SHORT COMMUNICATION
UDC 614.878:615.285.7:631.544

ASSESSMENT OF HUMAN EXPOSURE TO PESTICIDES IN GREENHOUSES AND EFFECTIVENESS OF PERSONAL PROTECTIVE DEVICES

LAURA IORIZZO[1], ANDREA BIANCHI[1], GASTONE GAMBERINI[1], ALDO RUBINO[1], MAURILIO MISSERE[2], GIOVANNI JR. MINAK[1], SANTE TABANELLI[2], FRANCESCO S VIOLANTE[2], GIOVANNI B RAFFI[2]

Public Service of Preventive Medicine and Occupational Hygiene, Rimini, Italy[1], Postgraduate School of Occupational Medicine, University of Bologna, Italy[2]

Received December 20, 1995

The exposure to pesticides in a group of workers growing vegetables in greenhouses in farms near Rimini in Italy was evaluated. The pesticides used were organophosphorus compounds, organochlorine compounds, carbamates, pyrethroids, amide and anilide derivatives. Measurements were carried out in seven greenhouses randomly selected. The environment was free of atmospheric agents which could have influenced the pesticide concentrations in the indoor air. Two types of chemical sampling were performed: environmental and personal. The latter was done in the liquid for washing hands and by means of pads applied directly to the worker's skin and to the clothes. The aim of the determination of airborne pesticide concentrations was to evaluate mean environmental exposure to pesticides in the sprayed areas. The sampling went on from a fixed point during the entire spraying period. The aim of individual sampling was to determine the active ingredients as contaminants. The values obtained showed a risk of exposure for the greenhouse personnel working without using personal protective devices (masks, gloves and waterproof clothes), considering that pesticides could be absorbed through the skin in between the spraying intervals.

Key terms:
environmental airborne pesticides, greenhouses pesticide pollution, pesticide exposure, skin pesticide contamination

The effectiveness and selectivity of pesticides are very often related to microclimate and to previous use. In greenhouses with controlled microclimate many varieties of parasites are known to change susceptibility to pesticides. For

Presented at 1st Croatian Congress on Occupational Health with International Participation, Opatija, Croatia, October 26–28, 1995

Arh hig rada toksikol, Vol 47 (1996) No 1, pp. 25–33

this reason new pesticides are being used (1, 2). In greenhouses first and second class pesticide formulations are mainly used; increasing doses are applied and so is the number of applications, to the detriment of workers and consumers.

The aim of this study was to evaluate pesticide exposure of workers whose job was to spray pesticides by means of manual sprayers.

SUBJECTS AND METHODS

The study took place in greenhouses near Rimini in Italy. Seven greenhouses out of 19 were randomly selected for the study. The exposure to pesticides of the workers employed to grow vegetables was evaluated (one sprayman in each greenhouse). As closed environments the greenhouses were free from the effect of atmospheric agents which could influence the results of pesticide levels in the air.

Table 1 *Sampled active ingredients*

Active ingredients	Chemical formula	Chemical group	Toxicological class	TLV-TWA mg/m^3	LD_{50} mg/kg	ADI mg/kg
Primicarb	$C_{11}H_{18}N_4O_2$	Carbamate compounds	Ic		107	0.02
Clorothalonil	$C_8Cl_4N_2$	Organochlorine compounds	IIa		300	0.005
Metalaxyl	$C_{15}H_{21}O_4N$	Amide derivates	IIc		670	0.03
Copper oxychloride	$3CuOCuCl_2\ 3H_2O$	Copper compounds	IId		1440	
Methomyl	$C_5H_{10}SO_2N_2$	Carbamate compounds	Ia	2.5	17	
Endosulfan	$C_9H_6C_{16}O_{3S}$	Organochlorine compounds	Ic	0.1 skin	80	0.008
Methyl parathion	$C_8H_{10}NO_5PS$	Organophosphorus compounds	Ia	0.2 skin	6	0.02
Thiram	$C_6H_{12}N_2S_4$	Dithiocarbamate compounds	IIb	1 skin	560	0.005
Iprodione	$C_{13}H_{13}O_3N_3Cl_2$	Anilide derivatives	III		3500	0.3
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	Pyrethroid	Ic		135	0.01
Heptenophos	$C_9H_{12}ClO_4P$	Organophosphorus compounds	Ic		96	

Pesticide exposure was determined by measurements in the air and also on the skin and clothes of the workers. Two kinds of chemical sampling was carried out: environmental and personal (3, 4). The environmental sampling in the air was performed using a unit (pump and bubblers) placed in the centre of the greenhouses and personal sampling was carried out using a personal sampling pump to collect the air from the worker's breathing zone. Seven workers, one from each greenhouse (marked 1 through 7 in the tables), who sprayed pesticides, were subjects to personal sampling. Environmental sampling was continuous and lasted throughout the spraying period (Table 1); it was conducted from the height of 1.50–1.60 m. Two pairs of bubblers in succession were used, one containing acetone and the other acidulous water to sample active ingredients soluble in water or in solvent. The pesticide concentration in the air of the worker's breathing zone was measured with a personal sampler with two glass fibre filters placed in succession. The evaluation of pesticide on the skin was made directly from the dosage of pesticides in the washing liquid (ethanol 95%) at the beginning and at the end of the spraying treatment.

Another type of pesticide sampling involved the application of pads to the worker's chest, back, forearms and legs, as well as to the inside and outside of the working clothes. This enabled us to assess also the protection provided by working clothes. The active ingredients were dosed by Perkin Elmer gas chromatographs models 8700 and 8500 with capillary columns (length 30 m); for dosing copper compounds an atomic absorption spectrophotometer was used.

RESULTS

Table 2 shows average pesticide concentrations in the environment when sampling was done with the two bubblers. For some pesticides (Metalaxyl, Thiram, Iprodione) the sampled amounts were found to be below the detection limits, mainly because of short sampling time. The detection limit values were not constant for the same active ingredient as they depended on sampling time.

Environmental sampling was carried out in only one greenhouse (No. 7). Table 3 shows the results of personal air sampling which was carried out in the worker's breathing zone and on the hands. Some workers had higher values at the beginning of work than at the end. This could probably be due to irregular use of gloves or because they did not clean their hands before using gloves so that a cumulative effect from previous exposures might have been involved. The results of pesticide determinations on pads are reported in Table 4.

Arh hig rada toksikol, Vol 47 (1996) No 1, pp. 25–33

Table 2 *Environmental sampling (air concentration of active ingredients)*

Active Ingredients	Bubbler with acidolous water, μg/m³	Bubbler with acetone, μg/m³	Greenhouse No.
Pirimicarb	13.2	13..68	1
Chlorothalonil	11.85 42.0 26.0	19.6 22.9 152.3	1 3 5
Metalaxyl	< 54.5 < 28.1 < 56.1 < 18.7	< 54.5 < 28.1 < 56.1 < 18.7	1 2 5 6
Copper oxychloride	73 130.4 225.0	24.4 65.3 24.2	2 3 6
Methomyl	182.8	65.3	3
Endosulfan	19.1	44.2	4
Methyl parathion	16.9	19.3	4
Thiram	< 33.8	< 33.8	4
Iprodione	< 20.6	< 20.6	6
Deltamethrin	141.9	< 26.4	5
Heptenophos	49.2	69.7	7

Values preceded by < refer to detection limits. The limit values are not constant for the same active ingredient; they depend on sampling time.

Arh hig rada toksikol, Vol 47 (1996) No 1, pp. 25–33

Table 3 *Personal sampling in the worker's breathing zone and on hands*

Active ingredients	Air in the worker's breathing zone ($\mu g/m^3$)		Hands cleaning liquid* (μg)		Greenhouse No.
	Filter 1	Filter 2	Beginning of work	End of work	
Pirimicarb			49.3	29.7	1
Chlorothalonil	9.7 3.74	<1.3 <0.26	<0.03 8.8 18.7	8.07 120.7 63.2	1 3 5
Metalaxyl	<0.8 <15.3 <5.1	<0.8 <15.3 <5.1	9.5 <1.1 69.3 <1.1	20.0 <1.1 <1.1 3.2	1 2 5 6
Copper oxychloride	63.5 10 20.2	<5.2 <10.0 <3.3	1.8 12.2 <0.7	5.7 3.0 <0.7	2 3 6
Methomyl	15.5	13.8	2.9	3.0	3
Endosulfan	17.3	3.2	6.4	0.9	4
Methyl parathion	8.9	6.7	6.9	0.5	4
Thiram	<33.8	<33.8	<4.7	<4.7	4
Iprodione	<5.9	<5.9	<1.3	7.6	6
Deltamethrin	22.6	<20.5	40.0	16.9	5
Heptenophos	18.8	16.2			

Values preceded by < refer to the detection limits.
For the environmental sampling limit values are not constant for the same active ingredient as they depend on sampling time
* The active ingredients were detected after ethanol evaporation

Arh hig rada toksikol, Vol 47 (1996) No 1, pp. 25–33

Table 4 *Personal sampling on pads applied to the inner (A) and outer side (B) of working clothes (values of active ingredients are in µg/dm²)*

Active ingredients	Right forearm		Left forearm		Right leg		Left leg		Chest		Back		Greenhouse No.
	A	B	A	B	A	B	A	B	A	B	A	B	
Pirimicarb	0.90	5.7	1.25	1.78	1.05	2.44	0.46	1.25	0.87	1.16	BL	1.45	1
Chlorothalonil	0.27	3.2	1.76	1.88	1.50	4.76	BL	1.58	BL	0.16	0.03	3.66	1
	3.8	16.0	4.5	6.0	2.3	516.0	7.2	845.9	BL	26.0	BL	7.4	3
	BL	3.40	BL	BL	BL	11.9	BL	3.2	BL	BL	BL	BL	5
Metalaxyl		BL	BL	BL	BL	3.05	BL	2.20	BL	BL	BL	5.23	1
	BL	BL	BL	BL	BL	9.34	BL		BL	BL	BL	6.0	2
	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	BL	5
	BL	BL	BL	BL	BL	220.8	BL	86.4	BL	BL	BL	BL	6
Cooper oxychloride	19.5	19.5	15.5	21.0	26.0	65.5	21.5		11.5	14.0	15.5	23.5	2
	41.5	48.0	35.5	42.5	62.0	343.0	47.0	392.0	32.5	38.0	36.5	41.0	3
	18.1	27.5	20.0	22.5	26.3	774.3	25.0	741.2	20	21.9	16.9	20.0	6
Methomyl	3.0	4.1	1.4	2.1	4.3	4.8	2.9	3.0	2.7	5.2	2.8	3.0	3
Endosulfan	1.6	10.3	BL	6.1	1.5	3.1	1.7	19.0		BL	2.6	4.9	4
Methyl parathion	1.8	3.9	0.5	5.2	2.1	31.4	3.0	28.7	0.9	2.9	1.4	4.0	4
Thiram	BL	85.2	BL	119.9	BL	227.0	BL	215.5	BL	31,2	BL	43.7	4
Iprodione	BL	BL	BL	BL	BL	208.1	BL	118.9	BL	BL	BL	BL	6
Deltamethrin	BL	BL	BL	BL	BL	BL	BL	5.6	BL	10.3	BL	BL	5

BL=below limits of detection. The limits of detection (µg/dm²) are: Primicarb 0.43, Chlorothalonil 0.02, Metalaxyl 2.4, Endosulfan 0.2, Thiram 9.5, Iprodione 2.5, Deltamethrin 0.53

Considering that the whole body surface is 1,70 square metres, with chest 18%, back 18%, upper limbs 18% and lower limbs 18%, we obtained a hypothetical deposit on the skin as reported in Table 5.

The personal protective devices used by the workers in the selected greenhouses are reported in Table 6.

Table 5 *Hypothetical total deposit on the skin during spraying*

Sampled active ingredients	Total amount of active ingredients in μg	Greenhouse No.
Pirimicarb	*160.13 – 173.29	1
Chlorothalonil	*79.08 – 79.10 *429.53 – 429.93 ≤1.7	1 3 5
Metalaxyl	≤ 370.26 ≤ 465.12 ≤ 387.1 ≤ 387.1	1 2 5 6
Copper oxychloride	2815.2 6357.15 3473.1	2 5 6
Methomyl	488.07	3
Endosulfan	*210.74 – 211.14	4
Methyl parathion	261.63	4
Thiram	≤ 1598.85	4
Iprodione	≤ 420.75	6
Deltamethrin	≤ 89.2	5

Values were obtained utilizing those from Table 4 considering: $y=a \cdot b \cdot c$ where: y=referred values in Table 5, a=sampling values (Table 4) or limits of detection, b=170 dm^2, c=% of body surface.
* Theoretical range

Table 6 *Protective equipment*

Greenhouse No.	Protective equipment	Active ingredients	Exposure time (min)
1	rubber gloves, cotton coverall, *mask**	Primicarb, Metalaxyl, Chlorothalonil	50
2	cerate trousers, rubber boots, thick filling cotton jacket, rubber gloves**, *mask**	Metalaxyl, Copper oxychloride	60
3	thick filling cotton coverall, rubber gloves, rubber boots, *mask**	Chlorothalonil, Methomyl, Copper oxychloride	40
4	rubber gloves, thin filling cotton coverall, cotton hat, *mask	Endosulfa, Methyl parathion, Thiram	60
5	cotton coverall, rubber boots, rubber gloves, *mask**	Deltamethrin, Metalaxyl, Chlorothalonil	35
6	cerate trousers, rubber boots, thick filling cotton jacket, rubber gloves**, *mask**	Metalaxyl, Copper oxychloride, Iprodione	100
7		Heptenophos	94

* mask with an activated-carbon gas filter cartridge; ** put on during the spraying

Arh hig rada toksikol, Vol 47 (1996) No 1, pp. 25–33

DISCUSSION AND CONCLUSIONS

Pesticide air concentrations measured in the environment and on the worker's skin showed that greenhouse workers were exposed to toxic compounds and that even a short exposure to those compounds may have caused health damage. Moreover, exposure to pesticides through skin absorption which may take place between the spraying intervals should also be considered (5).

Obviously, wearing personal protective devices during pesticide spraying does not guarantee an effective protection against skin contamination. For this reason we consider that personal protective equipment (masks, goggles, boots and clothes), even when correctly used, do not provide adequate safety to the sprayers, as their choice and use are conditioned by factors such as comfort, durability and low cost.

The aim of protective equipment is to exclude pesticides from all possible contact with the body surface or breathing system. Whether this aim is actually achieved will depend on the proper use and technical validity of the equipment. In our study the workers very often failed to observe normal preventive measures.

Protective clothing (whose efficacity varies greatly according to fabric, pesticide and the interaction between tissue fibers and chemical compounds) has to be thermally comfortable and impermeable (6). Previous treatment of cotton and polyester/cotton with water repellent products may improve impermeability (6).

According to some authors the fabric previously treated with water repellent or cleaning products reduced pesticide absorption by about 90% (6, 7). Pesticides can be absorbed through fasteners, zips and seams. Clothes must not be too tight and must permit free movement.

Clothes have to be cleaned immediately after every exposure to pesticide; they require precleaning with water and washing at high temperature, use of bleach and repeated rinsing.

Protective gloves must have a good abrasion resistance, elasticity, fit and failure time (interval between external contact with pesticide and its internal detection) and rate of permeability (the amount of pesticide that penetrates inside the glove is in linear correlation with the square root of permeability time) (7).

Respiratory protective devices are very important. The ones most often used are half-masks and air-purifying helmets both based on an activated-carbon gas filter cartridge providing protection for a given number of working hours. The efficiency of filters is affected by environmental humidity: values over 65% quickly reduce holding time. Information about filter substitution is mainly empirical: in fact it is recommended to renew filters as soon as workers smell the pesticide used. For occasional use it is recommended to use a new filter every six months, for continuous use to replace them after 40 hours or after a week (7).

A typical problem with the use of mask concerns possible inhalation of toxic vapours if the mask does not fit properly. The problem may arise with bearded people. For people with a beard contaminated air penetration may be as high as 8% against 0.03% in people without a beard.

REFERENCES

1. *Archibald BA, Solomon KR, Stephenson GR.* Estimation of pesticide exposure to greenhouse applicators using video imaging and other assessment techniques. Am Ind Hyg Assoc J 1995;56:226-35.
2. *Adamis Z, Antal A, Fuzesi I, Molnar J, Nagy L, Susan M.* Occupational exposure to organophosphorus insecticides and synthetic pyrethroid. Int Arch Occup Environ Health 1985;56:299-305.
3. *Mesters R, Francois C, Causse C, Vian L, Winnet G.* Survey of exposure to pesticides in greenhouses. Bull Environ Contam Toxicol 1985;35:750-6.
4. *Stamper JH, Nigg HN, Mahon WP, Nielsen AP, Royer MD.* Pesticide exposure to greenhouse foggers. Chemosphere 1988;17:1007-23.
5. *Brouwer R, Marquat H, de Mik G, Hemmen JJ.* Risk assessment of dermal exposure of greenhouse workers to pesticides after re-entry. Arch Environ Contam Toxicol 1992;23:273-81.
6. *Raheel M.* Dermal exposure related to pesticides. The barrier effectiveness of protective clothing. J Environ Health 1988;5:82-4.
7. *Betta A, Desideri E, Londini P.* Efficacia delle protezioni personali in agricoltura. Lavoro Sicuro 1992;19:57-62.
8. Valori limite di soglia ACGIH 1994-95. Giornale degli Igienisti Industriali 1995;20(Suppl. 1).

Sažetak

PROCJENA IZLOŽENOSTI LJUDI PESTICIDIMA U STAKLENICIMA I DJELOTVORNOSTI OSOBNE ZAŠTITNE OPREME

Istraživana je izloženost pesticidima u skupini radnika zaposlenih u staklenicima za uzgoj povrća u blizini Riminija u Italiji. Primjenjivani pesticidi bili su organofosforni, organoklorirani, karbamatni spojevi, piretroidi te derivati amida i anilida. Mjerenja su provedena u sedam slučajno odabranih staklenika. Unutrašnjost staklenika bila je izolirana od vanjskih utjecaja kako pesticidi u vanjskoj atmosferi ne bi utjecali na koncentracije u atmosferi staklenika. Provedene su dvije vrste sakupljanja uzoraka tijekom razdoblja raspršivanja pesticida: iz okoliša i sa ispitanika. U uzorcima zraka sakupljenim u atmosferi staklenika izmjerene su prosječne koncentracije pesticida u području raspršivanja pesticida. Također je sakupljena tekućina za ispiranje ruku radnika i pasivni upijači zagađivala s kože radnika i sa odjeće. Svrha individualnog sakupljanja bila je odrediti aktivne sastojke zagađivala. Dobiveni rezultati pokazuju rizik za izloženost radnika u staklenicima kada rade bez zaštitne opreme (maske, rukavice i vodootporna odjeća) imajući na umu da se pesticidi mogu apsorbirati kožom i u razdoblju između raspršivanja pesticida.

Ključne riječi:
izloženost pesticidima, onečišćenje kože pesticidima, onečišćenje pesticidima u staklenicima, pesticidi u zraku okoliša

Requests for reprints:

Prof. Giovanni Battista Raffi
Via Degli Orti n. 45
40137 Bologna, Italy