From:	Lin Fritschi
To:	Community Affairs, Committee (SEN)
Subject:	RE: Senate inquiry public hearing - issues on notice
Date:	Friday, 20 November 2020 3:26:26 PM
Attachments:	mono112-07.pdf ATSDR tp154.pdf Tuomainen2002_Article_PotentialExposureToPesticidesI.pdf

Please see attached the information on malathion from the International Agency for Research on cancer which was requested by the Inquiry.
You can also find it at https://publications.iarc.fr/549

There is also information in the ATSDR toxicological profile which is attached and can be found at https://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=522&tid=92).

Information on the level of exposure to malathion in community members, such as the young girl who rode her bicycle through clouds of insecticide spray can be found in section 1.4 (b) of the IARC monograph 112 and section 6 of the ATSDR profile.

- **Air** levels of exposure to the community when they are in areas where spraying is carried out were between 0 and 62 nanograms per meter cubed (IARC). It is difficult to put this into context as there is little comparison information on air levels in occupationally exposed workers. One study (Tuomainen et al, 2002 attached) suggests that greenhouse sprayers are exposed to air with about 26 micrograms of malathion per meter cubed (which is 26000 nanograms per meter cubed). Also note that the duration of exposure would be much longer in the occupationally exposed people.

- **Urinary** levels in occupationally exposed workers (Table 1.2 in IARC) are also much higher than those in the general population (table 1.3 in IARC). But I can't find any measures of urinary exposure in people who are in areas when spraying is carried out.

Please let me know if more information is required.
Regards
Lin Fritschi

Lin Fritschi
MBBS, FAFPHM, PhD
John Curtin Distinguished Professor

Please note I work Monday and Wednesday only

School of Public Health
Curtin University
Tel | +61 8 9266 9476

Email | lin.fritschi@curtin.edu.au
Web | www.curtin.edu.au

Curtin University

Bull. Environ. Contam. Toxicol. (2002) 69:342–349

DOI: 10.1007/s00128-002-0068-8

Bulletin of Environmental Contamination and Toxicology

Potential Exposure to Pesticides in Nordic Greenhouses

A. Tuomainen,[1] M. Mäkinen,[1] R. Glass,[2] J. Kangas[1]

[1] Finnish Institute of Occupational Health, Post Office Box 93, FIN-70701 Kuopio, Finland
[2] Central Science Laboratory, Sand Hutton, York, YO41 1LZ, United Kingdom

Received: 3 January 2002/Accepted: 15 May 2002

In European Union countries, the Council Directive on Plant Protection Products, EC 91/414 (CEC 1991) requires regulatory authorities to evaluate levels of operator and worker exposure to active ingredients of pesticides before releasing them to the common market. This has created a growing interest in predictive exposure modelling. Many European countries have developed such predictive models during recent years (JMP 1986; Lundehn et al. 1992; van Hemmen 1992). Exposure assessment by modelling relies on predictions of exposure levels based on generic databases. In the early 1990's, an idea of developing a common, harmonized exposure model was established in the EU countries. The first version of European Predictive Operator Exposure Model was introduced in 1997 (EUROPOEM 1997). The EUROPOEM databases contain measurements from peer reviewed studies performed comprehensively in European agricultural conditions.

However, for indoor applications in greenhouses, only 19 data points are available in EUROPOEM and they are all from one study done in the Netherlands (EUROPOEM 1997). As the reliability of the exposure models is mostly dependent on the underlying databases, there is a constant need to enlarge them with data produced with valid studies. In our study the potential inhalation, hand and dermal exposure to pesticides was measured during the mixing and loading (M&L) and application periods in the greenhouses. The pesticides studied were malathion, deltamethrin (insecticides) and iprodione (fungicide), which were applied to rose crops in four different Finnish greenhouses. The ultimate aim of this study was to produce data of good quality from the Nordic climatic conditions to be added to the EUROPOEM database and compare the measured exposures with the data already available in that model.

MATERIALS AND METHODS

Four greenhouses growing roses were selected in different parts of Finland. The area of the studied greenhouses ranged from 500 to 2500 m^2 and the application method used was a hand held lance. The relative humidity and temperature in the greenhouses ranged from 60 to 95 % and from 14 to 20 °C, respectively. The mean concentrations of malathion, deltamethrin and iprodione in the spraying

Correspondence to: A. Tuomainen

solutions were 1337, 12.5 and 500 mg/L, respectively. The products were tank mixed and the applied volume was on the average 170 L for malathion, 366 L for deltamethrin and 143 L for iprodione. The studied pesticides were sprayed into the greenhouses at different times. The mixing and loading time for the pesticides varied from 6 to 12 min and that of the application from 58 to 68 min. The greenhouse workers, who participated in the study were all experienced certified applicators. Seven of them were men and two were women. There was one mixer-loader and one applicator at each studied greenhouse and each pesticide was mixed, sprayed and sampled once in the greenhouses.

The pesticide products used in the study were from following sources: malathion (Malasiini Spray Liquid) was from Kemira Agro (Helsinki, Finland) and deltamethrin (Decis 25 EC) and iprodione (Rovral) from Aventis CropScience Nordic A/S Finland (Helsinki, Finland). Pure pesticide standards for the analysis were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Ethyl acetate was from E. Merck (Darmstadt, Germany) and ethanol (99.9 %) from Alko Co. (Helsinki, Finland).

The potential exposure of the workers to the pesticides via inhalation was studied by measuring the concentration of the compounds at the workers' breathing zones separately during the mixing and loading (M&L) and application periods of the pesticides. Iprodione was collected with a glass fiber filter (IOM samplers, SKC Inc., PA, USA, aerosol portion) and an XAD-2 adsorption tube (SKC Inc., volatile portion). Malathion and deltamethrin were collected with XAD-2 adsorption tubes. The aerosols were collected with an SKC 224 sampling pump at a sampling rate of 2.0 L/min and the volatiles with an SKC 222 sampling pump at a sampling rate of 0.1 L/min. The air sampling times always covered the whole working period both during M&L and application. After the sampling the air samples were transferred to the laboratory, where they were stored tightly capped at + 4 °C for not more than two days. The pesticides were eluted from the samplers with 3 mL of ethyl acetate and analyzed as earlier described (Kangas et al. 1993; Manninen et al. 1996). The recovery of malathion, deltamethrin and iprodione from the fortified air samples was 76, 96 and 102 %, respectively and the within-run coefficient of variation (CV%) was 12, 3 and 11, respectively. The limits of detection (LOD, in final organic extracts) both in air, patch and glove samples were 0.01, 0.05 and 0.01 μg/mL for malathion, deltamethrin and iprodione, respectively. However, these LOD can be further decreased e.g. by injecting more than 1 μL of the final solution in the gas chromatograph.

The pesticide exposure of the bystander was studied by collecting air samples outside the greenhouse during the whole period of M&L and application. The air sampling sites (one or two at each four greenhouses) were chosen so that they were situated at the most probable area of a random bystander (e.g. customer, other worker) in the studied greenhouse area. The sampling height was about 1.5 m from the ground. Otherwise the sampling and analysis method was similar with the breathing zone sampling of the pesticides.

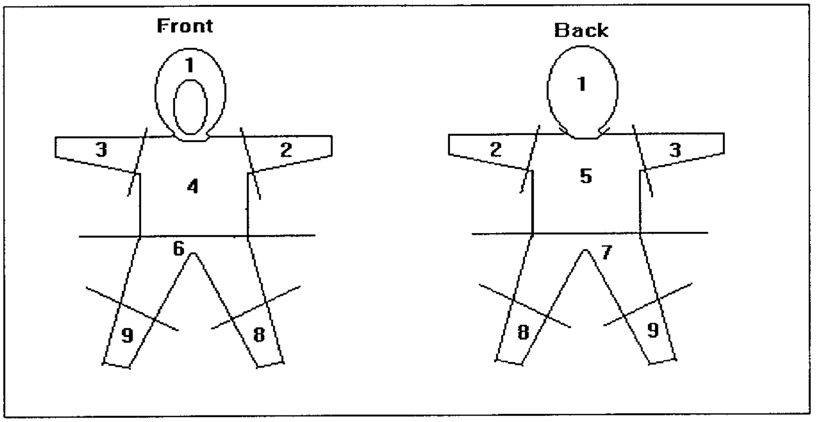


Figure 1. Placement of the alpha cellulose patches in the workers' coveralls during mixing-loading and application periods of the pesticides.

To measure the potential dermal exposure of the workers to pesticides, the workers had alpha cellulose patches (size 10x10 cm) attached to a clean, unused Tyvek coveralls (Tyvek Pracktik, Apparel SL100MP elasticated hooded coverall) (Fenske 1993). Separate samples were collected during the M&L and application periods. The patches were carefully attached by tape to the coveralls. The number of patches distributed over the coverall was 14 (Figure 1) and their location was according to the OECD guidance document (1997). After the working period, the patches were removed and each patch was transferred to a tube containing 25 mL of ethanol. The samples were stored at -18 °C until the analysis according to Kangas et al. (1993) and Manninen et al. (1996). The recovery of malathion in the patch samples was determined to be 106 % and that of deltamethrin and iprodione 96 % and 103 %, respectively. The CV% was 10 for malathion, 3 for deltamethrin and 11 for iprodione.

The contamination of workers' hands was measured with thin cotton gloves (Famon Ltd., Finland) worn over clean, unused nitrile rubber gloves. New cotton gloves were pretested and prewashed before the study and separate samples were again collected during M&L and application. After sample collection in the field, the cotton gloves were transferred to glass bottles containing 80 mL of ethanol and stored at -18 °C before the analysis. Right and left hand gloves were analyzed separately (Zweig et al. 1985). The recoveries from the fortified samples were 69, 124 and 104 % for malathion, deltamethrin and iprodione, respectively. The within-run coefficient of variations for the pesticides were 14, 14 and 11 %.

The total potential dermal exposure of the workers was calculated from the measured pesticide concentrations of the patch and glove samples. The amount of the exposure in different body parts was calculated by using the areas of the body parts according to the OECD guidance document (1997). Then the pesticide concentrations measured in different body parts were calculated together, and this gives the amount of pesticide in the whole body. Finally, the total potential exposure means the body, hand and inhalation exposure calculated together.

Every sampling time, field blanks (air samples, gloves, patches) were also used to monitor possible pesticide contamination. All the pesticide standards and sample blanks were treated and analyzed in duplicate in the same manner as the samples (also done in duplicate). Malathion was analyzed with a Hewlett Packard 5890 gas chromatograph equipped with an FPD (flame photometric) detector in the phosphorus mode. The column used was an HP1 cross linked methyl silicone gum (25 m, 0.32 mm inner diameter, 0.52 μm film thickness). Deltamethrin and iprodione were analyzed with a Hewlett Packard 5890 Series II gas chromatograph equipped with an EC (electron capture) detector. The column was similar as in the analysis of malathion (Kangas et al. 1993; Manninen et al. 1996). The basis of EUROPOEM is the assumption that the level of operator exposure, both inhalation and dermal, is influenced by the physical properties of the pesticide formulation, the mixing, loading and application techniques used, work methods, application rate, environmental conditions and the hygienic measures taken by the worker. The chemical or toxicological properties of the substance are not considered important in that sense (van Hemmen 1992). The result of the modelling, i.e. the surrogate value for exposure, can be given as milligrams per kilograms of active ingredient (a.i.) handled or millilitres of spray liquid applied per hour.

RESULTS AND DISCUSSION

The identification of the compounds was always based on the authentic standards and their retention times in the chromatograms. Every times the several field blanks collected were found to be clean from pesticides. The mean concentration of malathion, deltamethrin and iprodione at the workers' breathing zone during M&L was 155, 18 and 99 $\mu g/m^3$, respectively and during application 26, 1 and 49 $\mu g/m^3$, respectively. The exposure seemed to be highest during the M&L of malathion. This might be due to that both in the commercial formulation and in the spraying solution of malathion the concentration of the active ingredient was much higher than that of the two other pesticides; deltamethrin and iprodione. During the application, the highest concentration was measured for iprodione. On the other hand, the inhalational exposure to deltamethrin was much lower at both work phases. When estimating the bystander exposure, there were no measurable amounts of studied pesticides in the bystander air samples. In any case, the inhalational exposure to the pesticides was quite small and considered to be insignificant when compared to the dermal exposure.

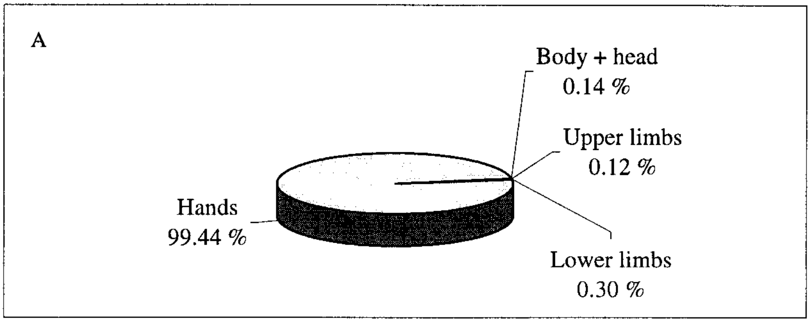
The mean potential dermal exposure of the workers to malathion and iprodione was highest during the application of these pesticides (Table 1). Conversely the potential dermal exposure to deltamethrin was marginally greater during the mixing and loading period than during application. In the studies with malathion, there was an accidental contamination in one right hand sample. This value (outlier) was not included when later comparing the Finnish results to the available EUROPOEM data. During pesticide mixing and loading in the greenhouses over 99 % of the potential dermal exposure was accounted for by the workers' hands. During the application period lower (60 %) and upper limbs (21 %) were the body parts, which were mostly contaminated. The contamination via hands was 18 % during the application of the pesticides (Figure 2). In practice, the proper selection and use of personal protective gloves is very important to reduce (or mitigate) exposure to pesticides. Furthermore, suitable protective clothing and respiratory protection are needed during pesticide application in the greenhouses. The clothes and equipment should also be carefully washed and maintained after every use (Edelman 1991). The absorption of pesticides into the body usually continues for some time after the dermal exposure events. Therefore careful wash up and changing of clothes after the application is very important to minimize the exposure.

Table 1. Potential exposure (mg/kg a.i.) of mixer-loader and applicator to malathion, deltamethrin and iprodione. Every value is a mean of three consecutive measurements, except for deltamethrin mixer-loader, where it is a mean of two measurements.

Exposure via	Mixer-loader exposure (mg/kg a.i.)			Applicator exposure (mg/kg a.i.)		
	malathion	delta-methrin	iprodione	malathion	delta-methrin	iprodione
total body	0.3	5.1	2.5	665.4	133.6	1413.0
hands	201.1	930.4	68.4	6053.5[a]/234.1	211.8	46.1
left hand	100.9	754.2	32.6	158.9	109.5	26.8
right hand	100.2	176.2	35.7	5894.6[a]/75.1	102.4	19.3
total dermal	201.3	935.4	70.8	6718.9[a]/899.5	345.5	1459.1
inhalation	0.005	0.009	0.004	0.01	0.018	0.024
total potential	201.4	935.5	70.9	6718.9[a]/899.5	345.5	1459.1

[a] contamination of the right hand sample

It is necessary to use a high percentile value (even the maximum value), when there is only a limited amount of data available in the database (van Hemmen 1993). In the case of indoor applications the maximum value has been recommended to ascertain safety of the operators. The potential surrogate exposures modelled with EUROPOEM using the current database from indoor activities and the measured exposures of this study are presented in Table 2. Our measurements were performed separately for mixing-loading and application, but in order to compare the results with the EUROPOEM database values, they had to be combined. As the current database is very limited, not only by the number of data points but also in the variety of scenarios, it was not surprising that the exposure levels were quite different from each other. It was seen that the measured exposures of this study were significantly higher than the surrogate



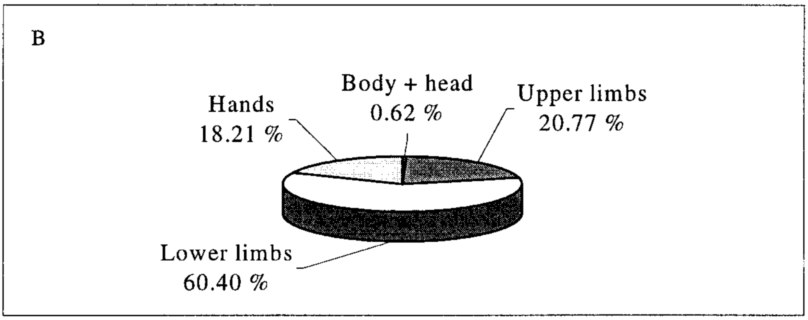


Figure 2. Potential dermal exposure to pesticides in Finnish greenhouses A. during mixing and loading and B. during application with a hand held method.

Table 2. Comparison between exposure estimates (mg/kg a.i.) in the EUROPOEM database and the Finnish field study, characteristics of the data sets.

	Hands		Body		Total dermal		Inhalation	
Characteristics of the data sets	EURO-POEM	Finnish field study	EURO-POEM	Finnish field study	EURO-POEM	Finnish field study	EURO-POEM	Finnish field study
number of data points	16	7	17	7	16	7	17	7
geometric mean	30	234	15	502	57	1261	0.05	0.006
75th percentile	56	623	28	1553	94	2116	0.12	0.048
90th percentile	199	1184	42	2424	268	2600	0.20	0.040
maximum	1346	1920	131	2940	1372	3190	0.34	0.040

values of the database, probably due to different crop characteristics, e.g. high plant densities, height of the roses, and narrow row spacing in the Finnish study. Different measurement methods were also used in the studies: in the database study the body exposure had been measured with cotton coverall. It is possible, that patch and glove sampling used in our study overestimate the exposure especially when handling concentrated formulations or spraying with hand held lance. Uneven distribution of the contamination may lead to a sampling error with the patch method (DelgadoCobos et al. 2000), and during the application the proximity of the hands to the nozzles, together with possible leakages may cause saturation of the cotton gloves. It is also suggested that the extent and pattern of deposition of pesticides on Tyvek represents that on other work clothes. However, this assumption was not further investigated in this study and therefore is a source of uncertainty in the exposure assessment.

It is clear that the EUROPOEM databases must be enlarged drastically, before they can be used to reliably predict the operator exposure in all indoor scenarios. It might even be more practical and reliable in the future to divide the database of indoor activities into more specific "sub-databases" according to the different exposure determinants. One shortcoming of the existing EUROPOEM database is also that the data on mixing-loading and application is combined. The exposure involved with these tasks is, however, very different, as spraying leads to dermal exposure to less concentrated liquids than during mixing-loading, where concentrated liquid (or solid) formulations are handled. This also has consequences for the exposure management and designing personal protection. Validated, uniform methods for occupational hygienic measurements of dermal exposure of pesticide operators are also urgently needed.

Ackowledgments. The study has been financially supported by the European Union Standards, Measurements and Testing Programme, Project SMT4-CT96-2048 "The Assessment of Operator, Bystander and Environmental Exposure to Plant Protection Products", the Finnish Work Environmental Fund and the Occupational Health and Safety Department of the Ministry of Social Affairs and Health in Finland.

REFERENCES

CEC (1991) Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market; OJ L230 19.08.91. Commission of European Community, Belgium

DelgadoCobos P, Nocete Merelo FJ, Arechabala Anaya M, Castro Barrio S, Glass CR (2000) Comparison of potential dermal exposure during olive tree treatment with dimethoate using patch and whole body methods. Proceedings of the 1st International Conference on Occupational Risk Prevention, Tenerife, Spain, February 23rd to 25th

Edelman PA (1991) Prevention of injury by pesticides. In: Hayes WJ, Laws ER (eds) Handbook of Pesticide Toxicology, vol 1. Academic Press Inc, San Diego, pp 405-451

EUROPOEM (1997) The Development, Maintenance and Dissemination of a European Predictive Operator Exposure Model (EUROPOEM) Database, Final report, BIBRA International, Carshalton, UK

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

JMP, Joint Medical Panel of the scientific subcommittee on pesticides (MAFF) and British Agrochemicals Association (1986) Estimation of Exposure and Absorption of Pesticides by Spray Operators, SC 8001, Ministry of Agriculture, Fisheries and Food, Harpenden, Herts, UK

Kangas J, Laitinen S, Jauhiainen A, Savolainen K (1993) Exposure of sprayers and plant handlers to mevinphos in Finnish greenhouses. American Ind Hyg Assoc J 54:150-157

Lundehn JR, Westphal D, Kieczka H, Krebs B, Löcher-Bolz S, Maasfeld W, Pick ED (1992) Uniform Principles for Safeguarding the Health of Applicators of Plant Protection Products. Mitteilungen aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft. Heft 277, Berlin, Germany

Manninen A, Kangas J, Tuomainen A, Tahvonen R (1996) Exposure to insecticides in the use of cold fog generators in greenhouses. Toxicol Environ Chem 57:213-224

OECD (1997) Guidance document for the conduct of studies of occupational exposure to pesticides during agricultural application. Series on testing and assessment, no 9. OECD/GD (97) 148, Paris, France

van Hemmen JJ (1992) Estimating worker exposure for pesticide registration. Rev Environ Contam Toxicol 128:43-54

van Hemmen JJ (1993) Predictive exposure modelling for pesticide registration purposes. Ann Occup Hyg 37:541-564

Zweig G, Leffingwell JT, Popendorf W (1985) The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues. J Environ Sci Health B20:27-59