, 86% on soft polymers and 17% on leaves. The recovery for triadimefon are on hard polymer 88%, on soft polymer 2.0% and on leaves 79%. The remaining part in the pores of the leaves are estimated to be 15%.

SAMPLING PLAN

Greenhouse Experiments

Temperature, humidity and light intensity were measured both inside and outside the houses during the experiment period. In experiment A air samples were taken during the first 24 hours. In addition, one person carried air sampling equipment during harvest work on the fourth day after application. Samples on acrylic sheets and leaf areas were taken during one week after application. On plastic sheets samples were taken on day 1, 3 and 6 after application and on day 1, 2, 3, 4, 6 and 7 after application of the fungicide on leaves.

Samples in experiment B were taken on leaves and plastic sheets on the floor on days 1, 4, 7, 14, 21 and 28 (Figure 2 in Paper II). Air samples were taken until harvesting started on the fourth day after application, (see Table 3 in Paper II). On the fourth day the harvester carried air sampling equipment.

In experiment C only leaf samples were taken on day 1, 4, 7, 14, 21 and 28.

The greenhouses used measured 528 m^2 in floor space (16 x 33) in experiments A:1, A:2, B:1 and C:1 and 360 m^2 (12 x 30) for the others. The applications performed are shown in Table 1 in Paper II.

Climate Chamber Experiments

The effect of climate on the declination of fungicide vinclozolin was studied in climate chambers (the Biotron, Alnarp). The temperatures and humidities in the experiments are shown in Table 2 in Paper II.

The chambers are 2.5 x 3 m in area with a height of 2 m and were equipped with artificial light and possibilities to control temperature, humidity and light intensity.

Light intensity was 10.000 lux (140 μmol/m^2s) and CO_2 concentration was about 350 ppm (natural level).

Exposure Study

During experiments C and D, we also studied the exposure on clothes for workers harvesting cucumbers. Samples were taken on cotton gloves, overalls and sleeves. Three different harvesters participated in the study on eight harvesting occasions (Table 1 in Paper II, p.3)

RESULTS AND DISCUSSIONS

The results of the greenhouse experiments are presented first, then the climate chamber experiments and finally the exposure studies. The thesis closes with conclusions drawn from the results.

DECLINATION STUDIES IN GREENHOUSES

In experiment A both triadimefon and vinclozolin were studied and in experiment B-D only vinclozolin.

Experiment A

After *triadimefon* application concentrations in greenhouse *air* were not detectable. Concentrations on leaves and plastic floor and wall areas were low. *On leaves* after low volume spraying, the concentrations were close to the detection limit (0.0014 µg/cm^2). After high volume spraying the residues were on average 0.01 µg/cm^2 the day after spraying and the concentration was about the same after on week. *On floor* areas the concentration was 0.01 µg/cm^2 after low-volume spraying and 0.013 µg/cm^2 after high volume spraying. *On walls* the concentrations were 0.01 µg/cm^2 after low-volume spraying and 0.011 µg/cm^2 after high volume spraying.

Air concentrations during the first 24 hours lie in average on 40 µg/m^3 for low-volume application and 15 µg/m^3 after high-volume application. Air sampling during tomato picking showed no concentrations of vinclozolin when carried out on the third day after application.

One week after low-volume spraying there was 67% of the initial concentration of *vinclozolin* (6,83 µg/cm^2, SD 2,55) left on leaves and after high-volume spraying 86% left (initial concentration 2,51 µg/cm^2, SD 2,07). The relatively short sampling period, the limited number of samples and the large variation between blocks made the determination of any declination rate too uncertain. This was the reason that experiments B and C were performed during a longer period and with greater number of sample.

After spraying with both sprayers the highest concentrations were found *on the floor* (ratio leaf/floor: 3,7 for low-volume, 4,25 and high-volume). Only one sample/block was taken which did not allow testing between blocks. The high concentrations on floor areas were expected since the off-target deposition from the sprayers is known to be high.

Experiment B and C

After *vinclozolin* application there was a higher concentration *in air* after low volume spraying than after high-volume spraying, 445 µg/m^3 air compared with 5 µg/m^3 one hour after application (Table 3 in Paper II). After 2-24 hours the concentrations in the air were in average 24 µg/m^3 after low-volume spraying and 3 µg/m^3 after high volume spraying. In the interval 48-84 hours after application the concentration was about 1.5 µg/m^3 air for both spraying techniques.

The declination rate on floor areas was similar to the ones on leaves. The time constant for the decay, using a least square fit ($y = Ae^{-t/T}$), on polythene sheets was 9.52 after low-volume spraying and 7.3 after low-volume spraying and on acrylic sheets 9.4 after low-volume and 10.2 after high-volume spraying. Under laboratory conditions (normal indoor climate) the declination rate was slower, T = 4.26.

The uneven distribution of the two sprayers caused problems when we wanted to draw conclusions about the differences in concentration on different surfaces, and also makes it harder to find significant differences between the declination rate and between the efficiencies of the two sprayers. Both sprayers distribute a great part of the pesticide on non-target areas. The low-volume sprayer produces a spray mist which reaches all parts of the house while the high-volume sprayer contaminates mainly the floor areas. As in experiment A the highest concentration was detected on the floor in experiment B. The ratio for leaf/floor concentrations was 2,1 for the low volume-sprayer and 2,4 for the high-volume sprayer.

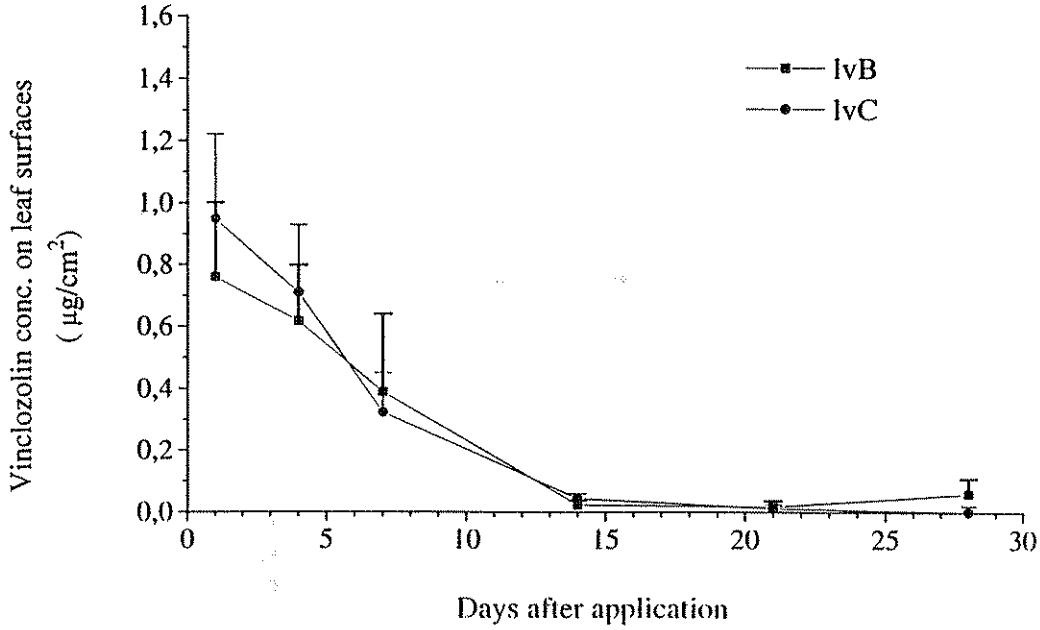
Concentrations and declination curves for vinclozolin on leaf surfaces are shown in Figure 3. In experiments B and C the amount left after four days, when harvesting began, was 80 % for both spraying techniques. After one week about 50 per cent, with a variation between 46% to 73%, remained. The declination rate in experiments B and C seemed to be more rapid than in experiment A (67% left after one week after low-volume spraying and 86% after high-volume spraying) where the declination was hard to observe. After four weeks the concentrations of vinclozolin were almost zero for both application techniques.

We found a significantly lower time constant on the 95% significance level for the *low volume sprayer* compared with the high-volume sprayer, which indicates a faster declination rate for the high-volume sprayer. The difference may be due to the difference in droplet sizes; smaller droplets with larger surface to volume ratio, which increases the accessibility for oxidation reactions, hydrolyze and the evaporation rate. This could, as we found, lead to a faster declination for low-volume spraying with the smaller pesticide diameter compared with the larger from high-volume.

The consequence of the faster declination after low-volume spraying is that the effect of the treatment lasts for a shorter period and it has to be more frequent if the plant protection effect is to remain. To obtain better effect increased dosages are required.

After low-volume spraying there were significant differences on the 95% confidence level between blocks one and three in all experiments. The air assistance in the low-volume sprayer is supposed to distribute the small pesticide droplets evenly throughout the house but does not seem to succeed in achieving an even deposit between the blocks. The block farthest away, block three, from the sprayer (placed stationary), receives less deposit on leaves than the others.

In most cases, except for high-volume spraying in experiment C, there were significant differences in declination rate between different blocks in the greenhouse. These differences may be explained by how the manual application is carried out.



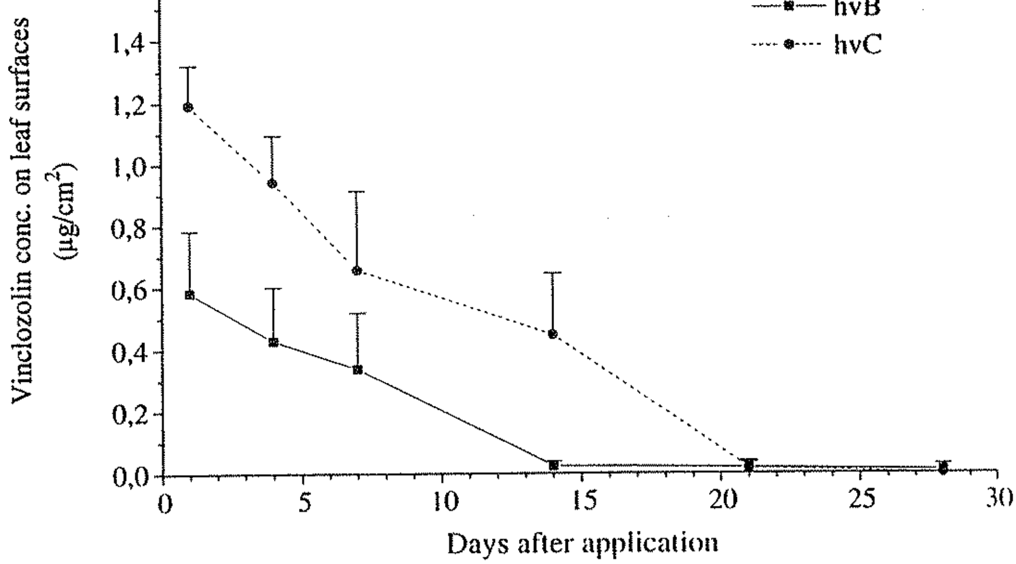


Figure 3.a and 3 b. Declination of vinclozolin on leaves (µg/cm²) in greenhouse after low-volume (a) high-volume (a) and application in experiment B and C.

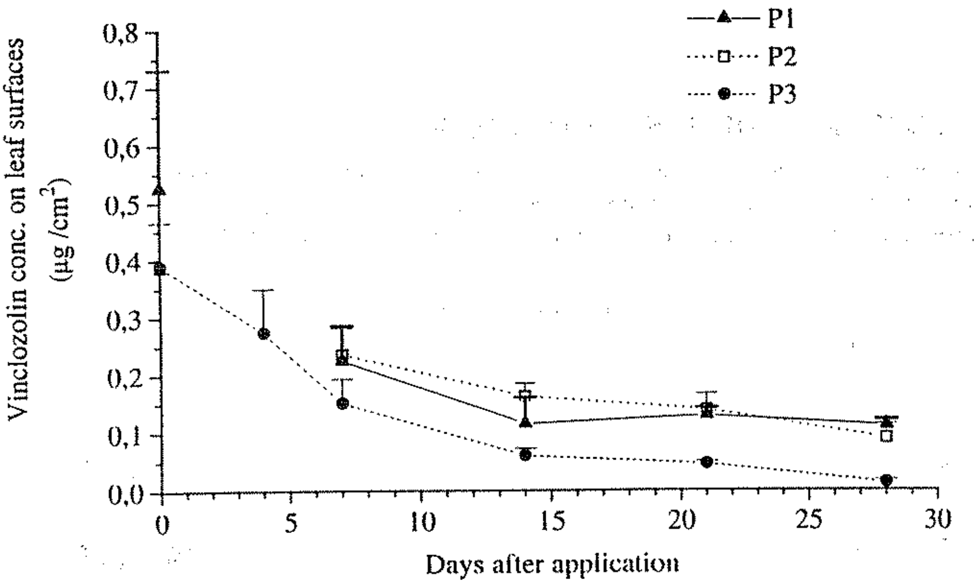
Experiment D

The concentration on the uppersides of cucumber leaves was 1.47 μg vinclozolin/cm^2, SD: 0.73, n=7) and on the undersides of the leaves 0.146 μg/cm^2 (SD: 0.278, n=8). When tested the deposits, on upper and undersides of the leaves were significantly different at the 99% confidence level. The approximately tenfold difference corresponds to similar results in other studies; Nielsen & Kirknel (1990) showed that low-volume spraying in greenhouse deposited 95% on the upperside and 5% on the under side of the leaves in the top part of a pot plant (Chrysanthemum). Use of upperside sampling for estimation of concentrations on leaves is therefore reasonable since the main part is deposited on this side. Also in DFR-sampling the upperside is used as the area when estimating the residues/cm^2 (Zweig, 1985).

DECLINATION IN CLIMATE CHAMBERS

Our hypothesis was that the higher biological activity present, at elevated temperatures, would produce a faster declination. We also assumed that a higher vapor pressure deficit would give a more rapid declination caused by the increased evaporation of water and pesticide from the leaf areas. The declining study in climate chambers showed little variation in declination rate between the different climatic conditions in the experiment and no pattern related to humidity or temperature dependence was found. The difference in declination rate between the highest and lowest temperature, or between the highest and lowest humiditiy, was not significant.

Figure 4 shows the declination of vinclozolin on leaves with time under different experimental conditions (see Table 2 in Paper II). The initial concentration varied between 0.31 to 0.59 g/cm^2 leaf area, Figure 4.



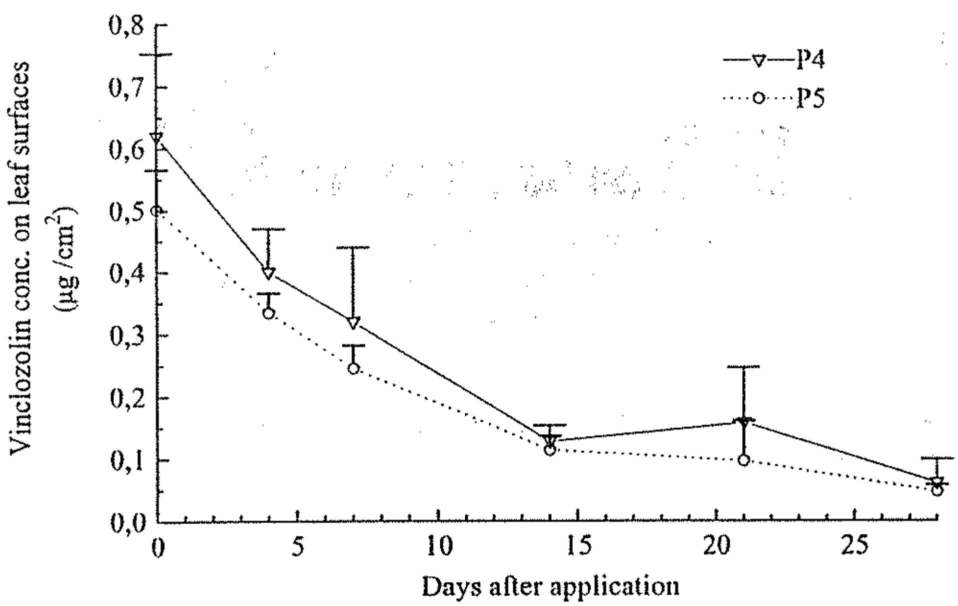


Figure 4a and 4b. Declination of vinclozolin on leaves (µg/cm²) during period 1 (a) in climate chamber (experiments P1, P2 and P3). and during period 2 (b) in climate chamber (experiments P4 and P5).

EXPOSURE STUDIES IN GREENHOUSES

The exposure on clothes varied a lot between workers and between experiments for the same worker. An average exposure, Figure 5, was estimated from the eight experiments presented in Paper III (three different workers participated in the study).

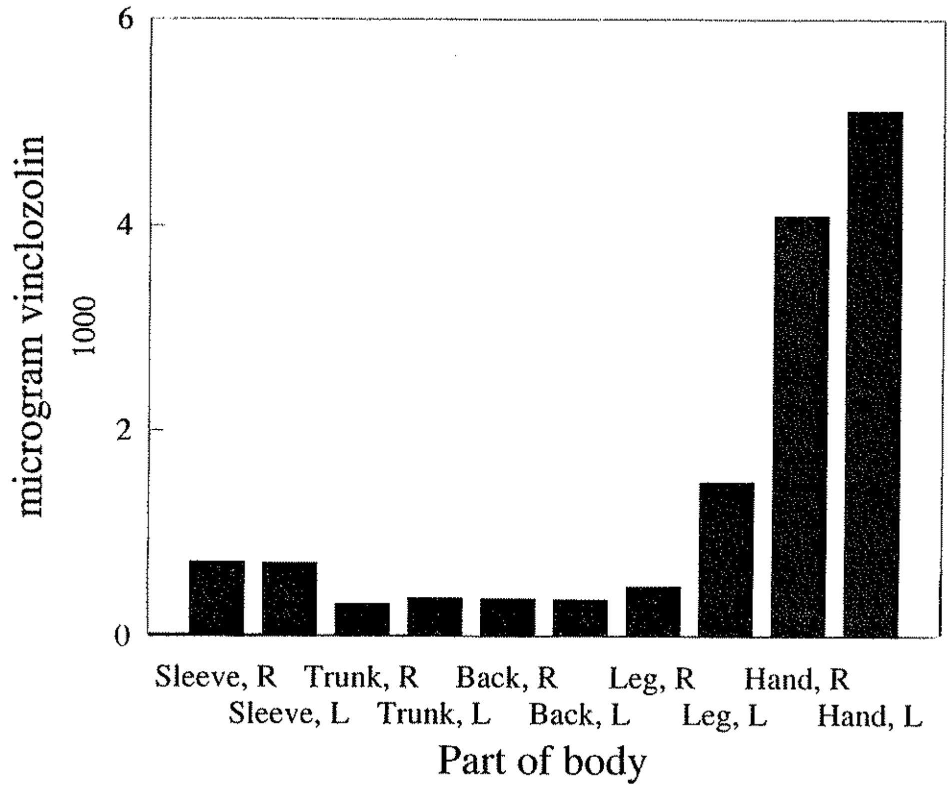


Figure 5. Average exposure in 1000s of μg/day obtained on cucumber harvester's clothes during an 8 hour working day .

Figure 5 shows, as expected in harvest work, that the highest exposure is on the hands. The total calculated average exposure on clothes was 15.54 mg. If we estimate that 10% of the exposure on clothes goes through the skin 1.55 mg of vinclozolin gets into the body. The World Health Organization's (WHO) limit for acceptable daily intake (ADI) through food is 4.2 mg a day (0.07 mg/kg body weight) and the Environmental Protection Agency US's (EPA) limit is 1.5 mg a day (0.025 mg/kg body weight). The calculated value lies just above the EPA limit. Most of the exposure can be avoided through wearing clothes that protect the skin. Wearing gloves is especially effective since most of the exposure in harvest work such as picking cucumbers is on the hands. With these measures taken, the risk for a healthy person to work in the greenhouse seem to be low.

Another question asked was if there is a connection between exposure time and exposure/hour. A longer *exposure period* give lower exposure per hour. In Table 3 a smaller amount/hour was absorbed by the gloves worn over a longer period of time, harvesters 1, 2, 7 and 8, while harvesters 3, 4, 5 and 6 who have worked for about one hour had in comparison a higher amount/hour on their gloves. The reason could be that the cotton gloves absorb less after a while because the small pores in the gloves have been filled with particles.

The difference in exposure between inner and outer gloves (Table 3) shows that more than 50% of the exposure stays on the outer glove.

Table 3
Percentage of vinclozolin on inner gloves of the total of glove exposure for each harvester after high-volume (hv) and low volume (lv) spraying.

Sampled harvester	*Left inner (%)*	*Right inner (%)*	*Hours of work*	*Application technique*	*Dosage ratio*	*Exposure on gloves µg/hour*
1	no inner glove		4^{30}	lv	1.32	584
2	no inner glove		3^{00}	hv	1.5	424
3	28	32	0^{55}	hv	1	2.233
4	28	15	1^{05}	hv	1	2.721
5	6	33	1^{00}	hv	1	2.569
6	31	22	0^{45}	hv	1	1.499
7	45	44	5^{30}	lv	1.04	210
8	38	44	2^{00}	lv	1.04	437

The percentage that reaches the inner glove varies between 6% and 45% in the investigation, and it seems that a longer exposure time results in a higher percentage reaching the *inner* glove. The person harvesting for 5.5 hours (harvester 7) receives 44-45% of the exposure on the inner gloves while persons harvesting for about one hour receive 6-31% on the inner gloves. The correlation dermal dose/concentrations on leaves (cm^2/hour) estimated for subjects in experiment 1, 2, 7, and 8 are given in Table 4. In experiments 3 - 6 no leaf concentrations are available.

Table 4.

The ratio for dermal exposure/concentration of vinclozolin on leaves. The dermal exposure is estimated as exposure on gloves for harvesters (four day after application). In experiment 7 and 8 the leaf concentration has been estimated as 80% of the concentration of day one (marked *).

Experiment	*Dermal dose (mg/hour)*	*Conc. on leaves* $\mu g/cm^2$	*Ratio dermal exposure/leaf conc* $(cm^2/hour) \times 10^{-3}$
1	0,48	0,71	0,68
2	0,42	0,94	0,45
7	0,21	1,2*	0,18
8	0,44	1,2*	0,37

The dermal exposure/hour are higher (about 6 times) for experiments 3 to 6 where the harvesters worked a shorter period. The dosage of vinclozolin, g/L, are in the same magnitude as the others. The longer working time/glove makes the exposure seem lower/hour than a shorter time/glove. With an estimated concentration on leaves in experiments 3 to 6 of about the same as for experiment 2 the estimated ratio is 2.7 cm^2/hour.

Other factors that influence the exposure/hour are differences in harvesting performance and the humidity in the house. A rougher handling of the fruit, and a more humid climate, are expected to give higher exposure than gentler handling and a drier climate. The influence of spraying technique on amount of exposure/hour is lost in the large effect of exposure time/glove.

CONCLUSIONS

CONCENTRATIONS ON SURFACES

Triadimefon concentrations are low, both in air and on surfaces after an application, and our judgment is that the health risks related to working in treated greenhouses should be small for a person with no allergic problems.

The concentration of vinclozolin after application in greenhouses is still high 4 days after application; as much as 80 % of the substance remains from day one after application. Other fungicides can be expected to behave in the same way. With DFR-technique Zweig found a half-life period of four days for vinclozolin to compare with our results of a half-life of about one week. The difference can depend on that the decomposition by UV-light is low in a greenhouse.

Variations in initial concentration in the experiments might depend on the status of the leaves. A poorer leaf status causes less fungicide to reach the skin. This variation does not disturb the aim of the investigation, since the status of the leaves also should be considered when studying the degree of exposure on the worker's skin.

Declination rates do not differ much between the different climatic conditions in our investigation. It is therefore possible to give a reasonable estimate of the declination rate for different climatic conditions within these climate ranges based on the decay results from our study. Within the greenhouse the temperature varied between 20-30°C, the humidity between 50-90%.

A considerable part of the declination can be explained by evaporation from the leaves as a result of the low vapor pressure of vinclozolin. With a vapor pressure of 0.13×10^{-8} Pa (20°C) evaporation is estimated to explain about 10% of the declination between day one and four.

EXPOSURE OF PERSONNEL TO SPRAYED FUNGICIDES

The trouble with long-term effects are that they are not recognized in connection with the exposure which makes it difficult to motivate the worker to wear protective garments in the current situation. To make the workers themselves feel responsible for their working environment and personal protection is a good way of improving the work environment.

Protective gloves give better protection if they are changed before they get too humid. The study shows that after a long working period the calculated exposure/hour is lower than after a shorter period. If the worker wears a glove the whole day, a greater percentage is found in the inner gloves which would lead to higher exposure on the workers skin.

The fast declination from the greenhouse air, of both fungicides, reduces the health risks caused by inhalation after only two hours. However, during the first two hours after low-volume spraying the concentrations of vinclozolin are rather high, 445 $\mu g/m^3$, and entrance during this time should be avoided unless a protective mask is worn.

RECOMMENDATIONS

In general, alternative working methods can be used to avoid work in treated houses or to come into contact with treated material. For ornamental cultivation, except for some cut flowers, it is often possible to avoid work in the house for a week or two after application and thereby diminish the exposure. After one week the concentration of fungicides is considerably lower in for example the case of vinclozolin half of the concentration remains.

Unnecessary contact with contaminated equipment could be avoided by covering of permanent installations and moving equipment as far as possible out of the greenhouse before treatment.

It is recommended that the skin is protected from contamination by pesticides during the first week after application. For harvest work the hands and arms should be protected. The warm and humid greenhouse climate increases the demand for light and comfortable protective garments. Cotton material or tight plastic material in gloves and sleeves are recommended. If plastic garments are used one must be careful of torn garments, which is worse than wearing no protection at all, because of the humid conditions on the skin inside the garment. Cotton materials are comfortable and cheap to use but it is important to change gloves and sleeves when working many hours a day. To wear soaked garments is worse than working without since the humid conditions on the skin make the uptake of the pesticide more efficient.

Good hygiene in general is a preventive measure which avoids uptake through the skin. Keeping the hands in good shape and washing them before eating is an easy way of diminishing exposure.

Even though the concentrations in air are low immediately after high-volume spraying, it is recommended not to work in the house during or right after application. After 12 hours the house should be ventilated. It can then be re-entered.

FUTURE RESEARCH

The sampling methods used in these experiments could also be suitable for other substances and crops. It would be interesting to study insecticides or other fungicides in rose cultivation. Work in rose cultivation is another situation where the workers are frequently exposed to pesticide during harvesting and other tasks. The results of these studies could be compared with this study.

In this study we found that the gloves became soaked after a while and a higher percentage of the substance penetrated the outer glove and reached the inner one, which can symbolize the human skin inside the glove. How long it would be possible to use different types of gloves before the pesticide penetrates the material is another area that would be interesting to research

ACKNOWLEDGMENT

I wish to thank all the colleagues on the Department of Agricultural Engineering at Alnarp who has assisted me with the experiments, laboratory work and reading of manuscript. A great thank to my supervisors, Thomas Nybrant and Lennart Mathiasson for their support, not at least for all reading of my papers. Thanks also to Margareta Papantoni for helping me to get the papers in publicizing shape before print deadline! Also many thanks to my friends Susanne, Berit and Knut-Håkan and an *enormously huge* thank you to Anna for the last nights reading and support!

I am also thankful to the nice and enthusiastic badminton players and to the "Friskis & Svettis" in Lund who helped me stay in physical fitness through the winter. Music by Wolfgang Amadeus Mozart enhanced my inspiration and improved my concentration (not *of* the fungicides, but on) during the writing of the thesis, I am very grateful, W. A. Mozart.

REFERENCES

Adams, A.J.; Palmer, A. 1986. Deposition Patterns of Small Droplets applied to a Tomato Crop using the Ulvafan and two Prototype Electrostatic Sprayers. *Crop Prot.* (1986) 5 (5), 358-364

Adams, A.J., Palmer, A. & Abdelbagi, H. 1986. The Influence of Droplet Size and Air Assistance upon the Distribution of Electrostatically Charged Sprays on Tomatoes. *Br. Crop Prot. Conf. - Pests and diseases*, 251- 254

Adams, A.J.; Lindquist, R.K. 1991. Review of the Performance of Air-assisted Sprayers for use in Glasshouses. *Br. Crop Prot. Council (BCPC) Monograph* 46, Air-Assisted spraying in Crop Protection, pp. 227-235

Andersson, K.; Gudehn, A.; Levin, J. O.; Nilsson, C. A. 1983. A Comparative Study of Solvent and Solvent-free Sampling. Methods for Airborne 4,4-diphenylmethane diisocyante (MDI) generated in Polyurethane Production. *Amer. Ind. Hyg. Assoc. J.* 44, 802-808

Autio, S. 1991. Ecotoxicological Evaluation of Triadimefon. Vatten- och miljöstyrelsen, Finland 6.5.1991 (Swedish)

Bergkvist, P.; Isaksson, B.; Tillberg, A.; Törnlund, M. 1991. PM 1991-12-18 Ronilan FL reg. no 3629. Authority for Chemicals, Division of Pesticides, Solna, Sweden,

Branson, D. H.; Sweeney, M. 1991. Pesticide Personal Protective Clothing. *Rev. Environ. Contam. Toxicol.*, 122, 81-109,

Chester, G.; Adam, A.V.; Inkmann-Koch, A.; Litchfield, M.H.; Tuinman, C.P. Field Evaluation of Protective Clothing Equipment for Pesticide Operators in Tropical Climate. *La Medicina del Lavoro*. 1990, 81, 6, 480-488,

Eriksson, K.; Grip, L.; Kolmodin-Hedman, B.; Törnqvist, A. 1988. Exposure and Symptoms of Tolylfluanid at Handling *Picea* Plants. Investigation Report National Institute of Occupational Health, Sweden, 5 (Swedish)

Fransson, R. 1988. Toxicological Validation of the Fungicide Imazalil. Department of Environmental Medicine, Institute of Karolinska, Stockholm, Sweden, (Swedish)

Garcia-G, J.-E. 1991. Improved Method for the Determination of Triadimefon, Triadimenol-A and Triadimenol-B in Wheat Plants (triticum aestivum L.) and Soil Samples by Gas Chromatograph. *Fresenius'J. Anal. Chem.*, 339-, 402-404

Garå, A. Exposure for Pesticides in Berry Cultivation. Investigation Report, Swedish Board for Occupational Safety and Health, Umeå, 1984 (Swedish)

Giles, D. K., Blewett, T. D., Saiz, S. G., Welsh, A. M. & Krieger, R. I. Foliar and Nontarget Deposition from Conventional and Reduced-volume Pesticide Application in Greenhouses. *J. Agric. Food. Chem.* 1992, 40, 2510-2516

Giles, K. D. ;Blewett, C.; Saiz, S.; Welsh, A.; Krieger, R. Greenhouse Applicator and Harvester Exposure to Pesticides. ISHS International Symposium on Engineering as a Tool to Reduce Pesticide Consumption and Operator Hazards in Horticulture August 8 - 13 (14) 1993, Ulvik, Norway

Gunther, F. A.; Barkley, J. H.; Westlake, W. E. 1971. Worker Environment Research. II. Sampling and Processing Techniques for Determining Dislodgable Pesticide Residues on Leaf Surfaces. *Bull. Environ. Contam. Toxicol.* , 641-644

Iwata, Y.; Knaak, J. B.; Spear, R. C.; Foster, R. J. 1977. Worker Re-Entry into Pesticide-Treated Crops. I. Procedure for the Determination of Dislodgeable Pesticide Residues on Foliage. *Bull. of Environ. Contamin. Toxicol.*18, 649-655

Jarrett, P., Burges, H. D. Matthews, G. A. 1978. Penetration of Controlled Drop Spray of *Bacillus thuringiensis* into *Chrysanthemum* Beds compared with High-Volume Spray and Thermal Fog. Symposium on Controlled Drop Application. *Br. Crop Prot. Council Monograph* 22, 75-81

Kolmodin-Hedman, B.; Åkerblom, M.; Alex, G.; Flato, S. 1992. Preliminary Report "Exposure to Chemicals in Crops", Huddinge Sweden, (Swedish)

Liesivuori, J.; Liukkonen, S.; Pirhonen, P. 1988. Re-Entry Intervals after Pesticide Application in Greenhouses. *Scand. J. of Work Environ. & Health*, 14 (1988): suppl 1, 35-36,

Lundbergh, I. 1991. Ecotoxicological Evaluation of Transformation and Degradation of the Fungicides Triadimefon and Triadimenol. Swedish Authority for Chemicals, Solna

Lundqvist, P. 1985. Near Accidents in Greenhouse Work - Experiences and Opinions of Owners of Business and Safety Representatives. Department of Biosystems and Technology, Internal Report, Swedish University of Agricultural Sciences, Lund

Lundqvist, P. 1982a. Near Accidents in Greenhouses. Department of Biosystems and Technology, Report 22, Swedish University of Agricultural Sciences, Swedish University of Agricultural Sciences, Lund

Lundqvist, P. 1982b. Personal Protective Equipment for Greenhouse Work. Department of Biosystems and Technology, Special Message 113, Swedish University of Agricultural Sciences, Lund

Maibach, H.I.; Feldmann, R.J.; Milby, Th.H.; Serat, F. 1971. Regional Variation in Percutaneous Penetration in Man. *Arch. Environ. Health*, 23, 208-211

Newsome, H. H.; Collins, P. 1989. Multiresidue Method for Fungicide Residues in Fruit and Vegetables. *J. Chromatogr.* 472, 416-421

Nielsen, S-L.; Kirknel, E. 1990. Deposition Patterns by High and Low Pressure High Volume Spraying in Glasshouse Pot Plant Crops. *Tidsskrift for Planteavl* 94, 517-525

Nickless, G.; Spitzer, T.; Pickard, J.A. 1981. Determination of Triadimefon in Grape Juice and Capillary Gas Chromatography. *J. Chromatogr.*, 208, 409-314

Persson, G.; Palmqvist, I. 1992. Chemical Pesticides in Forestry. Exposure for Maneb, Vinclozolin and Propikonazol in Forestry Nurseries and at Planting in Forestry. (Swedish) *Occupational Inspection Board in Härnösand, Sweden, Report* Yi-Hä 3-92

Popendorf, W. J.; Spear, R.C.; Selvin, S. 1975. Collecting Foliar Residues related to Potential Airborne Exposure of Workers. *Environ. Sci. & Technol.* vol 9:6, June, 583-585

Ramaswamy, G. N.; Boyd, C. R. 1991. Protective Apparel Survey of Agricultural Workers in Cotton Growing Regions. *Bull. Environ. Contam. Toxic.* 1991, 47, 529-536

Slahck, S. C. 1985. Liquid Chromatographic Determination of Triadimefon in Technical and Formulated Products. *J. Assoc. Off. Anal. Chem.* 68, 586-589

Waldron, 1985. Minimizing Pesticide Exposure Risk for the Mixer-loader, Applicator and Field Worker. *Amer. Chem. Soc. (ACS)*, 409-411

Winterlin, W. L.; Kilgore, W.W.; Mourer, C.R.; Shoen, S.R. 1984. Worker Reentry Studies for Captan Applied to Strawberries in California. *J. Agric. Food Chem.*, 32, 664-672

WHO. 1991. IPCS - International Programme on Chemical Safety. Summary of Toxicological Evaluations performed by the Joint FAO/WHO Meeting on Pesticide Residues 1991, JMPR (UNEP, ELO, WHO)

Zweig, G.; Gao, R.; Popendorf, W. 1983. Simultaneous Dermal Exposure to Captan and Benomyl by Strawberry Harvesters. *J. Agric. Food Chem.*, 31, 1109-1113

Zweig, G.; Gao, R.; Witt, J.M.; Popendorf, W.; Bogen, K. 1984. Dermal Exposure to Carbaryl by Strawberry Harvesters. *J. Agric. Food Chem.* 32. 1232-1236 (2 ex)

Zweig, G.; Leffingwell, J.T.; Popendorf, Wm. 1985. The Relationship between Dermal Pesticide Exposure by Fruit Harvesters and Dislodgeable Foliar Residues. *J. Environ. Sci. Health*, B20(1), 27-29

Personal messages

Margareta Littorin, Department of Occupational Medicine, University of Lund