Procedures to Evaluate the Efficiency of Protective Clothing Worn by Operators Applying Pesticide

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The evaluation of the efficiency of whole-body protective clothing against pesticides has already been carried out through field tests and procedures defined by international standards, but there is a need to determine the useful life of these garments to ensure worker safety. The aim of this article is to compare the procedures for evaluating efficiency of two whole-body protective garments, both new and previously used by applicators of herbicides, using a laboratory test with a mannequin and in the field with the operator. The evaluation of the efficiency of protective clothing used both quantitative and qualitative methodologies, leading to a proposal for classification according to efficiency, and determination of the useful life of protective clothing for use against pesticides, based on a quantitative assessment. The procedures used were in accordance with the standards of the modified American Society for Testing and Materials (ASTM) F 1359:2007 and International Organization for Standardization 17491–4. The protocol used in the field was World Health Organization Vector Biology and Control (VBC)/82.1. Clothing tested was personal water repellent and pesticide protective. Two varieties of fabric were tested: Beige (100% cotton) and Camouflaged (31% polyester and 69% cotton). The efficiency in exposure control of the personal protective clothing was measured before use and after 5, 10, 20, and 30 uses and washes under field conditions. Personal protective clothing was worn by workers in the field during the application of the herbicide glyphosate on weed species in mature sugar cane plantations using a knapsack sprayer. The modified ASTM 1359:2007 procedure was chosen as the most appropriate due to its greater repeatability (lower coefficient of variation). This procedure provides quantitative evaluation needed to determine the efficiency and useful life of individual protective clothing, not just at specific points of failure, but according to dermal protection as a whole. The qualitative assessment, which is suitable for verification of garment design and stitching flaws, does not aid in determining useful life, but does complement the quantitative evaluation. The proposed classification is appropriate and accurate for determining the useful life of personal protective clothing against pesticide materials relative to number of uses and washes after each use. For example, the Beige garment had a useful life of 30 uses and washes, while the Camouflaged garment had a useful life of 5 uses and washes. The quantitative evaluation aids in determining the efficiency and useful life of individual protective clothing according to dermal protection as a whole, not just at specific points of failure.

Keywords: ASTM 1359:2007; ISO 17491:2008; operator safety; property, plant, and equipment efficiency testing; tracer

INTRODUCTION

Personal protective clothing for dermal protection

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uses as a protective layer between the pesticide and the surface of the worker's body. The protective nature of the clothing is relative to high repellency or low absorption, retention and penetration of pesticides in porous materials and seams. The penetration of protective materials is defined as the flow of chemicals through holes or imperfections
in the material of which the garments are made, called pores (Obendorf et al., 2003).

The methods for assessing dermal exposure to pesticides are grouped into three general categories: qualitative, semiquantitative, and quantitative. Semiquantitative and qualitative methods (Fensk, 1988) are usually based on observation of the presence or absence of skin exposure marked with colored or fluorescent pigments. The quantitative methods consisted of quantifying exposures to pesticides themselves or to the tracers added to the sprays used.

The protective water-repellent clothing is qualitatively assessed through method A (low-level spray test) and impermeability to materials through method B (high-level spray test) against pesticides. The qualitative assessment used the International Organization for Standardization (ISO) 17491–4 (ISO, 2008) procedure. This procedure is used to evaluate the full set of requirements in the standard ISO 27065 (Brasil, 2004; ISO, 2011). The protective clothing used by pesticide applicators can be evaluated by ISO and American Society for Testing and Materials (ASTM). The level of protection provided by personal protective clothing is evaluated qualitatively through the ASTM procedure F 1359 (ASTM, 2004).

These two procedures use colored or fluorescent tracers to characterize the penetration of sprayed liquid, especially through seams, gaps, and interfaces with other components (gloves, boots, hood, and respiratory protection). The penetration of sprayed liquid is evaluated visually with internal dosimeter coveralls worn under protective clothing. In the ASTM procedure, inner dosimeter coveralls and protective clothing are placed on a mannequin; in the ISO procedure, they are worn by a person. In accordance with ISO 27065 (ISO, 2011), approved protective clothing should not present stains greater than 3 cm in diameter. Quantitative methods computed penetration of pesticides, metallic or semimetallic tracers in the inner dosimeter coveralls worn beneath the individual protective clothing, under field conditions, as in the World Health Organization (WHO) Vector Biology and Control (VBC)/82.1 standard protocol (WHO, 1982).

The performance of protective clothing is determined by dermal exposure measurements of pesticide applicators in different pesticide application situations in the field (Machera et al., 2009; Protano et al., 2009; Tsakirakis et al., 2011).

Different spraying techniques using rear-mounted sprayers and trailer sprayers (Lebailly et al., 2009) influenced dermal exposure. It is not possible to uniformly evaluate the efficiency of protective clothing under field conditions. Garment design is another important factor in protective clothing, which requires the evaluation of possible openings in the seams or inadequate overlapping that may reduce the level of protection (Brouwer et al., 2001). The efficiency of protective clothing can be defined as a reduction in dermal exposure by penetration of pesticides.

The standard requirements of ISO 16602 (ISO, 2007) classify personal protective clothing against chemicals based on the percentage of penetration and repellency of these substances in the clothing materials. The standard ISO 27065 (ISO, 2011) classifies the personal protective clothing against pesticides according to levels of protection based solely on penetration percentage of the test substance through the material and the seams of clothing. In the ASTM F 1359 (ASTM, 2007) procedure, the efficiency evaluation of personal protective clothing is done using a spray volume higher than the standard established by ISO 17491–4 (ISO, 2008).

Baker (2005) highlights as a disadvantage that efficiency evaluation of personal protective clothing using ASTM F 1359–99 (ASTM, 2004) is done only qualitatively. This evaluation is carried out by viewing stains of a dye added to the spray as a tracer of exposure on inner dosimeter coveralls worn under protective clothing. It evaluates the liquid that penetrates protective clothing, gloves, and boots after exposure to the spray. Baker (2005) highlights subjective criteria as a disadvantage of the qualitative evaluation of the efficiency of protective clothing. This disadvantage is also observed in the procedure of ISO 17491–4 (ISO, 2008). Other disadvantages of the qualitative evaluation include the inability to quantitatively determine percentage dermal exposure control or to classify and differentiate the efficiency of clothing. In quantitative evaluations, these disadvantages do not exist because the efficiency may be calculated as the percentage of pesticide or tracer retained by the barrier of the work clothing layer. It is believed that the evaluation of the efficiency of personal protective clothing will be more properly measured using quantitative procedures in laboratory conditions, as specified in the procedure VBC/82.1 (WHO, 1982) established for the field. Efficiency classification can be established from this quantitative evaluation to determine the useful life after different numbers of decontamination/washes.

The objectives are to compare the procedures for evaluating efficiency of whole-body protective
Procedures to evaluate the efficiency of protective clothing for applicators of herbicides, for new and used, on mannequins versus operators; evaluate the efficiency both by quantitative and qualitative methodology; and propose effective classification to identify the useful life of the personal protective clothing against pesticides.

MATERIAL AND METHODS

Study site

The assessment of dermal exposure and efficiency of personal protective clothing was performed in both the field and laboratory. The field studies were conducted in the sugar cane plantations of Cosan/Bonfim unit in the municipality of Guariba in 2008. Laboratory evaluations were performed in the laboratory of Ecotoxicology of Agrochemicals and Occupational Health 2010/2011.

Sets of personal protective clothing, uses, and washes

Description. Personal protective clothing evaluated were Beige garment, made with fabric composed of 100% cotton and weighing 143.4 g m$^{-2}$, and Camouflaged garment, made with fabric composed of 31% polyester and 69% cotton and weighing 82.2 g m$^{-2}$. Fabrics were pretreated with fluorocarbon to provide water repellence. The Beige garment was composed of pants, a long-sleeved shirt, and cap-type hood with fabric to protect the neck and shoulders. The Camouflaged garment was composed of pants, a long-sleeved shirt, and a hood sewn into the collar. The pants of both garments were reinforced with waterproof material on the lower front portion starting at the knees.

Uses and washes. Both personal protective garments were used and washed 30 times. They were used by field workers without the addition of glyphosate herbicide in applications for weed control. Not adding glyphosate to the herbicide spray was due to its noninterference in the evaluation of protective clothing efficiency. The workers who applied herbicide walked between plant rows. The plants had 1.4 m between them and were 1.5–2.5 m tall.

A knapsack sprayer was used to apply spray for weed control. Workers were equipped with a flat fan nozzle that sprayed at an average pressure of 35 psi. The application lance was placed on the right side of the worker and the nozzle kept at 0.5 m above the highest leaves of the weeds.

After each 7-h workday of exposure, personal protective clothes were washed with neutral liquid coconut soap in an SLE-50M washer from SITEC. The protective clothing was then dried in the SP-30M centrifugal extractor. Only the Beige garments were ironed after drying at 110°C, according to the manufacturer’s recommendation.

Evaluation of potential dermal exposure in the inner dosimeter coveralls

The potential dermal exposure (PDE) under field conditions was quantified using the inner dosimeter coveralls, worn by workers exposed to tracers, using the whole-body dosimetry method (WHO, 1982; Chester, 1993). In laboratory conditions, coveralls were worn by mannequins. The inner dosimeter coveralls were made of woven 100% cotton, pre-washed in an industrial washer to remove the repellency of the fabric again, and had a hood. To quantify the dermal exposure of workers’ faces, feminine sanitary towels (Carefree®) were used on a half mask (respiratory protective device) by workers in the field. In laboratory conditions, the mannequin was only wearing the whole-body garment made of 100% cotton. These suits were also washed prior to removal of repellency of new fabric.

Dermal exposure to herbicide by applicators in the sugar cane plantations was quantified in 10 repetitions. Under laboratory conditions, five repetitions were performed with the mannequins, in accordance with the requirements of ASTM F 1359 (ASTM, 2007) and ISO 17491–4 (ISO, 2008).

After spraying, the inner dosimeter coveralls were cut to quantify dermal exposure in the following body parts: head + neck, front torso, back torso, arms, front leg, back leg.

Evaluation of the efficiency of the sets of personal protective clothing

Field conditions. The efficiency of personal protective clothing was evaluated quantitatively in the sugar cane plantation under the same conditions of use.

Laboratory conditions. The efficiency of personal protective clothing was evaluated qualitatively and quantitatively in a closed chamber isolated with metal sheets on the sides and ceiling (Fig. 1). The floor was composed of corrugated metal sheet, which allowed the passage of the...
spraying liquid. Below the floor structure a metal sheet was used to direct and collect the sprayed liquid to a fiberglass container of 1.0 × 1.0 m dimension and with a capacity of 300 l beneath the chamber. The chamber was equipped with a turntable of 1.0 m diameter, 0.05 m centrally above the floor, and two spray bars in accordance with ASTM F 1359 (ASTM, 2007) and ISO 17491–4 (ISO, 2008).

The inner dosimeter coveralls and garments were worn by the mannequin and placed in the center of the turntable spray chamber, in accordance with the procedure set by ASTM F 1359 (ASTM, 2007), including replacing the person used in two ISO methods. This was to avoid variations in the characteristics of handling by a test person, which does not occur with the mannequin.

**Modified ASTM F 1359.** The spray volume of ASTM F 1359 procedure was modified to a flow similar to the one used in field conditions and specified in ISO 17491–4 (ISO, 2008). The reason for this change in the flow was to completely soak the protective clothing and the coveralls worn underneath them.

For this procedure, the spray bar of the chamber was of an inverted U shape on the turntable center. The number of the nozzles and their position on the bar described in the standard were modified. In the ASTM F 1359 procedure (ASTM, 2007), five nozzles were used: one at each end of the pole near the floor, one at each of the upper corners, and one at the top center of the turntable. The spray bar used in the modified ASTM F1359 is represented in Fig. 1B. This modification was necessary for the spray to be evenly distributed throughout the vertical extent of the bar. The bar was equipped with FS-110 01 spray nozzles (Jacto Brazil) at a pressure of 40 psi.

The spraying time of the standard procedure was also modified. Spraying for 15 min in each quadrant from 90° to 360°, would result in 1-h total spraying time, with nozzles calibrated for a flow rate of $3.0 \pm 0.2$ l min$^{-1}$; this was reduced to 20 s in a complete rotation of the turntable.

**ISO 17491–4:2008.** For procedures using these standards, the chamber was composed of a 1.8-m vertical spraying bar, with four spray nozzles, and set 1.45 m from the center of the turntable (Fig. 1C). Methods A and B refer to the spraying of low and high levels, respectively. For low-level spraying, hollow cone nozzles were used, consisting of disc DC-03 and core CR-23 (US Hypro Ltd) at a pressure of 30 psi. For high-level spraying, hollow cone nozzles were used, consisting of disc DC-04 and core CR-25 (US Hypro Ltd) at a pressure of 40 psi. In this procedure, a mannequin was used.

**Field workers and mannequin**

Dermal exposure under field conditions was evaluated on 5 workers, with 10 repetitions for each personal protective garment. Workers also
used rubber boots, nitrile gloves, and half masks. The evaluation of personal protective clothing was performed on different days. Replications for each garment were performed on the same day, five workers at a time. Each worker was in different rows of the sugar cane plantation.

In addition to the inner dosimeter coveralls and personal protective clothing, mannequins wore cotton gloves under the nitrile ones, but not for quantification purposes. The three mannequins used were 1.82 m tall and wore the inner dosimeter coveralls, covering the entire body except for feet and hands.

After spraying, the inner dosimeter coveralls were cut into parts and stored in glass containers for subsequent quantification of tracers.

Quantitative assessments of dermal exposure

Tracers of sprayed liquid. Field conditions: Cations of manganese from sulfate manganese (3 g l\(^{-1}\)) were used as tracer (Oliveira and Machado-Neto, 2003) in the procedure for quantitative assessment of dermal exposure of workers performing the spraying of the herbicide glyphosate with the knapsack sprayer to control weeds in sugar cane plantations.

Laboratory conditions: In the standard procedures, the tracer used in the sprayed liquid was Cu of copper hydroxide (3 g l\(^{-1}\)). The surface tension of the spray liquid was adjusted by adding 1% of active sodium lauryl ether tense sulfate, (CAS 009004-82-4) to the ASTM procedure and method B of ISO, and 0.40% to method A of ISO.

Nozzle information flow, such as the total volume sprayed, spraying time, physical–chemical parameters of sprayed liquid and environmental conditions used during the evaluation of each procedure, are listed in Table 1.

The conductivity of the liquid spray was measured because the presence of ionic charges (positive or negative) that are present in pesticide formulations, which dissociate in water, can interact with the charges of the fabric of protective clothing. Polyester fibers hardly absorb water due to the low conductivity of the water (Wang et al., 2009).

Cu and Mn cations were extracted from each of the sectioned inner dosimeter coveralls with the extraction solution of HCl. The solution's concentration was 0.2 N for the samples obtained in field evaluations and 2 N for the samples obtained in evaluations under laboratory conditions. The volume of HCl solution was 600 ml for the hood, 900 ml for the front and back torso, and 1400 ml for

<table>
<thead>
<tr>
<th>Method</th>
<th>Flow/nozzle (l min(^{-1}))</th>
<th>Total volume sprayed (l)</th>
<th>Time of sprayed (min)</th>
<th>Tension of the liquid spray (dyn cm(^{-1}))</th>
<th>Viscosity (cP)</th>
<th>Conductivity (s cm(^{-1}))</th>
<th>Temperature (ºC)</th>
<th>Relative humidity (%)</th>
<th>Wind speed (m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field sugar cane</td>
<td>1.70</td>
<td>33.4</td>
<td>20.00</td>
<td>1.20</td>
<td>1200</td>
<td>28.0–31.9</td>
<td>35.7–52.0</td>
<td>1.0–1.8</td>
<td>1.0–1.8</td>
</tr>
<tr>
<td>ASTM F 1359-modified</td>
<td>0.33</td>
<td>1.98</td>
<td>0.33</td>
<td>1.00</td>
<td>31.00</td>
<td>292.2</td>
<td>25.3–28.7</td>
<td>56.2–71.0</td>
<td>28.5–29.3</td>
</tr>
<tr>
<td>ISO 17491-method A</td>
<td>0.47</td>
<td>1.88</td>
<td>1.88</td>
<td>1.00</td>
<td>50.20</td>
<td>290.0</td>
<td>28.5–29.3</td>
<td>57.2–62.1</td>
<td>28.5–29.3</td>
</tr>
<tr>
<td>ISO 17491-method B</td>
<td>1.14</td>
<td>4.56</td>
<td>4.56</td>
<td>1.00</td>
<td>60.30</td>
<td>291.0</td>
<td>29.5–31.6</td>
<td>59.2–71.2</td>
<td>29.5–31.6</td>
</tr>
</tbody>
</table>

Table 1. Parameters of applications and environmental conditions during spraying to evaluate protective garments in laboratory and field procedures, with inner dosimeter coverall and the protective clothing.

Procedures to evaluate the efficiency of protective clothing
leg front and leg back. The samples immersed in HCl solution were agitated in a shaker, model TE 421 (Tecnal, Brazil), for 3 h at 40°C and 120 rpm rotation. After stirring, 100 ml of extraction of cations were removed. Later, filtration was performed to read the concentration of cations collected from spraying. The cations in the extraction solutions were quantified by atomic absorption spectrophotometry (Oliveira and Machado-Neto, 2003).

Dermal exposure to cations was used as substitute data for determining the exposure to the sprays (Jensen, 1984).

**Tracers and analytical conditions:** The copper hydroxide used in the laboratory assessment was Supera® (Suspension Concentrate; SC, 53.7% w/v) commercial formulation, manufactured by Oxiquimica Agrociência Brazil Ltd. To prepare the analytical curve, a solution of copper chloride was used (Tritisol, Merck, Darmstadt, Germany). The primary solution of 1000 mg l−1 was prepared in 2 N hydrochloric acid. Manganese sulfate (CoML Metalloys & Chemicals Ltd, Brazil) was used in field evaluations. To prepare the analytical curve, a solution of manganese chloride was used (Tritisol, Merck, Darmstadt, Germany). The primary solution of 1000 mg l−1 was prepared in 0.2 N hydrochloric acid. The standard solutions were prepared from the stock solution.

The measurements of Cu and Mn were performed in an atomic absorption spectrophotometer (GBC 932 AA) in air/acetylene. For the Mn cation, a hollow cathode lamp with a current of 5.0 mA was used and adjusted to 279.5 nm, with a 0.5 nm slit. For the Cu cation, a hollow cathode lamp with a current of 3.0 mA was used and adjusted to 324.8 nm, with a 0.5 nm slit.

The linearity range of the determination for the Cu cation is between 0.25 and 10.0 mg l−1 (R² > 0.992) and for the Mn cation, between 0.125 and 2.0 mg l−1 (R² > 0.992). For the Cu cation, the detection limit was 0.062 mg l−1 and quantification was 0.186 mg l−1.

The detection limit for the Mn cation was 0.237 mg l−1. Quantification limits were calculated according to International Union of Pure and Applied Chemistry (Currie, 1999).

The recovery of Cu cation from inner dosimeter coveralls was 96.2% and of the Mn cation was 91.2%. Mean average concentrations of Mn in sprayed liquid in sugar cane plantations was 782 mg ml−1.

The average concentration of Cu cation in test solutions used in the chamber ranged from 955 to 1092 mg ml−1 for the procedures of ASTM standard F1359 (ASTM, 2007) and both methods of ISO 17491–4 (ISO, 2008).

PDE was calculated based on the quantification of the spraying liquid cations in accordance with Harris (2003) by the following formula:

\[ V_2 (\text{ml}) = \frac{C_1 (\text{mg l}^{-1}) \cdot V_1 (\text{ml})}{C_2} \]

Where, \( C_1 \) refers to concentration of the cation of the sprayed liquid; \( V_1 \), volume of spray solution collected; \( C_2 \), concentration of the cation in inner dosimeter coveralls; and \( V_2 \), volume of solution sprayed on inner dosimeter coveralls.

For every experiment conducted within the chamber or in the field, 100 ml of spray solution was collected.

**Calculating efficiency of individual protective garment**

The efficiency of protective garments was assessed with the procedures for field and laboratory before use and after being used 5, 10, 20, and 30 times by glyphosate applicators in the sugar cane plantations, and washed after each use. The calculations were performed for each body part, and for the average of the total percentage differences between dermal exposures of inner dosimeter coveralls (without protective clothing) − PDE and dermal exposures of inner dosimeter coveralls that are not controlled [dermal exposure not control (DENC)] by protective garments over the PDE in accordance with Tácio et al. (2008) through the following formula:

Efficiency (%) = [(PDE − DENC)/PDE] × 100.

**Statistical analysis**

The calculated efficiency values were analyzed statistically using a completely randomized design using F test for variance, and Scott and Knott analysis for the comparison of averages (Scott and Knott, 1974). Sisvar program was used (Ferreira, 2000).

**Qualitative assessment of dermal exposure**

The qualitative assessment of dermal exposure was performed only in laboratory conditions, using a mannequin, through observation of fluorescence of a tracer in the sprayed liquid. The fluorescent tracer used was Luxcor AML 200® yellow. After garments were sprayed, a fan was used to dry the sprayed liquid on protective garments, to prevent contamination of the inner dosimeter coverall.
Then the pieces of protective garments were collected for evaluation of the inner dosimeter overall. With only fluorescent lamps on, penetration of the sprayed liquid was observed and recorded at junction points, overlap of protective garments, and the openings of seams of clothing in different parts of the mannequin’s body and internal parts of the protective clothing in accordance with the procedures described in ASTM F 1359 (ASTM, 2007) and ISO 17491–4 (ISO, 2008).

**Proposal for classification of individual protection garments based on efficiency and percentage of penetration for determination of useful life**

According to ISO 27065-11, manufacturer’s protective garments shall recommend the number of times that a garment can be worn. For this, the protective clothing shall be tested and classified by level of protection, based on the material and seams of the protective garment, prior to being submitted to a low-level spray test of the whole garment.

There is no reference value in bibliographic references, standards of reference, or test procedures to determine the useful life of the whole protective clothing according to the number of uses and washes. ISO 27065 (ISO, 2011) classifies the garment material based on the penetration of pesticides ≤5%; above this value garments are failed. However, ISO16602 (ISO, 2007) classifies the material and seams based on repellency and penetration of chemicals. The classification proposal was based on two levels according to these standards. This article proposes classifying and determining the useful life of washable protective clothing according to two levels (or class) derived from these standards, based on performance provided in Table 2.

Personal protective clothing coveralls with efficiency <80% and penetration >10% is fail.

**RESULTS AND DISCUSSION**

**Potential dermal exposure**

Spraying was carried out under field conditions and with a mannequin. The data for skin exposure was expressed in ml h−1 (Table 3). The position of the nozzle and application techniques (nozzle flow rate, distance from the operator/mannequin, and structure of the spray bar) for liquid spray in the procedures provided variations in dermal exposure measured on inner dosimeter coveralls in the chamber test (Table 3). The average PDE of workers applying spray herbicide in sugar cane plantations was 126.70 ml h−1. For the modified ASTM F 1359 procedure, the average PDE for the mannequin was 21426.50 ml h−1; for method A of the ISO 17491–4 standard (ISO, 2008), it was 587.10 ml h−1; for the method B, it was 2265.35 ml h−1. Quantification of cations for calculating dermal exposure was based on the analytical curve.

The average of PDE herbicide applicators is similar to the value of 128.15 ml h−1 calculated by Machado-Neto et al. (1998) for workers spraying the herbicide paraquat for weed control in corn fields. These values are slightly lower than 140 ml h−1 for PDE for workers spraying pesticides using a hand-held lance in broccoli crops (Hughes et al., 2008).

The higher dermal exposure provided by the ASTM F 1359 procedure (ASTM, 2007), in relation to the ISO 17491–4 procedures (ISO, 2008), may be due to the shorter distance between mannequin and nozzle (1.45–1.07 m); the number of nozzles (6 and 4, respectively); and the position of the nozzles in the upper and lower corners of the bar. The 45-degree inclination of the nozzles at the corners of the bar in the ASTM F 1359 procedure (ASTM, 2007) may have contributed to the increased deposition of sprayed liquid on the mannequin since the discharge nozzle was approximately the same, as shown in Table 1. This effect was also observed in studies of pesticide application technology, where the inclination of the nozzles in relation to the target increases the deposition of spray droplets (Bauer and Raetano, 2004; Foqué and Nuyttens, 2011). The difference of the types of nozzles used in knapsack sprayers interfered in the distribution of dermal exposure (Lesmes-Fabian et al., 2012).

The differences in the amount of exposure for the front and back torso sections were found to be not significant with the Scott–Knott test. The same can be said for front and back leg in the mannequin procedures (ASTM and ISO; Table 3). However, the average volume of exposure of front leg was significantly higher than the other parts in the field tests.

The distribution of percentage dermal exposure in parts of inner dosimeter coveralls provided by the four procedures was similar on the mannequin in laboratory conditions, and it differed little from the field on the workers’ bodies.

This difference occurs because of the position of nozzles in the chamber and on the sprayer in the field. The average height of 50 cm from the ground favors the exposure of the legs while walking. In the field, 93.90% of dermal exposure reached the legs (front and back) of the worker. However, the average amount of dermal exposure was lower than in other procedures.
### Table 2. Evaluations of repellency and penetration of pesticides in protective clothing made of water-repellent materials by standard 16602 (ISO, 2007) and proposed classification by the percentage of reduction of dermal exposure provided by the set of clothing, assessed quantitatively.

<table>
<thead>
<tr>
<th>Class</th>
<th>Classes of ISO 16602 to classify protective clothing by testing the material and seams</th>
<th>Classes proposals to classify protective clothing by control by dermal exposure reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Penetration</td>
<td>Repellency</td>
</tr>
<tr>
<td>1</td>
<td>&lt;10%</td>
<td>&gt;80%</td>
</tr>
<tr>
<td>2</td>
<td>&lt;5%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>3</td>
<td>&lt;1%</td>
<td>&gt;95%</td>
</tr>
</tbody>
</table>

In field conditions, similar to spraying pesticides in broccoli crops, PDE of the front part of legs was 107 ml h\(^{-1}\), which corresponded to 76% of total exposure (Hughes et al., 2008). In similar conditions in tomato plantations, legs and feet of workers were affected between 60 and 80% of total exposure dermal potential (EDP) (Nuyttens et al., 2009).

**Procedure variation coefficient**

The variability of PDE in field procedures and in laboratory tests using a mannequin, no facial protection was used.

### Table 3. PDE by ml h\(^{-1}\) in the field and mannequin in accordance with modified ASTM 1359, A and B methods of ISO 17494-4.

<table>
<thead>
<tr>
<th>Body parts</th>
<th>Potential dermal exposure (ml h(^{-1}))</th>
<th>Field</th>
<th>Mannequin</th>
<th>Test F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Modified ASTM (n = 5)</td>
<td>ISO 17491-4 method A (n = 5)</td>
<td>ISO 17491-4 method B (n = 5)</td>
<td></td>
</tr>
<tr>
<td>Head(^a)</td>
<td>1.2 C c</td>
<td>23.6 C d</td>
<td>54.3 B d</td>
<td>923.5</td>
</tr>
<tr>
<td>Arms</td>
<td>3.1 C c</td>
<td>119.2 C b</td>
<td>364.3 B b</td>
<td>1009.5</td>
</tr>
<tr>
<td>Front torso</td>
<td>1.5 C c</td>
<td>65.7 C c</td>
<td>334.3 B c</td>
<td>1500.6</td>
</tr>
<tr>
<td>Back torso</td>
<td>1.9 C c</td>
<td>58.5 C c</td>
<td>292.8 B c</td>
<td>1480.6</td>
</tr>
<tr>
<td>Front leg</td>
<td>93.4 C b</td>
<td>147.5 C a</td>
<td>595.8 B a</td>
<td>4006.0</td>
</tr>
<tr>
<td>Back leg</td>
<td>25.5 D a</td>
<td>172.6 C a</td>
<td>623.9 B a</td>
<td>4191.5</td>
</tr>
<tr>
<td>Test F</td>
<td>86.0</td>
<td>326.2</td>
<td>374.0</td>
<td>—</td>
</tr>
<tr>
<td>Total</td>
<td>126.7 D</td>
<td>587.1 C</td>
<td>2265.3 B</td>
<td>15284.1</td>
</tr>
</tbody>
</table>

\(^a\)Head + neck + face.

Averages followed by the same lower case letter, compared with the corresponding column for each procedure, and capital letter, compared in the line corresponding to each body part, do not differ by Scott–Knott (P = 0.05).

The greater range of dermal exposure for different body parts of the inner dosimeter coverall occurred for herbicide applicators in the field, resulting in higher CV% in the data (Fig. 2).

The variations of exposure data between the ASTM and ISO procedures were not significant by Scott–Knott test, i.e. they are similar. Coefficients of variation were less than 10% for spatial and temporal distribution of aerosol particles by mass tested in a closed chamber (Lundgren et al., 2006).

Dermal exposure in field conditions is not uniform as there are variations among replications due to various spraying techniques, types of spraying, worker’s experience (Hines et al., 2011), and interfering environmental influences such as wind and relative humidity (Marquart et al., 2003).

The average CV% for the level of dermal exposure in the field was 27%, significantly larger than for the exposures on the mannequin (CV% = 3–4). Ramos et al. (2010) found large PDE variability (6.8–188.2 ml h\(^{-1}\)) using the knapsack sprayer in tomato greenhouses, with a CV of 45%. The PDEs of the applicator in spraying cucumber and tomatoes in a greenhouse using visible tracers...
Procedures to evaluate the efficiency of protective clothing

were between 84 and 526 ml h$^{-1}$ (Machera et al., 2002). The CV% of PDEs for the body parts of the herbicide applicator with a knapsack sprayer ranged from 30 to 106% (Machado-Neto et al., 1998). In citrus, these values were between 17 and 29% for handgun and air-assisted applications (Oliveira and Machado-Neto, 2003).

Driver et al. (2007) found coefficients of variation ranging from 67 to 163% for evaluation of protection garments in the field using 22 spraying techniques. The distribution of respirable dust exposure showed low variability in relation to the mannequin evaluated in a closed chamber (Lundgren et al., 2006).

Most PDEs under field conditions show high variability (high CV%), found by different researchers worldwide. However, PDE evaluated on a mannequin in an automated test chamber can reduce interference and climatic variations of the techniques applied by operators in the field. Furthermore, the chamber can provide the advantage of future tests simulating weather conditions.

Comparison between quantitative and qualitative procedures to evaluate the efficiency of protective clothing

The efficiency of Beige and Camouflaged garments, used by herbicide applicators with a manual knapsack sprayer (applied on weeds in sugar cane plantations) and used in the mannequin tests, was calculated based on the average of their PDE (Tables 4 and 5).

A comparison of quantitative and qualitative methods for assessment of efficiency of coveralls for protection used in sugar cane plantations and evaluated on the mannequin and in the field are shown in Tables 4 and 5.

The useful life, according to the qualitative assessment of the Beige garments is 10 uses and washes. For the Camouflaged garment, it is of five uses and washes in sugar cane plantations in spray applications of glyphosate directed to weeds. These results differ from the classification proposed based on ISO 16602. In this case, the qualitative method is more restrictive, since the useful life of the Beige garments evaluated on the mannequin through the quantitative method is greater than 30 uses and washes (Table 4), and for the Camouflaged garments, it is 5 uses and washes (Table 5). However, the useful life for the Beige and Camouflaged garments evaluated in the field was greater than 30 uses and washes.

Therefore, the qualitative visual assessments complete a quantitative evaluation assessing the efficiency of protective clothing. The visual assessments indicated that the seams and closures of both protection garments showed greater penetration of the fluorescent tracer. However, the visual assessment is necessary for manufacturers to

Fig. 2. CV% of PDE in the field and mannequin according to modified ASTM F1359, methods A and B of ISO 1749-4.
Table 4. Mean values of the percentage reduction in dermal exposure (%), visual evaluation of fluorescent dye stain through Beige garment, used by glyphosate applicators in a sugar cane plantation with the knapsack sprayer, evaluated in the field and with mannequin in the laboratory.

<table>
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*, >3 cm; +, presence of stain; −, no stain; AP, approved; F, failed.

A = Head + neck.

Means followed by same capital letter, compared column for each body part of the coverall, do not differ by Scott-Knott (P = 0.05).

The mean percentage reduction in dermal exposure of the Beige garment was greater than 95.4 and 94% for 30 uses and washes, for evaluation on the mannequin and for the herbicide applicator, respectively (Table 4). For the Camouflaged garment, these values were greater than 94.3% and 75.8% for 30 uses and washes, for evaluation on the herbicide applicator and mannequin, respectively (Table 5).

The results of the percentage reduction in dermal exposure of the Beige and Camouflaged garments agree with those found by Protano et al. (2009), in which the efficiency of cotton protective coveralls ranged from 84.1 to 92.5% by using a tractor equipped with a boom sprayer for different pesticides. The penetration of different pesticides in cotton coveralls ranged from 11 to 26.8% (Vitali et al., 2009). Nigg et al. (1992) found ethion penetration of 2.5–3% in polyester/cotton coveralls treated with water-repellent substances.

The percentage reduction in dermal exposure of the back of the leg on the Beige garment evaluated in the field was significantly lower for 0, 5, and 20 uses and washes than for the mannequin tests. This was probably due to the experience of the applicator. Coveralls in these conditions of use evaluated in the mannequin test showed no presence of the fluorescent tracer greater than 3 cm in diameter. This
shows that this variation of stain was not due to use of clothing, except for 20 uses and washes. The protective factor of the back torso for the Beige garment evaluated in the field was significantly lower for 10 and 20 uses and washes than for the mannequin. In this case, leakage may have occurred. Parts of the back of the torso may suffer more dermal exposure when there is leakage from the knapsack sprayer used by the worker (Blanco et al., 2005).

For qualitative assessment, stains over 3 cm in diameter were identified in all parts of the body of the Beige garment after 30 uses and washes. However, for the Camouflaged garment, stains over 3 cm in diameter appeared in the torso and leg after 10 uses and washes.

Throughout 30 uses and washes, the efficiency of the Camouflaged garment was lower than that of the Beige garment in the test chamber. This is probably due to its smaller weight and fabric composition when in contact with the lower surface tension of the spray and also contact with pesticides. The penetration of the pesticide methamidophos in jeans fabric (0.75 mm, 458.66 g m⁻²) was smaller than the Beige fabric (0.25 mm, 153.49 g m⁻²) after 0, 10, 20, and 30 washes, due to increased weight and thickness of the jeans fabric (Oliveira and Machado-Neto, 2005).

Few studies in laboratory take into account the modeling of protective clothing. The gaps, seams, and overlapping of the parts to be covered on the worker’s body interfere with the penetration of liquid sprayed on the protective clothing, and further on the composition of fabrics.

In further work, it would be important to assess other molecules of different pesticides in protective clothing to improve the new ones coming to the market. Efficiency studies of protective clothing performed on the mannequins can minimize risk of contamination for workers applying pesticide in the field evaluation.

The efficiency evaluation of protective clothing in a closed chamber provides less variability in results due to noninterference from the use of pesticides by the worker, height and spacing of culture, and environmental conditions such as wind and temperature (Zimmerli, 2000).

Classification of sets of individual protection for the quantitative evaluation

The protective Beige and Camouflaged garments were classified by the efficiency of protection assessed quantitatively (Table 6). Garments were classified into two levels according to a new proposed classification based on the ISO 16602 for water-repellent materials.

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Table 5. Mean values of percentage reduction in dermal exposure (%), visual evaluation of fluorescent dye stain through Camouflage garments, used by glyphosate applicators in a sugar cane plantation with the knapsack sprayer, evaluated in the field and with mannequin in the laboratory.

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*Means followed by same capital letter, compared column for each body part of the coverall, do not differ by Scott–Knott (P = 0.05).

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*Head + neck.

*bMeans followed by same capital letter, compared column for each body part of the coverall, do not differ by Scott–Knott (P = 0.05).
The proposed classification for the efficiency of the Beige garment evaluated quantitatively in the field and on the mannequin were the same up to 20 uses and washes. For 30 uses and washes, the assessment done with the mannequin was more severe than in the field. The Camouflaged garment failed after 10 uses and washes in the mannequin evaluation, presenting penetration greater than 10%. However, for the evaluation in the field, classification was 2 for 20 uses and washes and 1 for 30 uses and washes.

The evaluations for both protective garments are different, indicating that the proposed classification is suitable to evaluate different protective garments after use and wash.

The classification proposed by quantitative evaluation is useful for selecting the best protection clothing to be used in relation to the pesticide to be applied by the operator, ensuring their protection.

**CONCLUSIONS**

The most suitable procedure to evaluate the efficiency of the personal protective clothing against pesticides is the modified ASTM F 1359, due to greater repeatability (lower CV%).

The quantitative evaluation is needed to determine the efficiency and useful life of individual protective clothing, according to dermal protection as a whole, and not only at specific points of failure.

The qualitative assessment is suitable for verification of garment design and stitching flaws, not for determining the useful life, but still complements the quantitative assessment.

The proposed classification is appropriate and accurate for determining the useful life of personal protective clothing from agrochemicals with material composition and numbers of uses and washes. With this proposal, the useful life of the Beige garment is 30 uses and washes and for the Camouflaged garment, 5 uses and washes.

**FUNDING**

<table>
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<sup>a</sup>Class 2: Efficiency> 90% and Penetration <5%.

<sup>b</sup>Class 1: Efficiency> 80% and Penetration <10%.

F, failed.

Acknowledgements—We thank the Cosan/Bonfim Unit for conducting the field research.

REFERENCES


Procedures to evaluate the efficacy of protective clothing


