Bull. Environ. Contam. Toxicol. (2003) 70:415–421

DOI: 10.1007/s00128-003-0002-8

Bulletin of Environmental Contamination and Toxicology

Use of Manganese as Tracer in the Determination of Respiratory Exposure and Relative Importance of Exposure Routes in the Safety of Pesticide Applicators in Citrus Orchards

M. L. Oliveira, J. G. Machado-Neto

Department of Crop Protection, Faculty of Agrarian and Veterinarian Sciences, State University of São Paulo, Via de Acesso Prof. Paulo Donato Castellane, s/n, 14.884-900, Jaboticabal, São Paulo State, Brazil

Received: 10 June 2002/Accepted: 20 January 2003

Citrus orchards are the fifth major user of pesticides in Brazil, corresponding to 4% of the total sales of $ 2.5 B in 2000 (SINDAG 2000). Conventional pesticide application on citrus have low efficiency, with 47 to 50% retention of the 10 L of spray applied per plant with handgun sprayer and 30 to 45% of 7 L applied with air-assisted sprayer (Matuo 1988). Therefore, the large quantity of spray not retained by the plants is dispersed in the surroundings and could reach workers and cause intoxication.

Occupational exposure to pesticides can be controlled by reducing contact of these products to the exposure routes of the body. Quantification of skin and respiratory exposures and determination of its relative importance in total exposure are fundamental in the selection of effective, comfortable and economical safety measures. Generally more than 99% of the total exposure occurs through the dermal route and less than 1% through the respiratory route in the field conditions (Wolfe et al. 1972; Van Hemmen 1992).

Occupational exposure to pesticides can be quantified by measuring tracers added to the application spray (Jensen 1984). Metallic cations are known to be excellent tracers in sprays because of their low toxicity. They do not degrade during testing, transport and storage of the samples and are usually selective for cultivated plants. Metallic cations have a low cost and their recovery from samplers by analytical procedures is highly efficient. Copper cation from copper oxychloride fungicide was utilized very efficiently as tracer in the determination of dermal exposures of workers in staked tomato plants (Machado-Neto 1990). In a similar manner Mn^{+3} from manganese sulfate could be utilized as tracer in the quantification of respiratory exposure to pesticides.

The purposes of this study were to determine the effectiveness of Mn^{+3} from manganese sulfate as tracer in determining respiratory exposure to pesticides, the relative importance of the dermal and respiratory exposure routes and their effects on total exposure and safety of the working conditions to workers applying pesticides on citrus orchards utilizing handgun sprayer and air-assisted sprayer.

Correspondence to: J. G. Machado-Neto

MATERIALS AND METHODS

Mixed cellulose ester filters (SKC) with 0.8 μm pore size and 37 mm diameter were utilized for sampling manganese cations (Mn^{+3}) in cassettes of individual air sampling pumps to determine respiratory exposure. Recovery of Mn^{+3} from the mixed cellulose ester filters was performed after adding increasing volumes of an aqueous solution of manganese sulfate containing 692 ppm Mn^{+3}. After drying under laboratory conditions the filters were placed in plastic flasks containing 20 mL 0.2 N HCl, for two hours for the solubilization and recovery of Mn^{+3}. Manganese cation was quantified in solutions by atomic absorption spectrophotometer (GBC 932AA). The recovery data were statistically analyzed by means of polynomial regression fitted to linear equation (Pimentel-Gomes 1963).

The safety of the working conditions was calculated from the data on the potential dermal exposure (PDE) and the potential respiratory exposure (PRE) during 1999 and 2000 in orchards located in the state of São Paulo. Application using handgun sprayer was carried out in Pêra-rio orchards with 2.5 to 3.0 m high plants and air-assisted sprayer in Valência orchards with 4.5 to 5.0 m high plants.

The handgun sprayer utilized was 2000-L capacity Rolanzir high pressure sprayer equipped with two 4-m hoses with D10 nozzle tips. In this type of spraying one tractor operator works together with two applicators that are positioned on a platform located at the rear of the spray tank at 0.5 m from the ground. Spraying is performed directing the jets to one side of each plant of two rows moving the spray jets in such a way that they reach the top and low parts of the plants.

Air-assisted sprayer utilized was 2000-L capacity Arbus 2000 Valencia (Jacto). J5-2 nozzle tips were alternated with J5-3 nozzles the lowest positioned at 1.2 m from the ground. In this type of spraying only the tractor driver is required.

The two types of sprayers applied 10 L of spray liquid per plant, at 21 bar of pressure. PDEs of the workers to the sprays containing copper fungicide Cuprogarb 500 WP were quantified through the copper cation as tracer (Machado-Neto 1997). The samplers utilized were overalls, cotton gloves and female hygiene pads. Exposure was determined for short periods of one hour of work and subsequently extrapolated to a whole day of six hours of effective exposure (Machado-Neto 1997). PREs were determined on mixed cellulose ester filters, with 0.8 μm pore size utilized in cassettes of continuous-flow air pumps (A. P. Buck) with 2 L/min flow rate. The cassettes were positioned in the breathing region of the workers exposed to the sprays containing Mn^{+3}, which was utilized as tracer. PREs were determined for periods of approximately three hours and extrapolated to a day of six hours of effective exposure. All the activities were assessed from data gathered from 10 repetitions.

After the exposures, the overalls were cut into pieces, the cotton gloves, the female hygiene pads and the mixed cellulose ester filters were immersed in 0.2 N HCl to extract the cations. The samplers remained in the solubilizing agent for two hours. Subsequently, an aliquot was filtered with qualitative filter paper and the tracers were quantified by atomic absorption spectrophotometer (Machado-Neto and Matuo 1989). Exposures to the sprays were calculated from the concentrations of tracer measured and the respective concentrations of the pesticides in the sprays, according to Jensen (1984). PDEs and PREs were calculated for the 21 most toxic and most utilized pesticides in citrus orchards, taking into account their respective recommended doses (Andrei 1999).

The safety of these working conditions was calculated using the formula for margin of safety (MOS) by Severn (1984) modified by Machado-Neto (1997), which is as follows: MOS = (NOEL x 70) / (QAE x 10), where: MOS = margin of safety, NOEL = no observed effect level (mg/kg/day) (Tomlin 1997); 70 = average body weight (kg); 10 = safety factor to compensate for the extrapolation of NOEL values obtained in laboratory animals to those for humans (Brouwer et al. 1990); and QAE = quantity absorbed exposure (mg/day). In the calculation of the MOS for the dermal route (PDE), a QAE = 10% of the PDE determined (0.1 x PDE) was considered, and for the respiratory route (PRE), a QAE = 100% of the PRE. For total MOS (PDE + PRE), QAE = [(0.1 x PDE) + (PRE)]. The criterion utilized for the classification of the safety of work conditions was the following: if MOS $\geq$ 1, safe conditions, acceptable exposure and tolerable risk; and if MOS $<$ 1, unsafe conditions, unacceptable exposure and intolerable risk (Machado-Neto 1997).

RESULTS AND DISCUSSION

The recovery of manganese cations (Mn^{+3}) from mixed cellulose ester filters was fitted to the linear equation $X = (Y - 0.06) / 0.92$ ($R^2 = 0.999$), where: X = concentration of Mn^{+3} in the sampling filter corrected for recovery, and Y = concentration of Mn^{+3} measured in the samplers (Table 1). Recovery of Mn^{+3} from filters previously contaminated was 91.2%.

The dermal exposure of the tractor operator applying pesticides with a handgun sprayer was 99.98% of the total exposure and only 0.02% was from the respiratory exposure. In pesticide applicators operating handgun, 99.99% of the total exposure was through the dermal route and only 0.0077% through the respiratory route. In applications using the air-assisted sprayer, dermal exposure was 99.99% of the total exposure and respiratory exposure just 0.0042%. The percentage values of the relative importance of the exposure routes of the pesticide applicators in citrus orchards (Table 2) are similar to those reported by others (Wolfe et al. 1972; Van Hemmen 1992).

Table 1. Concentrations of manganese cations (Mn^{+3}), from manganese sulfate, added to sprays and mean values of concentrations recovered from the mixed cellulose ester filters, with the respective linear predictions and fitted equation.

Concentration Added	Concentration Recovered	Linear Prediction
0.00	0.03	0.06
0.40	0.43	0.42
0.70	0.70	0.67
1.00	1.00	0.97
1.40	1.33	1.34
2.80	2.60	2.61
F Treatment	1,445.00**	
F Linear regression		7,224.00**
Fitted equation Y = 0.06 + 0.92 X (R^2 = 0.999)		

** (P < 0.01)

Table 3 shows that only respiratory exposure of the three activities examined was used to classify 21 pesticides at recommend doses as safe (MS ≥ 1). For the tractor driver working with handgun sprayer, dermal exposure (PDE) and total exposure (PDE + PRE) were used to classify fourteen pesticides at recommended doses as safe (acrinathrin, azocyclotin, benomyl, bromopropylate, chlorothalonil, cyhexatin, deltamethrin, fenbutatin oxide, fenpyroximate, hexythiazox, propargite, thiophanate methyl, trichlorfon and vamidothion).

Table 2. Mean values for potential dermal exposures (PDEs) and potential respiratory exposures (PREs).

Potential Exposure (mL/day)	Handgun sprayer		Air-assisted sprayer
	Tractor driver	Applicator	Tractor driver
Dermal	57.2	356.7	496.8
(S.D.)	(±16.57)	(±83.37)	(±84.13)
Respiratory	0.0138	0.0276	0.0209
(S.D.)	(±0.0008)	(±0.0014)	(±0.0025)

S.D. = standard deviation n = 10

For the applicator using handgun, dermal exposure (PDE) was used to classify nine compounds at recommended doses as safe (acrinathrin, benomyl, bromopropylate, fenbutatin oxide, fenpyroximate, hexythiazox, propargite, thiophanate methyl and vamidothion). However, considering the total exposure (PDE + PRE) of these pesticide applicators, it was only possible to deem propargite at the recommended dose as being safe.

For the tractor driver working with air-assisted sprayer, dermal exposure (PDE) and total exposure (PDE + PRE) were used to classify eight recommended compounds as being safe (acrinathrin, benomyl, bromopropylate, fenbutatin oxide, fenpyroximate, hexythiazox, thiophanate methyl and vamidothion).

For tractor driver working with the two types of sprayers, the PDEs were the determinant exposures for safety, independent of the PREs. The greater importance of the dermal exposure route compared to the respiratory exposure routes in these studies is also evident from the doses of active ingredients recommended as being safe, calculated from the PDEs and PREs, separate and combined.

Table 3. Classification of safety as a function of the MOS calculated for the exposure routes studied for 21 active ingredients at recommended doses.

Safety for exposure routes	Recommendations of active ingredient.		
	Handgun sprayer		Air-assisted sprayer
	Tractor driver	Applicator	Tractor driver
DERMAL ROUTE (Potential Dermal Exposure)			
Safe	1* - 5, 7, 8, 12 - 14, 17, 18, 20 and 21	1, 3, 4, 12 - 14, 17, 18 and 21	1, 3, 4, 12 - 14, 18 and 21
Unsafe	6, 9 - 11, 15, 16 and 19	2, 5 - 11, 15, 16, 19 and 20	2, 5 - 11, 15 - 17, 19 and 20
RESPIRATORY ROUTE (Potential Respiratory Exposure)			
Safe	1-21	1-21	1-21
Unsafe	-	-	-
TOTAL (Potential Dermal Exposure + Potential Respiratory Exposure)			
Safe	1 - 5, 7, 8, 12 - 14, 17, 18, 20 and 21	1, 3, 4, 12 - 14, 18 and 21	1, 3, 4, 12 - 14, 18 and 21
Unsafe	6, 9, 10, 11, 15, 16 and 19	2, 5 - 11, 15 - 17, 19 and 20	2, 5 - 11, 15, 16, 17, 19 and 20

Legend: 1=acrinathrin, 2=azocyclotin, 3=benomyl, 4=bromopropylate, 5=chlorothalonil, 6=chlorpyrifos, 7=cyhexatin, 8=deltamethrin, 9=dicofol, 10=dimethoate, 11=ethion, 12=fenbutatin oxide, 13=fenpyroximate, 14=hexythiazox, 15=methidathion, 16=parathion methyl, 17=propargite, 18=thiophanate methyl, 19=triazophos, 20=trichlorfon e 21=vamidothion.
*** numbers correspond to the above products.**

The safety of working conditions of pesticide applicators using a spray handgun was similar to that for tractor driver, except in the recommended doses of propargite, which was classified as safe (MOS = 1.09) at least with dermal exposure (PDE) and unsafe (MOS = 0.85) with total exposure (PDE + PRE). This exception is due to the fact that the calculated MOS value was close to one. In this case, the respiratory exposure value, being very low, made the working conditions with this acaricide unsafe.

These results showed that the safety of the exposures to pesticides at recommended doses for citrus orchards is influenced by the intrinsic toxicity of each pesticide and by the exposure due to the specific working conditions, in agreement with Turnbull (1985).

Acknowledgments. The authors extend their gratitude to the Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP, for the scholarship granted to the first author and for financial assistance making this study possible.

REFERENCES

Andrei E (ed) (1999) Compêndio de defensivos agrícolas: guia prático de produtos fitossanitários para uso agrícola. Organização Andrei Editora LTDA, São Paulo. 672p.

Brouwer DH, Brouwer R, De Vreede JAF, De Mik G, Van Hemmen JJ (1990) Respiratory exposure to field-strength dusts in greenhouses during application and after re-entry. Annual report 1990. TNO Health Research: 183 –184.

Jensen JK (1984) The assumptions used for exposure assessments. In: Siewierski M (ed) Determination and assessment of pesticide exposure. Elsevier, New York, p 147-152.

Machado-Neto JG (1990) Quantificação e controle da exposição dérmica de aplicadores de agrotóxicos na cultura estaqueada de tomate, na região de Cravinhos, SP. (Tese de Doutorado) - Faculdade de Ciências Agrárias e Veterinárias, Universidade Estadual Paulista. Jaboticabal.

Machado-Neto JG (1997) Estimativas do tempo de trabalho seguro e da necessidade de controle da exposição dos aplicadores de agrotóxicos. (Tese de Livre-Docência) - Faculdade de Ciências Agrárias e Veterinárias, Universidade Estadual Paulista. Jaboticabal.

Machado-Neto JG, Matuo T (1989) Avaliação de um amostrador para o estudo da exposição dérmica potencial de aplicadores de defensivos agrícolas. Ciência Agronômica, Jaboticabal 4/2: 21-22.

Matuo T (1988) Desenvolvimento de um pulverizador intermitente operado fotoelétricamente para tratamento de pomares de citros. (Tese de Livre-Docência) - Faculdade de Ciências Agrárias e Veterinárias, Universidade Estadual Paulista. Jaboticabal.

Pimentel-Gomes F (1978) Curso de estatística experimental. Gráfica Nobel Ltda, Piracicaba. 430p.

Severn DJ (1984) Use of exposure data for risk assessment. In: Siewierski M (ed) Determination and assessment of pesticide exposure. Elsevier, New York, p 13-19 (Studies in Environment Science, n.24).

SINDAG – Sindicato da Indústria de Produtos para Defesa Agrícola (2000) Vendas de defensivos agrícolas por cultura de destinação e classes. São Paulo. (<http://www.sindag.com.br/db/arqs/CULTURAS-9700.xls>, março de 2002)

Tomlin CDS (ed) (1997) The pesticide manual: a world compendium. 11o ed. London, The British Crop Protection Council, 1.606p.

Turnbull GL (1985) Current trends and future needs. In: Turnbull GL (ed) Occupational hazards of pesticide use. Taylor & Francis, London, p.99-116.
Van Hemmen JJ (1992) Agricultural pesticide exposure data bases for risk assessment. Rev Environ Contam Toxicol 126: 85.
Wolfe HR, Armstrong JF, Staiff DC, Comer SW (1972) Exposure of spraymen to pesticide. Arch Environ Hlth 25: 29-31.