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Pesticide potential dermal exposure during the manipulation of concentrated mixtures at small horticultural and floricultural production units in Argentina: The formulation effect

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HIGHLIGHTS

- A horticultural and floricultural worker's pesticide exposure study was done.
- A correlation between the pesticide formulation type and the exposure was found.
- Granulated formulations were the safest for the mix and load stage.
- The opening of the pesticide container is a risk operation for liquid formulations.
- External pesticide contamination of the containers could contribute to the exposure mechanism.

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ABSTRACT

Potential dermal exposure measurements of horticultural and floricultural field operators that handled concentrated pesticides showed a correlation with the types of formulations used (liquid or solid) during the mix and load stage. For liquid formulations, hand exposure was 22–62 times greater than that for solid ones. The dermal exposure mechanism was studied for this formulation under laboratory conditions, finding that the rupture of the aluminum seal of the pesticide container and the color of the liquid formulation are important factors. Additionally, significant external surface contamination of pesticide containers collected at horticultural farms was found. This could partially account for the differences between the exposure levels of field and laboratory experiments for liquid formulations.

1. Introduction

Crop productivity has experienced an important increase since the middle of last century (Dyson, 2000), as a result of better soil and water management, improved plant varieties, application of fertilizers and the use of pesticides (Cooper and Dobson, 2007). In the particular case of pesticides, the main beneficial effects of these products have been associated with the control of agricultural pests, having other indirect positive consequences such as the reduction of fungal toxins, and control of invasive species. Besides these positive aspects some negative characteristics have been observed, being the impact on the environment and human health the ones with more conspicuous repercussions. Despite these negative aspects, farmers continue to apply these products, in some countries in increasing quantities. This fact could be partially explained by the short term economic profit that derives from their use (Wilson and Tisdell, 2001), although at present concerns about sustainable use of pesticides are a matter of discussion between producers and regulatory authorities.

As mentioned above, one of the main negative effects of pesticide use is their effect on human health. In this respect it is well known that farm operators in particular are some of the most exposed subjects, especially when the pesticide application is done without the proper protection (Lesmes-Fabian et al., 2012). In an investigation done on 6300 cases with manual sprayers in 24 different countries, the effect of pesticide use on human health was studied (Tomenson and Matthews, 2009), finding that 1.2% of the operators experienced serious agrochemical related incidents (with hospitalization), while 5.2% of the total users had a moderate incident which required medical intervention. In another

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international study analyzing 8500 cases of operator's attitude and behavior regarding the use of pesticides (Matthews, 2008), in 26 different countries, it has been established that only 50% of the operators used gloves during the mixing stage of the concentrated pesticide. This occurred despite the recommendations of using personal protective equipment during this operation (International Labour Organization-WHO, 1991), perhaps because of climate stress factors such as high humidity and temperature (Park et al., 2009). In the same sense, in a study done among farmers in the Philippines, Lu (2009) has pointed out that 31.8% of the operators interviewed have experienced spillage on their hands.

The pesticide exposure risk is particularly important in small horticultural (Ramos et al., 2010) and floricultural (Flores et al., 2011) production units surrounding Buenos Aires city. There, working conditions are unfavorable, associated with lack of education, low technology and highly manpower-dependent tasks. In these cases we have previously shown that the mixing and loading operations could constitute a considerably risky stage. It has been pointed out that the type of pesticide formulation can modulate the toxicological effects on non-target systems and affect the pesticide's environmental fate (Cox and Surgan, 2006). In particular, for human exposure, the influence of the formulation type on dermal absorption has been studied from experimental (Aust et al., 2007) and modeling (Krüse and Verbek, 2008) perspectives. Moreover, it has been established that insecticides with the same active ingredient but different formulation have different biocide actions (Moreno et al., 2008).

Despite being recognized that the type of pesticide formulation may affect the operator's exposure (Damalas and Eleftherohorinos, 2011), to our best knowledge no quantitative analysis has been made studying the factors that modulate the exposure risk from this point of view. In this sense, the survey described in this report studied the exposure to pesticides under real working conditions in horticultural and floricultural production units and under controlled laboratory situations, analyzing the effect that the pesticide formulation has on the operator's exposure.

2. Methodology

2.1. Reagents and materials

For the preparation of each reference material, technical grade pesticides used in field trials were purified by recrystallization (95% pure by GC–FID), and the identity and purity of the active principles were confirmed by ^{1}H- and ^{13}C NMR. A primary solution of 300–1000 ppm w/w was prepared in acetone or cyclohexane, and all other working solutions were made by dilution as needed. Acetone and cyclohexane (Aberkon p.a. grade) used for all solutions and extracts, were previously distilled and chromatographically checked as suitable for GC–ECD use.

Commercial products used in the field trials were as follows:

- Captan ((3a,4,7,7a-tetrahydro-2-[(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione), CASRN [133-06-2]): Captan® (WP, 85% w/w) (Tomen-Chemiplant).
- Deltamethrin ((*S*)-α-cyano-3-phenoxybenzyl-(1*R*,3*R*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate, CASRN [52918-63-5]): Decis Forte® (EC, 10% w/v) (Bayer CropScience Argentina).
- Procymidone (3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo [3.1.0]hexane-2,4-dione, CASRN [32809-16-8]) liquid: Sumilex® (CS, 50% w/v) (Summit Agro Argentina); and solid: Sumilex® (WP, 50% w/w) (S. Ando Argentina).
- Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide), CASRN [115-29-7]): Thionex ® (EC, 35% w/v, Magan).

For the preparation of pesticide surrogates Brilliant Blue #1, CI Nº 42090 (Sensient — Ardennes S.A.), phenolphthalein (Sigma-Aldrich) and glycerine pharmaceutical grade (Química Wisconsin, Argentina) were used as provided.

2.2. Study sites

All field experiments were carried out by local operators following their usual practices using commercial pesticides, during normal activities in greenhouses or open field plantations in the following locations, in the province of Buenos Aires (Argentina):

H_1–H_3: maize field in Moreno district;
H_4–H_8: mixed vegetable fields in Moreno district;
H_9–H_{16}: tomato greenhouses in San Pedro district;
F_1–F_7: flower greenhouses in Moreno district

2.3. Measuring devices

In the case of liquid formulations, the amount of product measured out by the operators was defined by volume (e.g. 10 mL) and checked by weighing on a portable scale. In the case of solid formulations, the amount handled was measured by weight difference of the pesticide or surrogate original vessel. Measuring devices used in commercial plantations were varied: spoons, cups, measuring cylinders, Falcon-type centrifuge tubes, etc. In laboratory experiences, various devices were tested: i) 15 mL graduated plastic cup, similar to those provided with medicines; ii) Falcon tube, 50 mL graduated plastic centrifuge tube with screw-top; iii) 2 mL piston bottle pumps, with screw-top, used for soap dispensers; and iv) plastic disposable teaspoons.

2.4. Field procedures

All field trials were carried out by the operators that usually perform the pesticide application in each plantation, following their habitual measuring and dilution methods, without any indication about procedure or dose. All products used were dispensed from commercial containers, some with intact seals, while others were in use so their seals were already opened. Prior to starting, operators were equipped with clean cotton gloves (used as samplers), and asked to open the container and prepare the mixture needed in a 20 L backpack sprayer. In experiences H4–H8, after opening the container, the operator measured out the dose with a plastic spoon into a tank but did not actually add water. The amount measured out was weighed in a portable scale before transferring it to the tank. After closing the tank and container, the gloves were taken off and placed in separate bags (right or left hand) and then taken to the lab for analysis. The spoons used in experiences H4–H8 (solid formulations) were collected individually and placed in extraction flasks for analysis.

In the cases where the pesticide content on the outside of the commercial containers was measured, the external surface of the container was rubbed with a piece of tissue paper soaked in acetone or cyclohexane. This was repeated with a fresh tissue. Both tissues were placed in a 100 ml bottle, taken to the laboratory and frozen.

2.5. Laboratory sampling methods with pesticide surrogates

Laboratory procedures were done using formulations of a food dye (Brilliant Blue) or phenolphthalein as pesticide surrogates under controlled laboratory working conditions.

2.6. Surrogates preparation

2.6.1. Solid formulations

For the preparation of 100 g of water soluble granules, 20 g of Brilliant Blue was mixed with 70 g of a soluble carrier (ammonium sulfate), 5 g of wetting agent (sodium lauryl sulfate), 4.5 g of dispersing agent (sodium naphtalensulfonate) and 0.5 g of powdered antifoam. The mixture was homogenized by milling and 5.0 to 8.0 mL of water was added to form a wet paste. Then, it was transferred to a LCI Benchtop