Potential Operator Exposure to Procymidone in Greenhouses

E. Capri,*,[†] R. Alberici,[†] C. R. Glass,[‡] G. Minuto, and M. Trevisan[†]

Istituto di Chimica Agraria ed Ambientale, Università Cattolica del Sacro Cuore, 29100 Piacenza, Italy, Central Science Laboratory, MAFF, Sand Hutton, York YO41 1LZ, U.K., and Centro Regionale di Sperimentazione e di Assistenza Agricola, 17031 Albenga (SV), Italy

Recent legislation in the European Union requires regulators of member states to carry out risk assessments using data for actual or potential operator exposure, or estimates of exposure from models. However, the existing models have few datasets from studies carried out on greenhouse or indoor crops, particularly in southern Europe. In this study potential dermal and inhalatory exposures were measured in two trials in Italian greenhouses. The total potential dermal operator exposure of the applicator, measured with a whole-body passive dosimetry method, was 15.4 and 37.1 mL/h of the diluted pesticide mixture. The majority of the contamination was on the hands and on the lower part of the coverall. Approximately 0.003% of the active ingredient (ai) applied to the crop area contaminated the coverall worn by the operator. The potential dermal exposure during the mixing and loading phase accounted for 6-8% of the total potential dermal exposure during the whole process. Inhalation exposure accounted for only 0.05-0.07% of the total potential operator exposure. Model predictions of the potential operator exposure using a modified version of the German model overestimate the mixing-loading exposure while underestimating the application exposure. These data are evidence that the estimation coefficient set for hand-held application to ornamental and horticultural crops may be inadequate for the agronomic conditions of southern Europe.

Keywords: Chemical analysis; procymidone; potential operator exposure; greenhouse; exposure model

1. INTRODUCTION

The Common Acceptance Directive 91/414/EEC (Dec. Lgs. 194, 1995) deals with the authorization of plant protection products (pesticides) and the control of their use. This requires regulators of European Union (EU) member states to evaluate levels of worker exposure to pesticides during their intended use as part of the authorization process. The current Italian legislation (Dec. Lgs. 626, 1994) deals with protective measures in the working environment, and the need for workers to perform an assessment of the potential exposure to pesticides during their use, i.e., preparation and application, and the need for protective measures such as protective clothing. The evaluation of worker exposure by regulatory authorities also uses a variety of predictive modeling approaches (Glass and Gilbert, 1996). Examples of models have been developed in the U.K. with the predictive operator exposure model (POEM) (Martin, 1990) and also in Germany (Lundehn et al., 1992) and North America (PHED, 1992). In Europe a harmonized approach is being pioneered with the development of a EUROPOEM database (Chen and Watts, 1993) to support European pesticide approval under Directive 91/414/EEC (Dec. Lgs. 194, 1995).

New data to complete the database are required, especially from southern European conditions and for protected (indoor) crops. In such situations the unfavorable conditions of high temperature and relative humidity make the wearing of personal protective equipment (PPE) difficult for operators and associated workers. The lack of PPE use combined with the common use of handheld application techniques would tend to increase the risk to the operator from exposure to plant protection products (PPPs). Data for re-entry exposure are also required by regulators to evaluate the risk of exposure to workers from airborne pesticide droplets and vapors, in addition to dermal exposure from deposits of pesticides on leaves and working surfaces in the greenhouse.

In Italy a number of studies have been carried out to determine occupational exposure to pesticides, with the majority of studies dealing with the evaluation of exposure during the pesticide manufacturing processes (Aprea et al., 1997; Sciarra et al., 1994). Studies have also evaluated the dietary exposure of the population (Aprea et al., 1996a,b; Ferrari et al., 1998). The evaluation of exposure of workers during pesticide application has usually been done by means of biological monitoring (Aprea et al., 1997; Catenacci, 1988; Aprea et al., 1994a,b; Aprea et al., 1998), where samples of urine or blood have been analyzed for the presence of parent or metabolite compounds. However, there are few data available from studies which have evaluated the potential or actual dermal and inhalation exposure during pesticide application. Such studies allow more detailed assessments of the nature of the exposure, such as the evaluation of potential hand exposure or the influence of protective measures on dermal exposure (Russo et al., 1996; Valerio et al., 1993; Aprea et al., 1994a). Much of the data which have been generated are not suitable for the EUROPOEM database due to the lack of supporting quality assurance data concerning the field

[†] Università Cattolica del Sacro Cuore.

[‡] MAFF.

[§] Centro Regionale di Sperimentazione e di Assistenza Agricola.

Table 1. Chemicophysical Properties of Procymidone (Nicholson, 1993)

ne i. Chemicophysical Fi	operties of Frocymutone (No	(11015011, 1993)	
vapor pressure melting point molecular weight water solubility	0.01 Pa (25 °C) 166 °C 284 4.5 mg/L (25 °C)	Henry constant (Kaw) half-life in air (leaf) half-life in air (soil) half-life in soil	3.03E-4 (20 °C) 1.07 days (20 °C) 0.18 day (20 °C) 90 days

application and operating procedure adopted in the studies.

In the greenhouses of the Albenga region of Italy, ornamental crops such as hydrangeas and daisies are commonly cultivated in pots. One of the main sources of worker exposure to the procymidone used on these crops is likely to be the airborne pesticide. This exposure is likely to occur during the application itself and also during the re-entry periods afterward. There is also a risk of dermal exposure during mixing—loading and application, which can be evaluated by measuring potential dermal exposure. The aim of this study was both to measure potential dermal and inhalation exposure in the greenhouse and to evaluate the risk to workers in such a scenario.

2. EXPERIMENTAL PROCEDURES

2.1. Chemicals. The pesticide used for the studies was procymidone (patent no. US3903090, Sumitomo), a fungicide belonging to the dicarboximide group, formulated as a wettable powder (Sumislex 50 WG) by Cyanamid. Procymidone has an essentially protective activity against fungi such as Botritys, Sclerotinia, Monilia, Alternaria, and Sclerotium. The properties of procymidone are reported in Table 1. The analytical standard of procymidone was obtained from Labservice Analytica, solid standard (99.7% purity). The standard was dissolved in *n*-hexane (for analysis, Carlo Erba) to obtain a primary (stock) calibration solution (122 μ g·mL⁻¹), which was then stored in a freezer at -18 °C. Other solutions of lower concentration were prepared from the stock solution by further dilution with *n*-hexane. Acetone (for analysis, Carlo Erba) was used for the extraction of procymidone from experimental samples.

2.2. Equipment. Laboratory glassware was used for the extraction procedure. A Dani Model 8521 gas chromatograph equipped with an ⁶³Ni electronic capture detector and a fused-silica capillary column DB-17 by J. & W. Scientific (30 m × 0.25 mm i.d. and 0.25 μ m film thickness) was used for procymidone quantification. The GLC-ECD operating conditions were injector temperature 280 °C, detector temperature 289 °C, and initial temperature 180 °C for 3 min, increased at 4 °C min⁻¹ up to 210 °C for 10 min and 15 °C min⁻¹ up to 270 °C and held at 270 °C for 10.5 min. The carrier gas was He at 4 mL min⁻¹, the injection volume was 1 μ L, and the retention time of procymidone was 18.1 min. With these conditions the detection limit was 0.01 mg/kg, and good linearity was achieved ($R^2 = 0.992$).

2.3. Analytical Procedures. 2.3.1. Analytical Method for Procymidone Determination Extracted from Coveralls and Gloves. An analytical method has been developed for the extraction and quantification of procymidone from PPE worn by the operators during the field trials. During the field experiments Tyvek coveralls were used as both protective clothing for the operator and as sample media for the pesticide. From experience with earlier tracer studies the predicted rate of coverall contamination was low (<40 mL/h), and no runoff from the coverall surface was observed. The Tyvek Pro.tech coverall used by the operator during the application was dissected into several parts in the laboratory (Figure 1). Each coverall section and the cotton gloves worn by the operator carrying out the mixing-loading and the application were then extracted with 250 mL of acetone (350 mL for the largest sections) in a glass flask (500 mL) and then shaken for 30 min at 180 rev/min speed. After filtration with 30 g of anhydrous sodium sulfate, the samples were concentrated on a rotary evaporator to give a 25 mL (Tyvek sample) or 50 mL (gloves)



Figure 1. Sections of the coverall analyzed.

final volume. Each sample was then analyzed by GLC-ECD. The recovery of procymidone was determined by fortification of the different samples (Table 2).

2.3.2. Analytical Method for Procymidone Determination in Air. For the measurement of airborne procymidone, the samplers consisted of a glass tube of diameter 10 mm containing a plug of polyurethane foam (PUF). These were connected to personal air-sampling pumps (SKC LTD 224-PCEX4) which were operated with an air flow regulated at 2 L/min. The extraction procedure of PUF was carried using a triple extraction with acetone (50 mL for each extraction) by ultrasonic bath, followed by filtration with 10 g of anhydrous sodium sulfate. This was then concentrated under vacuum, and finally blown down to a volume of 1 mL under nitrogen flow. This 1 mL extract was used for the final GLC-ECD analysis.

2.3.3. Air-Sampling Validation. The air-sampling system adopted for the field study was developed by evaluating a number of different procedures following the air-sampling methodology reported by Martinez Vidal et al. (1997) and the American Society for Testing Materials (ASTM, 1988). Recovery tests were also evaluated for each procedure.

Static recovery is the ability of the sampling medium to retain the spike solution when the sampling cartridge is stored under clean, quiescent conditions for the duration of the test period. An aliquot of 25 μ L of a procymidone solution of concentration 122 μ g/mL (3.05 μ g) was added to each PUF plug, so that the liquid spread out over the surface, and then the extraction was performed. The test was carried out at room temperature (25 °C and 45% relative humidity). There were three replicates of samples, in addition to the control samples of laboratory blanks (untreated) and samples fortified with acetone alone.

Retention efficiency is the ability of the sampling medium to retain a compound when added in the form of a liquid solution. This test has been carried out to verify the absorption capacity of the active compound by the PUF during the sampling process and during air transition. PUF plugs were fortified and connected to the personal sampling pumps for 3 h in the dark, with a 2 L/min air flow (18.5 °C, 53% relative humidity). Controls were provided by PUF plugs fortified and stored at a low temperature (<5 °C) and by PUF plugs not connected to a personal sampling pump.

Sampling efficiency is the ability of the sampling medium to trap the vapor of a particular pesticide or metabolite. The proportion of the analyte of interest collected and retained by

Table 2. Recovery (%) of Procydimone in Different Worker Clothes Media and Paper Patches^a

	spike solution (1 mL, 1.6 ppm)	spike solution (1 mL, 7.3 ppm)		spike solution (1 mL, 1.6 ppm)	spike solution (1 mL, 7.3 ppm)
paper	89.2 ± 5.7	84.1 ± 7.3	gloves	86.8 ± 4.8	89.1 ± 9.9
Sontara	89.7 ± 2.3	86.3 ± 4.7	blank	97.3	
Tyvek	87.5 ± 3.1	89.5 ± 7.7			

^{*a*} Mean of three replicates.

Table 3. Air-Sampling Validation

trial	fortification ^a (µg/mL)	recovery (%)	volatilization (%)
static recovery	122	89.10 ± 8.84	
retention efficiency	122	91.31 ± 4.57	
sampling efficiency			
40% UR, 25 °C	122	89.21 ± 5.04	4.89 ± 0.69
40% UR, 45 °C, N ^b	122	76.46 ± 21.41	31.17 ± 22.34
100% UR, 40 °C	122	65.94 ± 7.43	29.60 ± 6.88
100% UR, 40 °C ^c	442.5	91.60 ± 8.76	6.06 ± 2.84

^a 25 µL. ^b Under N flux. ^c With commercial formulate Sumislex.

the sampling medium is determined by introducing the analyte as a vapor in air (or in nitrogen) into the air sampler. The sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended field use. This experiment allows a mass balance measurement of the pesticide distributed in the air phase and on the wall of the flask used to generate the vapor. Furthermore, it gives a good indication of the sorption breakthrough curve of the sorbent by means of different PUFs positioned along the tube. To evaluate the sampling efficiencies, several tests were carried out with both the formulation and the active ingredient (in the form of the analytical standard) in different conditions of temperature and relative humidity. An extreme test condition, favoring volatilization, was carried out by using only the active ingredient (Table 3).

2.3.4. Greenhouse Studies. 2.3.4.1. Trial Description. Two studies were carried out in greenhouses of the Experimental Centre in Albenga (CERSAA), in West Liguria, during the months of February and March 1998. The studies were done with two types of pot-grown plants, young plants of daisies (Argyrantherum Frutescens spp.) and mature hydrangea (Hydrangea Macrophylla spp.). Foliar applications were made using a hand-held application technique (adjustable hydraulic full cone nozzle supplied by hose from a stationary pump) with the commercial formulation, which was formulated as a wettable powder containing 50% w/w procymidone. The formulation is packaged and marketed in 20×30 cm multilayer polythene bags inside cardboard boxes. The main details of the field trials are reported in Table 4. A diagram showing the route of the operator and a plan of the crop layout is shown in Figure 2. In trial 1 the operator applied the pesticide from the central alley of the greenhouse, pointing the nozzle toward the plants. In the second trial the application was done by the operator walking up and down individual pathways which were partially covered with plants. In the second trial the operator also made applications to potted plants placed on suspended benches (1.7 m above the ground).

2.3.4.2. Measurement of Potential Dermal Exposure. The evaluation of the dermal exposure of the operator during the mixer/loading and the application of the pesticide was carried out using the whole body dosimetry method. This method involves analysis of the whole garments worn by the mixerloader and applicator. The operator wore a Tyvek coverall and a pair of cotton gloves worn over latex gloves. For the mixerloader, only the potential dermal hand exposure was measured as studies done to generate data for the U.K. POEM had shown that coverall contamination rarely occurred during the mixing and loading process. The same person carried out mixingloading and application operations. However, media were changed between the two operations, so that separate data sets are available. After the pesticide mixture preparation, the gloves of the mixer-loader were collected and then stored as described in section 2.3.4.5. In the laboratory the coverall of the operator was disected into nine parts for analysis (Figure 1). The cotton gloves were extracted and analyzed separately to give values for the left and right hands.

2.3.4.3. Measurement of Potential Inhalatory Exposure. The potential inhalation exposure was measured using a personal air sampler connected to glass tubes containing PUF plugs. These were positioned close to the neck of the operator. The pump was regulated and calibrated to give a constant flow rate of 2 L/min of air. After the pesticide application the PUF samplers were collected and stored as described in section 2.3.4.5.

2.3.4.4. Measurement of Procymidone Concentration in the Air. Procymidone concentrations in air were monitored by sampling the greenhouse atmosphere during distinct periods following the application. The same air-sampling technique which was used with the operator during the application was also used to sample the greenhouse atmosphere. The sampler was positioned in the center of the treated area at a height of 170 cm. The air was sampled at different times of the day, to cover a range that included the night period and periods during the whole of the week following the pesticide application (Figure 3). For each sampling period the air was sampled for 3 h, with a clean PUF sampler being used for each sample time. During the sampling time the greenhouse was managed as normal, i.e., following routine agricultural practices which included the opening of vents during the hottest hours of the day (between 11:00 am and 3:00 pm).

2.3.4.5. Field Sample Fortification, Transport, and Loading. All the samples collected were kept in plastic bags and stored at low temperature (<5 °C) until they arrived at the laboratory where they were kept at -20 °C. All the PUF samples were treated in the same way. For each step of the field trial, field blank and fortified samples were prepared and stored with the experimental samples.

3. RESULTS AND DISCUSSION

3.1. Potential Dermal and Inhalatory Exposure. In the first trial with pot-grown daisies, the rate of potential dermal operator exposure was measured as 15.4 mL/h of the diluted spray mixture. However, the majority of the contamination was on the hands at a rate of 13.8 mL/h, and only 1.6 mL/h on the whole of the coverall. For the application to hydrangea the potential dermal operator exposure was approximately twice that for the daisies, with a total rate of 37.1 mL/ h. However, in this case the majority of the contamination was to the body of the operator at a rate of 30.0 mL/h, and only 7.1 mL/h on the gloves (see Table 5). In each case approximately 0.003% of the active ingredient applied to the crop area contaminated the coverall worn by the operator. The size and structure of the crop and the application technique influence the level of operator contamination. In the second trial, on the crop with the greatest leaf area, the crop was repeatedly in contact with the operator (Figure 2). This was observed to increase the amount of contamination. In trial number 1 the application was done without entering the crop area, which considerably reduced the amount of operator contamination.

In general the potential dermal exposure is low if compared with the average values from applications to greenhouse crops such as tomatoes or cucumbers (Glass

	marguerite (trial 1) (25/02/98)	hydrangea (trial 2) (4/3/98)
greenhouse	plastic tunnel	glass/iron house
crop	pot 19 cm diameter, 50 cm intrapots into the line, 40% soil cover cropping	pot 18×30 cm diameter, 45 cm intrapots into the line, 90% soil cover cropping
plot treated	$304 \text{ m}^2 (38 \times 8)$	$620.5 \text{ m}^2 (17 \times 36.5)$
application length (min)	6	6
sprayer	hydraulic hand-held lance, 5 L/min output at 20 bar of pressure	hydraulic hand-held lance, 6.5 L/min output at 23 bar of pressure
climatic conditions (in the greenhouse)	20 °C, UR 10%	25 °C, UR 30%
mixture concentration (g/L)	0.8	0.8
amt of mixture used (L)	30	39
procymidone concentration (g/L)	0.4	0.4
total procymidone applied (g)	12	15.6
irrigation	drop per pot	drop per pot
operator	male, 24 years old, 160 cm height	male, 24 years old, 180 cm height
greenhouse volume (m ³) ^a	500	2000
^a Estimation.		

TRIAL 2



TRIAL 1



Figure 2. Scheme of the operator walks during the application.

et al., 1998), and similar to values obtained with applications to flower crops and vegetables in northern Europe (van Hemmen, 1992; Nilsson and Papantoni, 1996) with manual applications. The pattern of contamination of the body areas was found to differ in the two trials (see Table 5). In trial number 2 the most contaminated areas of the body were the chest, because of the upward direction of the application, and the lower legs due to contact with the crop. The head and back were the least contaminated. In trial number 1 the contamination was low for all areas of the body apart from the gloves, the front thighs, and the lower right

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Figure 3. Procymidone dissipation in air after the application in the greenhouses.

Table 5.	Mixer-	Loader	and	Applicator	Potential
Exposure	e by Pro	ocymida	one		

	tria	l 1		trial	2	
section	μg	%	mL/h	μg	%	mL/h
head and neck	0.3	0.1	0.01	24.1	1.6	0.6
left arm	0.8	0.2	0.02	116.3	7.7	2.9
right arm	0.8	0.3	0.02	111.3	7.4	2.8
chest	1.1	0.3	0.03	172.9	11.5	4.3
back	1.7	0.6	0.04	73.8	4.9	1.8
thighs/waist front	2.5	0.8	0.06	139.0	9.2	3.5
thighs/waist back	8.2	2.7	0.20	84.3	5.6	2.1
lower leg left	2.8	0.9	0.07	246.3	16.3	6.2
lower leg right	14.3	4.6	0.36	254.5	16.9	6.4
glove right applicator	0.8	0.3	0.02	139.5	9.3	3.5
glove left applicator	275.6	89.2	6.89	145.8	9.7	3.6
PUF applicator	0.2			1.1		
glove right mixer	24.0		0.60	91.5		2.3
glove left mixer	14.8		0.37	145.8		3.6
mixer–loader (potential dermal)	38.7			237.3		
applicator (potential dermal)	308.9		7.72	1507.5		37.7
applicator (notential inhalation)	0.2		33.3 ^a	1.1		218.8*

^{*a*} μ g of ai/h at a breathing rate of 2.5 m³/h.

leg (which was closest to the nozzle during the application). The potential dermal exposure during the mixing and loading phase is much lower than during the application itself, and accounts for 6-8% of the total potential dermal exposure during the whole MLA (mixer-loader/applicator) process. Datasets from a number of European countries (Glass et al., 1999) and also those in the German model (Lundehn et al., 1992) indicate great variability (coefficient of variation >100%) in the levels of total body contamination for different crop conditions and workers. Therefore, the two studies reported from Italy may not be representative, and additional studies could show that other parts of the body may be contaminated using different operators or crop conditions.

3.2. Potential Inhalation Operator and Re-entry Exposure. The potential inhalation exposure during the application was 0.16 and 1.05 μ g for trial 1 and 2, respectively (Table 5). An estimated breathing rate for moderate work activity can be taken as 2.5 m³/h. So considering that the application only lasted for 6 min, the potential inhalation exposure of the operator is lower than for workers re-entering the greenhouse in the days following the application. Such workers spend hours in the greenhouse, to carry out a range of activities such as the manual opening and closing of the windows, moving plants around, etc. For the greenhouse in trial 2 the potential inhalation exposure 3 days after the application is still 7.5 μ g per working hour.

The dissipation of procymidone in the air can be described according to first-degree kinetics:

$$C(t) = C_0 \mathrm{e}^{-kt}$$

The half-lives so calculated are 100 h in trial 2 and less than 1 h in trial 1 (Figure 3).

This difference may be due to a number of factors such as the ventilation systems in the two greenhouses, different crop canopy architecture and density, and the different indoor climatic conditions (Table 4). As a matter of fact the volatilization of procymidone is higher from leaves to air than from soil to air; therefore, the higher leaf area of the hydrangea is likely to increase rates of volatilization and subsequently the amount of active ingredient in the air. Furthermore, the higher temperature and relative humidity of trial 2 would also enhance the volatility, as shown by laboratory studies to measure the parameters which affect volatility (Table 3). In the case of the greenhouse used for trial 2, the safe re-entry time could be greater than 1 week, depending on the amount of time spent in the greenhouse.

3.3. Model Estimation. The potential exposure data have been compared to the data estimated by the generic database adopted in Italy (CCPF, 1996) derived from the German model, which does not consider handheld application to short crops. Worse case values are used by CCPF in the absence of values for the short crop and assume that the operator applies the pesticide to 1 ha/day. In the model the amount of the pesticide mixture used is the same for the applicator and the mixer-loader. The potential dermal exposure of the applicator is evaluated for the whole body on the basis of data from studies using the patch methodology. For the mixer-loader only the hands are considered as contributing toward dermal exposure. In both cases the inhalation exposure is estimated, and the total exposure from both routes is reported as the amount of active ingredient (ai) available for body absorption per kilogram of ai (mg/operator kg of ai).

The comparison between the model prediction and the measured levels of potential exposure shows a difference (Table 6). The estimated mixer—loader potential exposure, both dermal and inhalation, is higher than the values achieved from the field studies. However, the applicator potential exposure estimation is lower than the measured potential exposure by more than a factor of 20. This is evidence that the estimation coefficient set for the hand-held application to ornamental and

Table 6. Comparison between the Model Estimate and the Measured Potential Operator Exposure (mg/person/kg of ai)^a

			daisy		hydrangea	
operator	$exposure^b$	$\mathbf{cofficient}^d$	estd	measd	estd	measd
mixer-loader	D _M (h)	21	8.3	1.28	5.3	3.82
	I_M	0.02	0.008	nr	0.005	nr
	total	21.02	8.3	1.28	5.3	3.82
applicator	$D_A(h)$	0.38	0.15	9.08	0.09	4.59
••	D _A (c)	0.06	0.024	0.01	0.015	0.39
	D _A (ub)	1.6	0.63	0.14	0.40	7.64
	$D_A(lb)^c$			0.91		11.66
	IA	0.001	0.0004	0.11	0.0003	0.35
	total	2.041	0.80	10.3	0.51	24.6

^{*a*} The operator applies 986/ha and 628 L/ha of procymidone at 1 ha/day, respectively, for daisies and hydrangea. At a concentration of 0.4 g/L. ^{*b*} Inhalation (I) and dermal (D) potential exposure of the hands (h), head and neck (c), upper body (ub), and lower body (lb). ^{*c*} The amount of exposure (mg/person) per kilogram of ai. ^{*d*} Not considered by the model.

horticultural crops is inadequate. There would appear to be a reasonable case for exposure to pesticides in greenhouses to be measured in experimental studies rather then by extrapolation from existing data used for modeling purposes.

3.4. Procymidone Risk Assessment in the Albenga Scenario. Procymidone has a low acute toxicity in the species examined such as dogs and rats (LD50 > 10 000 mg/kg of body mass) for both oral and dermal routes. The human metabolism is via hydroxylation of the methyl group followed by oxidation to carboxylic acid and hydrolysis of the imide or amide linkage. In laboratory studies with oral administration to animals, procymidone was rapidly excreted via urine in a few hours (JMPR, 1989). The levels causing no toxicological effect, i.e., the no observed adverse effect level (NOAEL), have been set to 15 mg/kg for mice, 12.5 mg/kg for rats, and 100 mg/kg for dogs. The accetable daily intake (ADI) for humans, via dietary intake, has been set at 0-0.2 mg/kg of body mass/day.

To evaluate the operator risk, we have to take into account a number of parameters: the length time during which the operator is likely to be exposed, the amount of dose absorbed by the body (with or without protective clothing), and the threshold values. The typical lifetime of ornamental crops on farms is 6 months for daisies and 12 months for hydrangea. During this period seven procymidone applications would normally be made to the hydrangea and five applications to the daisy crop. From this it is possible to estimate the total potential exposure for each scenario evaluated in the field studies. The conservative scenario defined in Italy (CCPF, 1996) assumes that the operator uses the pesticide every day during the cropping season, at a work rate of 6 h/day, for a fixed period of life (50 years). A realistic scenario would be for the operator to apply to only 1 ha in a 6 h day, with five to seven applications per crop per crop season (Table 7). The Italian Pesticide Commission in the absence of experimental studies assumes an estimation of the absorbed dose in the absence of experimental studies equal to 100% of the potential inhalation exposure plus 10% of the potential dermal exposure for both the mixer-loader and the applicator (CCPF, 1996). In reality few operators use adequate protective clothing at all times, with occasional use of a face mask and gloves, but rarely specific coveralls to prevent contamination of normal workwear. In this case, with little use of PPE, a greater

Table 7. Comparison of Calculated Absorbed Dose Using the Model Estimated and Measured Potential Operator Exposure (mg/person/day)^a

		absorbed dose (mg/person/day)							
		daisy			hydrangea				
operator	$exposure^{b}$	real	estd	measd	real	estd	measd		
mixer-loader	D _M (h)	0.13	0.83	0.01	0.38	0.53	0.04		
	I_M		0.01			0.01			
	total	0.13	0.84	0.01	0.38	0.54	0.04		
applicator	D _A (h)	0.91	0.02	0.91	0.46	0.01	0.46		
	D _A (c)	0.00	0.00	0.00	0.04	0.00	0.04		
	D _A (ub)	0.01	0.06	0.01	0.76	0.04	0.38		
	$D_A(lb)^c$	0.09		0.05	1.17		0.58		
	I_A	0.11	0.00	0.11	0.35	0.00	0.35		
total	mg/person/kg of ai	1.25	0.92	1.08	3.16	0.59	1.85		
	mg/person/ha	0.49	0.36	0.43	0.79	0.15	0.46		

^{*a*} Key: real, data measured in the field and assuming personal clothes only (realistic scenario); estd, data estimated by the model for the Italian standard scenario with the use of PPE; measd, data measured in the field and assuming use of PPE. ^{*b*} See footnote *b* of Table 6. ^{*c*} See footnote *c* of Table 6.

Table 8. Operator Risk Evaluation of Procymidone Use on Daisy and Hydrangea Crops in the Albenga Scenario

		daisy			hydrangea		
index	real	estd	measd	real	estd	measd	
ADI (60 kg of body mass ^a /total exposure)	24.3	33.5	28.1	15.1	81.61	25.8	
tot exposure \times TF ^b /AOEL \times 70 kg of body mass	0.20	0.14	0.17	0.64	0.12	0.38	

^{*a*} According to the WHO limits for 1 day exposure (60 kg of body mass), this corresponds to 12 mg per human (men and women). ^{*b*} The time factor is the fraction of the days in the year in which the pesticide is used (160/365 and 365/365 for daisies and hydrangea, respectively) multiplied by the fraction of the years in the life in which the use is possible (50/70).

proportion of the potential dermal exposure will actually result in dermal exposure. Therefore, the potential risk is higher, and it may be more realistic to allow for 50% of the potential dermal exposure to result in dermal exposure.

In the absence of threshold values of worker exposure the evaluation of the risk may be carried out using indices. The comparison between the recommended values for ADI and the measured level of potential exposure, CCPF (1996), requires the rate of NOAEL measured with animals to be reduced by a safety factor. In both cases an index lower than or equal to 1 is acceptable.

The results obtained using the data estimated by the models with the use of PPE fall below 1, indicating no risk for the operator. For hydrangea with a realistic scenario, assuming the absence of PPE, the risk is evident (2.92 and 2.86) as the high potential exposure we measured in our experiment (Table 7).

4. CONCLUSIONS

The results of this trial confirm the high variability of the operators' exposure when they work in different crop conditions and applications. In particular, the crop architecture and density, the application techniques, and the greenhouse significantly influence the fate of the active ingredient during and after the application.

The risks to the operators as a consequence of procymidone exposure in the horticultural area of Albenga are likely to be low, both during the mixing– loading phase and during the hand-held application when adequate protective clothing is used. On the other hand, there is likely to be a greater risk for the occasional procymidone handler, when normal personal clothes only are worn. Despite the fact that the area of the greenhouse applications is low, with farmers typically involved with PPP application for only 30 min a day, the absorbed daily dose may exceed the AOEL. It is evident that more attention should be paid to protective clothing which is often not used because it is not comfortable to wear in the operating conditions of the greenhouse. With respect to this, it is useful to remark that, considering the exposure distribution all over the body of the operator, there is a need to create more comfortable protective clothing. Because of the exposure of the lower part of the body, special types of protective clothing could be manufactured with different materials that give greater protection to the lower part of the body than to the top. Air-breathable fabric on parts of the body would allow heat to escape from the body of the operator more easily, while impermeable material around the legs would prevent penetration of the PPP.

Adequate measures should be taken for protection against inhalation exposure during re-entry to the greenhouse after the application. In certain circumstances procymidone concentrations in the air can persist for more than 1 week.

The discrepancy measured between the predicted and the measured data is evidence that the exposure model should be improved with respect to the manual application to the small crops in the greenhouse environment.

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LITERATURE CITED

Aprea, C.; Sciarra, G.; Sartorelli, P.; Desideri, E.; Amati, R.; Sartorelli, E. Biological monitoring of exposure to organophosphorus insecticides by assay of urinary alkhyl phosphates: influence of protective measures during manual operations with treated plants. *Int. Arch. Occ. Environ. Health* **1994a**, *66*, 333–338.

- Aprea, C.; Sciarra, G.; Sartorelli, P.; Ceccarelli, F.; Maiorano, M.; Savelli, G. Valutazione dell'assorbimento di ometoato e fenitrothion durante lavorazioni esguite con l'uso di mezzi personali di protezione in ambienti confinati. *Med. Lavoro* **1994b**, *85* (3), 242–248.
- Aprea, C.; Sciarra, G.; Lunghini, L. Analytical method for the determination of urinary alkylphosphates in subjects occupationally exposed to organophosphorus pesticides and in general population. J. Anal. Toxicol. **1996a**, 20, 559–563.
- Aprea, C.; Betta, A.; Catenacci, G.; Lotti, A.; Minoia, C.; Passini, W.; Pavan, I.; Robustelli della Cuna, F. S.; Roggi, C.; Ruggeri, R.; Soave, C.; Sciarra, G.; Vannini, P.; Vitalone, V. Reference values of urinary ethylenthiourea in four regions of Italy (multicentric study). *Sci. Total Environ.* 1996b, *192*, 83–93.
- Aprea, C.; Sciarra, G.; Sartorelli, P.; Sartorelli, E.; Strambi, F.; Farina, G. A.; Fattorini, A. Biological monitoring of exposure to chlorpyriphos-methyl by assy of urinary alkyl phosphates and 3,5,6-trichloro-2-pyridinol. *J. Toxicol. Environ. Health* **1997**, *50*, 581–594.
- Aprea, C.; Sciarra, G.; Sartorelli, P.; Mancini, R.; Di Luca, V. Environmental and biological monitoring of exposure to mancozeb, etylenthiourea and dimethoate during industrial formulation. *J. Toxicol. Environ. Health, Part A* **1998**, *53*, 101–119.
- ASTM. Standard practice for sampling and analysis of pesticids and polychlorinated biphenyls in indoor atmospheres; designation D 4861-88, 1988; 14 pp.
- Catenacci, G.; Valoti, E.; Disilvestro, P. Impiego di esteri fosforici in pioppicoltura: inquinamento ambientale, indicatori biologici di esposizione e di effetto su addetti allo spargimento. Risultati di un monitoraggio ambientale ebiologico. In *Rischio da utilizzo di esteri fosforici in pioppicoltura*; La Goliardica Pavese: Pavia, 1988; pp 235–248.
- CCPF *Criteri di riferimento per valutare il rischio per l'operatore*; Commissione Consultiva per i prodotti fitosanitari, Ministero della Sanità, 1996; 13 pp.
- Chen, W.; Watts, P. *European Operator Exposure Database*, Health Canada and NATO Workshop on methods of pesticide exposure assessment, Ottawa, 1993.
- Dec. Lgs. 626. Attuazione delle direttive 89/391/CEE, 89/654/ CEE, 89/655/CEE, 89/656/CEE, 90/269/CEE, 90/270/CEE, 90/394/CEE e 90/679/CEE riguardanti il miglioramento della sicurezza e della salute dei lavoratori sul luogo di lavoro, Gazzetta Ufficiale della Repubblica Italiana, Supplemento ordinario 141, 1994.
- Dec. Lgs. 194. Attuazione della direttiva 91/414 CEE in materia di immissione di prodotti fitosanitari, Gazzetta Ufficiale della Repubblica Italiana, 122, 1995, 170 pp.
- Ferrari, M.; Ardigò, S.; Maccarini, L.; Roggi, C.; Trevisan, M. Urinary level of ethylenthiolurea in an adult population: epidemiological research; 2nd European Pesticide Residue Workshop, Almeria, Spain, 1998; Poster C17.
- Glass, C. R.; Gilbert, A. The use of predictive operator exposure models as regulatory tools. In *The Environmental fate of xenobiotics*; Del Re et al., Eds.; La Goliardica Pavese: Pavia 1996; pp 83–96.
- Glass, C. R.; Mathers, J. J.; Martínez Vidal, J. L.; Egea González, F. J.; Moreira, J. F.; Machera, K.; Kapetanakis, E.; Capri, E. Use of visible tracers for applications to greenhouse crops to evaluate pesticide fate and potential

operator exposure; 2nd European Pesticide Residue Workshop, Almería, Spain, May 24–27, 1998.

- Glass, C. R.; Martínez Vidal, J. L.; Degado Cobos, P.; Moreira, J. F.; Meuling, W.; Machera, K.; Kapetanakis, E.; Capri, E.; Wilkins, R. M.; Kangas, J.; Tuomainen, A. Second Annual Report EU SMT Project Contract number SMT4-CT96-2048 October 1997 to October 1998; report to the European Commission DGXII, Brussels, March 26, 1999.
- JMPR Evaluation of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Expert Group—Part II Toxicology; FAO: Rome, 1989; pp 161–181.
- Lundehn, J. R.; Westphal, D.; Kieczka, H.; Krebs, B.; Löecher-Bolz, S.; Maasfeld, W.; Pick, E. D. Uniorm principles for safeguarding the health of applicators of plant protection products; Mitteilungen aus der Biologischen Bundesantalt für Land -und Forstwirtscharf, Heft 277, Berlin, Germany, 1992.
- Martin A. D. A predictive model for the assessment of dermal exposure to pesticides. In *Prediction of percutaneous penetration. Methods, measurement and modelling*, Scott, Guy, Hadgragraft, Eds.; IBC Technical Services Ltd., 1990; 35 pp.
- Martinez Vidal, J. L.; Egea-Gonzàlez, F. J.; Glass, C. R.; Martinez-Galera, M.; Castrocano, M. L. Analysis of lindane, α - and β -endosulfan and endosulfan-sulphate in greenhouse air by gas chromatography. *J. Chromatog. A* **1997**, *765*, 99– 108.
- Nicholson, P. H. *Physicochemical evaluation: the environment, an expert system for pesticide preregistration assessment*, Proceedings of the 1994 BCPC Conference, Pest and Disease, Brighton, 1994; pp 1337–1342.
- Nilsson, U.; Papantoni, M. Long-term studies of fungicide concentrations in greenhouses: 3. Exposure risks after spraying in greenhouses. J. Agric. Food Chem. 1996, 44, 2885–2888.
- PHED. *Pesticide Handlers Exposure Database*; reference manual; Versar Inc.: Springfield, VA, 1992.
- Russo, E.; Galeotti, M.; Maramotti, R.; Achilli, F.; Bosi, A. Worker exposure to pesticides during agricultural practice. *The Environmental fate of xenobiotics*; Del Re et al., Eds.; La Goliardica Pavese: Pavia, 1996; pp 567–574.
- Sciarra, G.; Aprea, C.; Sartorelli, P. Valutazione dell'escrezione urinaria di etilentiourea in soggetti professionalmente e non professionalmente esposti ad etilenbisditiocarbammati. *Med. Lavoro* **1994**, *16*, 49–52.
- Valerio, F.; Ciccarellli, F.; Falcello, R. Indiividual dose indices: a model to classify greenhouse farmers according to their exposure to pesticides. In *IX Symposium Pesticide Chemistry—Mobility and degradation of xenobiotics*; Del Re, Ed.; Biagini: Lucca, 1993; pp 815–823.
- Van Hemmen, J. J. 1992. Agricultural pesticide database for risk assessment. *Rev. Environ. Contam. Toxicol.* 1992, 126, 1–85.

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