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## **Evaluation of Insecticides in Protective Clothing**

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#### **Abstract**

The exposure to insecticides causes several health problems, which can be aggravated by more toxicity. Therefore, to avoid this exposure, it is required to use protective clothing. The use of protective equipment against pesticides is indispensable and essential from the preparation/handling regulations of the pesticides spray to the application of diluted formulations. However, even with this protection, workers are not totally immune to the contamination of pesticides. There are several factors that contribute to the loss of efficiency of protective clothing against pesticides, such as field use, activity of application, the type of material, seam presence, clothing model, types of formulation used in the application, the process of washing, and the ironing of clothes after their use.

**Keywords:** insecticide, protective clothing, agrochemicals, exposure, contamination

## **1. Introduction**

The extensive exposure of insecticides, mainly from organophosphates (OPs), organochlorines, carbamates, and pyrethroids, causes several damages to the worker health, such as poisoning, neurotoxicity, cancer, and leukemia [1]. The exposure to pesticides can occur through the dermal and respiratory tract, by direct contact such as the application of pesticides in the control of pests and weeds, the handling of the formulation, the transportation of the products, and even in the removal of the protective clothing after its use, and by indirect contact such as re-entry into the culture after the application of pesticides and washing contaminated clothing [2].

The greatest risk of poisoning by agrochemicals occurs due to the lack of use of protective equipment, and as a consequence, serious diseases such as psychiatric disorders and respiratory problems are caused [3]. In general, the use of protective equipment is commonly used



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The use of protective equipment by rural workers is essential in Brazil, as can be seen in NR 6 [5]. However, it is common knowledge that the equipment marketed in Brazil, often supplied to workers by their employers according to the legislation, do not have adequate efficiency, exposing their users throughout the working day [6–9].

The manufacturer is responsible to sustain the quality of the personal protective equipment (PPE), which gave source to the Certificate of Approval (CA). Also, the producer should provide the information about the maximum permitted cleaning and hygiene procedures and indicate, when needed, the number of hygienization above which it is necessary to revise or replace the equipment, in order to guarantee the original level of protection [4].

To be marketed in the country, PPE must have the CA issued by the Ministry of Labor and Employment (MTE) and meet the pesticide protection requirements of International Organization for Standardization—(ISO) 27065: 2011 [10]. For the penetration test, the ISO 22608 (Protection Against Liquid Chemicals—Measurement of repellency, penetration and penetration of liquid pesticide formulations through protective clothing materials) is used [11]. In Brazil, the solution used in the tests is the herbicide Roundup Original® , classified as a soluble concentrate with 480 g/L glyphosate isopropylamine salt (48%) to replace the 5% solution of the pendimethalin active ingredient established in the procedure of ISO 22608: 2004 [5–7].

The 27,065 establishes that the evaluation of protective clothing must begin with materials and seam tests [10]. For impermeable materials, the ISO 6529 (determination of resistance of protective clothing materials to permeation by liquids and gases) is used [12]. In the permeation test, the chemical moves through the protective material by means of the molecular diffusion process with water, which is situated on the other side of the test cell [12].

The factors that may interfere in the permeability of pesticide penetration in the protective materials are air permeability (cm<sup>3</sup>/cm<sup>2</sup>/s), water vapor transmission rate (g/h m<sup>2</sup>), viscosity (η), stress (mN/m) of pesticides, and characteristics of the protective material [13].

The characteristics of the protective materials can be damaged through washing procedure, which influences the protective efficiency of the garments. The washing procedure causes breakage in the fibers and tissues due to mechanical agitation of the washing machines, water, temperature, the number of wash cycles, and tissue drying [14]. Fabrics with a higher coat of fluorochemicals can withstand more than 20 washes, depending on the type of wash [15].

The evaluation methods of the whole body of garments to agrochemicals are grouped into three categories: qualitative, semiquantitative, and quantitative [7]. Qualitative methods are usually based on visual observations of the presence or absence of dermal exposure labeled with colored or fluorescent pigments in accordance with procedures established by the American Society of Testing and Materials (ASTM) described in ASTM F 1359: 2007 [16] and ISO standard 17491-4: 2008 [17]. Quantitative methods are performed by quantifying the pesticides themselves or markers added to the sprayed grouts. Quantitative or qualitative methods

 are based on the penetration of pesticides, dyes, or traces added to the syrup and porous materials or possible openings in clothing.

The efficiency of the protective clothing involves the choice of material, design, field performance testing, and efficacy tests with various types of pesticides. This way, the field worker can use the clothing sanitizing for other types of pesticides, and not just one [7].

This chapter presents a brief review of the dermal exposure of pesticide applicators/manipulators, as well as the efficiency of the protective clothing used in this activity and the factors that undermine this efficiency.

## **2. Dermal exposure assessments to insecticides**

## **2.1. Field evaluation**

Field evaluation involves the predominance of dermal exposure measurements in the application of agrochemicals, whose purpose is to verify the performance of the spray system in contact with the crop and the applicator [18].

The whole-body dosimetry method documented by the Organization for Economic Cooperation and Development (OECD) is widely used in the evaluation of protective clothing in the Exposure to Pesticides during Agricultural Application in compliance with the Guidance Document for the Conduct of Studies of Occupational [18]. This method is an alternative to the patch method and uses cloth layers to measure the body exposure underneath protective clothing. Parts of the head or hands may be worn for the evaluation of dermal exposure [19].

Exposure levels can be expressed as mL of spray deposited on each body part per hour of application (considering the spray concentration and the application time). The exposed parts depend on several factors, such as spray drop size, greenhouse or open-field application, spray type, spray culture structure, and the type of formulation used in application [19].

Frenich et al. evaluated the dermal exposition with the whole-body dosimeter method of spraying with fenitrothion, methidathion, malathion, dimethoate, chlorpyrifos-methyl, and methamidophos under greenhouse conditions. Then, they checked that the legs were more exposed, and which fine droplets of spray increase the dermal exposure by the spray body [20].

The patch method has also been used to assess the dermal exposure of pesticides in different parts of the worker's body [21]. Leme et al. [22] investigated the dermal exposure and malathion penetration inside the dressing using patch method prior to each nebulization and placed absorbents under and on EPI dress in the chest and upper chest wall (back) (80% of the samples contaminated with malathion).

To evaluate the exposure of tractor operators during the application of fenitrothion (organophosphate) in apple cultivation in southern Brazil, absorbents were used on the protective clothing of the artificial operator, quantifying the exposure on the clothing with values below 0.18 mg/kg [23]. The efficiency of two water-repellent personal protection was 96.7 and 96.2% for the tractorsprayer in turbot sprays with turbopulverizer. The potential dermal exposures (in the most exposed areas of the spraying tractor) in the descending order were the feet, arms, thighs + front legs and trunk-back [24].

Goede et al. assigned scores to assess the effect of factors determining occupational exposure in order to correct and classify the dermal exposures of body parts. In tank preparation and tank-filling activities, dermal exposure in the hands is greater (per unit area) than in other parts of the worker's body [25]. The determinants of occupational exposure were viscosity and volatility of the applied substance, particle type, temperature during application, droplet size, particle size of the applied substance, the type of work performed (manual or automated), and was analyzed if the spray reaches the upper or the lower part of the body [26].

Some factors may increase the exposure of applicators in the field, as the structure and height of the crop increasing the spray volume applied in the same type of nozzle used in spraying, spray angle in relation to the worker [27], and correct worker clothing at the time of application [19].

Another exposure factor studied by Kasiotis et al. [28] is the re-entering of the treated crops, in which such exposure can vary according to the tasks of tying or pruning (pesticide residue can be transferred from the foliar surface of a plant to the worker). In this study, the difference in the exposure of SC insecticide (tebufenozide) and an EC fungicide (bupirimate) in tomato and pepper crops was verified. Workers' dermal exposure in applications of insecticide malathion at greenhouse pepper culture was higher in the upper body of the worker for waterrepellent cotton, cotton/polyester, and cotton garments. This fact occurred due to spraying directed toward the top and toward the aerial part of the plants cultivated in bench [29].

Through the assessment of dermal exposure with different spraying equipment, it is possible to classify the risk conditions (safe or unsafe) for the pesticides used, based on the Noel ratio of the substance used in relation to the exposure dose of the applicator [30].

## **2.2. Laboratory evaluation**

In Brazil, studies to evaluate the exposure and protection offered by PPE dressing have recently started and have been of great importance, since they analyze clothing marketed under local exposure conditions and can help in specific standards and tests according to the need of the country.

The evaluation of protective clothing against pesticides uses methods of dermal exposure assessment grouped into three categories: qualitative, semiquantitative, and quantitative. Qualitative methods are usually based on visual observations of the presence or absence of dermal exposure labeled with colored or fluorescent pigments in accordance with procedures established by the American Society of Testing and Materials (ASTM) described in ASTM F 1359:2007 [16] and ISO 17491-4:2008 [17].

Quantitative methods are performed by quantifying the pesticides themselves or markers added to the sprayed grouts. The quantitative evaluation described in ISO 16602 makes it possible to classify sets of protection against chemical substances and determine the useful life of these garments [31]. The process of evaluating the efficiency of the PPE starts with the selection of the materials that will be used in the manufacture of the set in laboratory tests.

International standards establish ways to evaluate the effectiveness of PPE dressings against agrochemicals. As of September 2009 in Brazil, the Ministry of Labor and Employment (MTE) by Ordinance No. 121/2009 established methods for the evaluation of these garments in relation to the repellency, permeation, and penetration of pesticides according to ISO 27065: 2011 [10], used internationally [32].

The type of the material and the seam of the parts determine the level of the PPE according to the protection requirements standard ISO 27065: 2011 [10]. The ISO 27065 sets that garments made are four levels: 1a, 1b, 2, and 3 against pesticides, and tests must be carried out on material, sewing, and whole garment [10].

In this requirement standard (ISO 27065), depending on the performance of materials and seams, full protection sets, or full-body garments and porous materials, the protector kits are classified in levels 1b or 2. According to this standard, for the sets to be classified at level 1b, the penetration of the test substance in the material and at the seam should be less than or equal to 40%, and for level 2, less than or equal to 5%, evaluated with the procedure of ISO 22608:2004 [10]. In this standard of ISO 27065:2011, requirement tests and criteria for minimum protection of materials, seams, and the complete sets themselves to assess the minimum safety and classify PPE against agrochemicals are defined.

The determination of the clothes classified at level 2 in performance is made with porous materials and seam with needles and thread, and level 3 is made with non-porous materials and welded seams, impermeable, as established in the norm of requirements [10].



**Table 1** establishes the criteria for the tests carried out with protective clothing for material types (level) according to ISO 27065.

**Table 1.** Requirement tests for level 1, 2, and 3 garments.

The protection criteria established in the ISO 27065: 2011 for PPE classified in level 2 [10] are materials and seams—penetration of <5% of the aqueous solution containing 5% of pendimethalin or glyphosate, evaluated with ISO 22608: 2004 standard, to the assessment of wholebody PPE (using automated closed chamber)—1-cm diameter stains of methylene blue dye, evaluated using the procedure of ISO 17491-4: 2008 [17]. The criteria for PPE at level 3 (impermeable material) are normalized in the final breakthrough time of ≥30 min: the final breakthrough time is standardized when the permeation rate normalizes at 1.0 μg/cm² min [10].

## *2.2.1. Toxicology and risk assessment*

The registration of insecticides or other agrochemicals is a complex process and goes through several stages, including biological tests with animals and microorganisms. This way, it is possible to know the causes of acute or chronic exposure to those who manipulate organisms affected by exposure. In **Figure 1**, a layout is described, which shows the registration of a new pesticide.

The efficiency tests to protective clothing against pesticides performed by ISO 22608 and according to ISO 27065 must have penetration to pesticides equal to or less than 5% and a herbicide with a low toxicological class was used (glyphosate) [10]. However, in these studies,



**Figure 1.** New pesticide registration process [33].

only the penetration of pesticide solutions is considered and not the pesticide toxicology. In Brazil, several agrochemicals are still commercialized, which have medium and high toxicity, such as the organophosphorus, organotin, chloroaromatic, and others. The margin of exposure (MOE) analysis is a tool to assess the risks in the exposure to pesticides, and animal toxicity tests are compared with levels of human exposure. The NOEL value is 500 mg/kg/ day for glyphosate according to USEPA [34]. To obtain a safety margin of exposure, the MOE is linked to NOEL in relation to the exposure dose ratio of pesticides. Some examples of MOE are chlorpyrifos, which have a value of 100 according to USEPA [35] and can change in 100– 820 rate if the applicator is wearing protective clothing. To the pesticide profenos, the MOE value is 300 [36]; to the acephate, the MOE (calculated as acute human NOEL of 1 mg/kg/day/ estimated human exposure) is <10, depending on the type of spraying used [37].

Thus, the calculation of the safety margin of exposure for the penetration of 5% active ingredients and 16 cm<sup>2</sup> area according to ISO 22608, the MOE value would be 0.5 mg. For acephate, which is an active ingredient more toxic than glyphosate, and assuming that the worker's body area is 21,050 cm<sup>2</sup> as defined by Nuyttens et al. [38], the ingredients actively penetrated would be defined by 657,81 mg (considering 1 day of work). This value is divided by the middle-weight (70 kg) results in condition mg/kg/day. The NOEL value divided by the exposure value calculated previously results in MOE, which is 0.7. This value is low, but it is considered as risk for workers.

Compared with the glyphosate risk used in the tests in Brazil, and using the same body area and the mean body weight data, but with NOEL of 500 mg/kg/day, and the mol of 52.46, a value below that recommended in the work by Lake [39] featured MOE for glyphosate applicators in a value of 83.

Researches about the potential risk of exposure of pesticide applicators have been studied in some European countries, in which the exposure was based on the Agricultural Operator Exposure Model (AOEM) by collecting the data in mg/person of the ingredients and comparing with Acceptable Operator Exposure Levels (AOELs) [40].

Most of the water-repellent materials found in the current market are treated with fluoride and carbon polymerization substances (**Figure 2**), combined in fluoropolymers, giving a high water repellency characteristic to the material [41].

The efficiency evaluation of protective clothing was performed in a laboratory by a closed chamber, which provides less variability in relation to the evaluation in field as environmental conditions and structure of crop. To evaluate the protective clothing in a laboratory, Espanhol-Soares et al. used tracers under field conditions in sugar cane culture and a dummy dressed in sampler clothes in an automated closed chamber. Also, a protective equipment was used to get a greater penetration for evaluation in camera. The penetration of the tracer in the clothes evaluated in the chamber was higher than in the field, ranging from 3.2 to 24% for 0–30 uses and washes, respectively [42].

Machado evaluated the efficacy of whole-body PPE used in the applications of insecticide malathion, for the control of the dengue mosquito. It has been checked that garments washed



**Figure 2.** Chemical structure of polytetrafluoroethylene polymer. C, carbon; F, fluor; and n, repeating units (polymer).



**Figure 3.** (A) A closed chamber used for assessment of protective clothing against pesticide. (B) Spraying layout according to ASTM 1359. (C) Spray layout (ISO 17491-4) [43].

under field conditions show a lower efficiency of clothes washed in the laboratory past and not only passed with 10 and 20 wash cycles, although the values are higher than 98%. Under laboratory conditions, the 30 cycles of washes and hot ironing do not significantly reduce the efficiency of PPE [6]. This result is due to the washing procedure number 8 - called gentle, established in ISO 6330: 2000 [6].

Espanhol-Soares et al. investigated the dermal exposure using a protective clothing applying the efficiency tests conforming to ASTM F 1359, under a spray bath using an exposure level greater than ISO 17491-4. The ISO 17491-4 procedure is required to evaluate complete protection sets in the standard ISO 27065. However, in this work, the ASTM standard was adapted to the flow similar to that of ISO 17491-4 for method A. Nevertheless, the total dermal exposure without the use of the protective clothing was 21426.5 mL L<sup>-1</sup>, according to ASTM 1359 (total volume sprayed 1.98 L). This value is higher than 2265.3 mL L−1, obtained for method B



**Figure 4.** Percentage and variation coefficient of potential exposure in the field and the dummy according to modified ASTM F1359, methods A and B by ISO 1749-4 [43].

(total volume sprayed 4.56 L) and 587.1 mL L−1, to the total exposition according to ISO 17491-4, using method A (total volume sprayed 1.88 L). **Figure 3** shows the spray methodology differences between ASTM 1359 and ISO 17491-4 [43]. These results imply in the comparison with the best methods to be chosen in the evaluation of clothing. In this work, a tracer was used, although the methods took into account the interfacial tension of the sprayed solution, but there may be differences if these tests were carried out with insecticides or other agrochemicals, due to their characteristics of the formulated product.

Espanhol-Soares et al. [42] evaluated the differences of dermal exposures in new protective clothing in field and laboratory conditions. The use of tracers in the evaluations enabled to obtain a coefficient of variation (CV%) in the field of 27%, and the variation for the dermal exposure in the laboratory using the dummy was between 3 and 4%, as shown in **Figure 4** [43].

## **3. Loss of efficiency**

#### **3.1. Pesticides (types of formulations, active ingredient, viscosity, etc.)**

The penetration of the pesticides is defined by the passage of a chemical compound, which passes through openings, pores of the materials, seams, holes, or other imperfections of overlapping of the clothing [43]. The movement of the pesticide molecule occurs in three stages: adsorption, absorption, and desorption. The adsorption is controlled by the ratio of the tissue surface energy to the surface tension of the spray mixture. Absorption is the way the pesticide interacts within the tissue structure. This movement is determined by the tissue structure and the size of the pesticide molecule. Desorption is the ability of the pesticide to penetrate the tissue [44].

The pesticides used in the ISO 22608 test, which were diluted and undiluted, are glyphosate, chlorpyrifos, and copper hydroxide in a water-repellent material, being greater penetrations for diluted solutions, mainly for solutions of chlorpyrifos and copper hydroxide. For the insecticide chlorpyrifos, the material was rejected after five uses and washes with the value of penetration of 5.5% for the diluted solution. For the solution undiluted material, it was disregarded after 20 washes of the material used in the field, but the evaluation with the glyphosate solution used in certification tests of garments was only reproved after 30 uses and washes after use in the sugar cane culture. These results indicate that it is necessary to carry out the tests with insecticides also for the clothing certification [45].

The penetration and retention of pesticides depend on the type of material: cotton (100%) retains more atrazine than other materials, due to the strong attraction of the molecules in tissue [46]. Nelson et al. evaluated that the differences on the retention of pesticides in protective materials are attributed to the type of the fiber of the material, since the retention of pesticides in cotton materials (100%) occurs in a greater proportion than in cotton/polyester materials (50/50%). The retention of carbaryl, in the formulation-concentrated suspension, and atrazine (concentrated suspension and wettable powder) is higher in cotton material; the cypermethrin (wettable powder) and the trifluralin (emulsifiable concentrate) are higher in cotton/polyester material [47].

## *3.1.1. Insecticides impregnated in protective clothing*

In addition to the evaluation of insecticides in protective clothing, the protective clothing has been impregnated by insecticides using the coating method [48]. Protective clothing used in areas with a higher incidence of diseases such as malaria, Chikungunya, dengue, Yellow fever, African tick-bite fever, *Aedes aegypti,* and Culex mosquitoes are generally impregnated with permethrin. The mixture of this insecticide with repellents may be 100%, depending on the applied dose and the type of coating applied on the clothes (as dip coating or spray). However, the use and wash decrease the efficiency, and it is suggested that after five uses, the insecticides must be reapplied in clothing [49].

The insecticide permethrin was impregnated in military uniform clothing (65% cotton and 35% polyester, weight of 220 g/m<sup>2</sup>) for prevention in malarious areas. After its use in the field, the residual concentration of permethrin is ≥200 mg permethrin/m<sup>2</sup> . The insecticide-coated clothing after 218 washes obtained the remaining permethrin at a concentration of 130 and 95 mg/m<sup>2</sup> . The established value for *A. aegypti* mosquito mortality was 200 mg/m<sup>2</sup> [50]. Clothing impregnated with a mix of repellent and organosorption inhibited 56.25% of bites. A group of the clothes were manually impregnated with the repellent KBR3023 (10  $g/m^2$ ) and another group were impregnated through the combination of pyrimiphos-methyl (150 mg/m<sup>2</sup> ).

#### **3.2. Washing and permeation processes**

An important factor in the loss of repellency of the protective materials against pesticides is the water temperature and the movements during washing used in garments. These facts affect the efficiency of cleaning agents and affect the protection of cotton fabrics as well [51].

The water repellency and the contact angle with the Teflon-treated polyester increase with the concentration of water-repellent substances applied to the fabric and decrease with the increase in the number of AATCC washes of 22 [52].

Obendorf et al. evaluated the adsorption of ionic surfactants present in soaps after washing processes in cotton fabrics. They found that the change in pH in the wash solution affects the adsorption of surfactants in the tissues. Cationic surfactants are adsorbed on cotton fabrics because of the negative charges [53]. This mechanism of adsorption may explain why certain pesticides are more retained in the tissues.

## **3.3. Design of the garments (type of material, presence of sewing, weight, etc.)**

For many times, the inefficiency of protective clothing is due to improper use or poorly constructed, and pesticides penetrate into clothing through openings, seams, zippers, folded sleeves, and poor overlaps of sleeves with gloves [54]. Such inefficiency of protection against pesticides may be absorbed by the skin of the worker [54].

The resistance to penetration of protective material against pesticides depends on the methodology used and the type of tissue. In fabrics made of 100% cotton with a water-repellent treatment (Phobol oil), penetrations below 1.6% have been found when evaluated by the trough, pipette, and atomizer test method. However, in cotton/polyester composite fabrics, the penetration is 12.8% with the pipette method, 16.5% with the gutter method, and no penetration with the atomizer method [42].

Although water-repellent fabrics cause discomfort to workers, especially in the hottest agricultural regions, it is believed that with the proof of EPI efficiency, the applicator distribution on the regions of the body, and with the methodologies of evaluation of the exposures, the EPI should be recommended for the most exposed areas of the body and provide safety and lesser discomfort to the worker as well [55].

Protective clothing has been studied through the ergonomic property testing in dummies in chambers with controlled environmental and exposure conditions [56]. In the dermal exposure, dummies can be used for assessment methods. Therefore, the penetration or retention of insecticides is evaluated, as in the evaluation of malathion spraying on protective clothing used to control dengue [22]. However, there are few studies in the literature that quantitatively evaluate the efficiency of closed-loop protection sets.

Machera et al. used the procedure of ISO 22608 to evaluate the penetration of pesticides in protective clothing materials. For materials containing cotton/polyester (50/50%) with 215  $g/m<sup>2</sup>$ treated with NanoTex® water repellent, the penetration was 2.4% after 15 washes. However, in cotton-dressing materials without water-repellent treatment with 287  $g/m^2$ , the penetration was 18.7%, after five washes [29]. Therefore, it has been found that the cotton yarns in the material provide the highest penetration of the test solution.

Shaw and Schiffelbein tested approximately 100 different fabrics used in the manufacture of pesticide applicator clothing and verified that the highest levels of protection were found on water-repellent garments [9].

Oliveira and Machado Neto evaluated the penetration of the insecticide methamidophos into two types of tissues: a cotton water repellent (153  $\rm g/m^2$  to 0.25 mm) fabric and another jeans fabric (458.66 g/m² to 0.75 mm). The authors noted that after 30 washes at manual washing with soap, more insecticides penetrated into lighter tissue (21.05%) than in the heavier tissue (0.12%) [57].

Marinho [7] evaluated the material of the protective clothing by ISO 22608 with seven types of washes with a machine programmed according to ISO 6330 and a manual washing as well. As a result, before the washing, all materials met the criterion of approval of the requirement rule ISO 27065 (ISO, 2011). After the 5, 10, 20, and 30 wash cycles, the penetrations of the test formulation (glyphosate) were higher than 5% for the materials without ironing process and no longer meeting the criteria of approval. All materials (cotton 100%, cotton 65% + polyester 35%), when ironing, had a penetration of <5%, in five uses and washes. However, the 50% cotton +50% polyester material had the same result in 20 uses and washes.

## **4. Conclusion**

It is noted, according to the study, that there are still several gaps to be studied regarding exposure to insecticides and other pesticides. Protective clothing tested according to international standards uses only one type of pesticide (pendimethalin or glyphosate), which do not emphasize the toxicity of the product in contact with the skin of the worker. The means of exposure to insecticides can occur without the use of clothing, but the exposure also occurs with the use of protective clothing. The loss of efficiency of clothing can be due to wear by insecticide applicators, washing, the use of soap at the time of washing, the presence of seams, and improperly made openings. Another exposure factor is the use of clothing by different types of pesticide formulations, which ensures wear. In addition, the factor discussed is the quality of the clothes that are put up for sale; even the certified clothing used in the application of insecticides does not present adequate exposure to the worker throughout the workday. There are differences in results between the tests carried out with the clothes in the laboratory and in the field, mainly due to wear factor by the use and contamination with other types of formulations that interact with the fabric or material of the dress. It is important to emphasize that many insecticides with high toxicity are still commercialized in the world, although many countries already prohibit their commercialization, as some organophosphates and organochlorines. This way, it is important to evaluate protective clothing with these types of pesticides.

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## **References**

- [1] Keifer MC, Firestone J. Neurotoxicity of pesticides. Journal of Agromedicine [Internet]. 2007;**12**(1):17-25. DOI: 10.1300/J096v12n01\_03
- [2] Nicolopoulou-Stamati P, Maipas S, Kotampasi C, Stamatis P, Hens L. Chemical pesticides and human health: The urgent need for a new concept in agriculture. Frontiers in Public Health. 2016;**4**:148-153. Available from: http://journal.frontiersin.org/Article/10.3389/ fpubh.2016.00148/abstract
- [3] Faria NMX, Fassa AG, Facchini LA. Pesticides poisoning in Brazil: the official notification system and challenges to conducting epidemiological studies. Ciência & Saúde Coletiva. 2007;**12**(1):25-38. Available from: http://www.scielo.br/scielo. php?script=sci\_arttext&pid=S1413-81232007000100008&lng=pt&tlng=pt
- [4] Rosa BT, Borges LAC, Pereira SP, Antonialli LM, Chalfoun SM, Baliza DP. Estudo sobre boas praticas agricolas em uma associaçaoo de cafeicultores familiares por meio da análise de clusters. Coffee Science. 2017;**12**(1):49-59
- [5] BRAZIL. Ministério do Trabalho e Emprego. Portaria no 3.214, de 8 de junho de 1978, Ministério do Trabalho e Emprego. Aprova as Normas Regulamentadoras – NR – do Capitulo V, Titulo II, da Consolidação das Leis do Trabalho, relativas a Segurança e Medicina do Trabalho. Norma Regulamentadora Equipamento de Proteção Individual-NR 6. Disponível em: http://trabalho.gov.br/images/Documentos/SST/NR/NR6.pdf [Accessed: 2018-01-10]
- [6] Machado AA. Efficiency of individual protection equipment with a certificate of approval. against aquosa and oleosa calle malathion used in nebulization [thesis]. Jaboticabal: São Paulo State University; 2017
- [7] Marinho MO. Loss of effectiveness of hydro-repellent materials in the protection against pesticides by washing process [dissertacion]. Jaboticabal: São Paulo State University; 2013
- [8] Espanhol-Soares M. Determination of efficiency and useful life of individual protection sets to pesticides according to the procedure for use and wash [thesis]. Jaboticabal: São Paulo State University; 2012
- [9] Shaw A, Schiffelbein P. Protective clothing for pesticide operators: Part II Data analysis of fabric characteristics. International Journal of Occupational Safety and Ergonomics. 2016;**22**(1):7-11
- [10] ISO. International Organization for Standardization. ISO 27065: Protective clothing— Performance requirements for protective clothing worn by operators applying pesticides. Geneva; 2011. 23 p
- [11] ISO. International Organization for Standardization. ISO 22608: Protective clothing protection against liquid chemicals: Measurement of repellency, retention, and penetration of liquid pesticide formulations through protective clothing materials. Geneva; 2004. 11 p
- [12] ISO International Organization for Standardization. ISO 6529: Protective clothing— Protection against chemicals—Determination of resistance of protective clothing materials to permeation by liquids and gases. Geneva; 2001. 21 p
- [13] Jain R, Raheel M. Barrier efficacy of woven and nonwoven fabrics used for protective clothing: Predictive models. Bulletin of Environmental Contamination and Toxicology. 2003;**71**(3):437-446
- [14] Daroux FY, Carr DJ, Kieser J, Niven BE, Taylor MC. Effect of laundering on blunt force impact damage in fabrics. Forensic Science International. 2010;**197**(1-3):21-29
- [15] Marek J, Martinková L. Protective clothing. In: Williams JT, editor. Waterproof and Water Repellent Textiles and Clothing. Elsevier Ltd; 2018. pp. 392-445
- [16] ASTM. American Society for Testing and Materials F 1359. Standard Test Method for Liquid Penetration Resistance of Protective Clothing or Protective Ensembles under a Shower Spray while on a Mannequin. West Conshohocken: ASTM
- [17] ISO. International Organization for Standardization. ISO 17491-4: Protective clothing— Test methods for clothing providing protection against chemicals—Part 4: Determination of resistance to penetration by a spray of liquid (spray test). Geneva; 2008. 9 p
- [18] So J, Ahn J, Lee TH, Park KH, Paik MK, Jeong M, et al. Comparison of international guidelines of dermal absorption tests used in pesticides exposure assessment for operators. Toxicology Research. 2014;**30**(4):251-260
- [19] Cao L, Chen B, Zheng L, Wang D, Liu F, Huang Q. Assessment of potential dermal and inhalation exposure of workers to the insecticide imidacloprid using whole-body dosimetry in China. Journal of Environmental Sciences (China). 2015;**27**(C):139-146
- [20] Frenich AG, Aguilera PA, Gonzalez FE, et al. Dermal exposure to pesticides in greenhouses workers: Discrimination and selection of variables for the design of monitoring programs. Environmental Monitoring and Assessment. 2002;**80**:51-63
- [21] Selmi G da FR, Trapé AZ. Health protection for rural workers: The need to standardize techniques for quantifying dermal exposure to pesticides. Available from: http://www. scielo.br/scielo.php?script=sci\_arttext&pid=S0102-311X2014000500952&lng=pt&tlng=pt
- [22] Leme TS, Papini S, Vieira E, Luchini LC. Evaluation of personal protective equipment used by malathion sprayers in dengue control in São Paulo, Brazil. Cadernos de Saúde Pública [Internet]. 2014;**30**(3):567-576. Available from: http://www.scielo.br/scielo. php?script=sci\_arttext&pid=S0102-311X2014000300567&lng=pt&tlng=pt
- [23] Barcellos M, Faletti MM, Madureira LA dos S, Bauer FC. Analytical evaluation of the protection offered by sealed tractor cabins during crop pulverization with fenitrothion. Environmental Monitoring and Assessment. 2016;**188**(12):660
- [24] Tácio MB, Oliveira ML, Machado-Neto JG. Efficiency of new clothes waterrrepelent int the protection of the tractor-driver in pesticides spraying in guava orchads with the air assisted sprayer. Revista Brasileira de Fruticultura. 2008;**30**:106-111
- [25] Goede HA, Tijssen SCHA, Schipper HJ, Warren N, Oppl R, Kalberlah F, et al. Classification of dermal exposure modifiers and assignment of values for a risk assessment toolkit. The Annals of Occupational Hygiene. 2003;**47**(8):609-618
- [26] Warren N, Goede HA, Tijssen SCHA, Oppl R, Schipper HJ, Van Hemmen JJ. Deriving default dermal exposure values for use in a risk assessment toolkit for small and medium-sized enterprises. The Annals of Occupational Hygiene. 2003;**47**(8):619-627
- [27] Foqué D, Nuyttens D. Effects of nozzle type and spray angle on spray deposition in ivy pot plants. Pest Management Science. 2011;**67**(2):199-208
- [28] Kasiotis KM, Tsakirakis AN, Richard Glass C, Charistou AN, Anastassiadou P, Gerritsen-Ebben R, et al. Assessment of field re-entry exposure to pesticides: A dislodgeable foliar residue study. Science of the Total Environment. 2017;**596-597**:178-186
- [29] Machera K, Tsakirakis A, Charistou A, Anastasiadou P, Glass CR. Dermal exposure of pesticide applicators as a measure of coverall performance under field conditions. Annals of Occupational Hygiene. 2009;**53**(6):573-584
- [30] Machado-Neto JG. Safety measures for handlers/workers against herbicide intoxication risk. In: Price A, Kelton J, Sarunaite L, editors. Herbicides, Physiology of Action, and Safety [Internet]. Rijeka: InTech; 2015. Available from: http://dx.doi.org/10.5772/61464
- [31] ISO. International Organization for Standardization. ISO 16602: Protective clothing for protection against chemicals—Classification, labelling and performance requirements. Geneva; 2007. 40 p
- [32] BRAZIL, Ministério do Trabalho e Emprego MTE, Portaria 121 de setembro 2009. Avaliable from: <http://www.quepia.org.br/site/portaria/2010\_1808/Portaria%20121.pdf>
- [33] Tordoir WF. The development of safe chemical pestice. In: Kee C, Jeyaratnam S, editors. Occupational Health In National Development. 1990
- [34] United States Environmental Protection Agency (USEPA). Reregistration Eligibility Decision (Red) Glyphosate. Office of prevention, pesticides and toxic substances. 1993. https://www3.epa.gov/pesticides/chem\_search/reg\_actions/reregistration/red\_ PC-417300\_1-Sep-93.pdf [Accessed: November 9, 2017]
- [35] US Environmental Protection Agency (US EPA) Human Health Risk Assessment Chlorpyrifos. Office of Pesticide Program, Health Effect Division. 2000. http://www.epa. gov/scipoly/sap/meetings/2008/september/hed\_ra.pdf
- [36] US Environmental Protection Agency (US EPA) Human Health Risk Assessment Profenofos. Office of Pesticide Program, Health Effect Division (7509C), 2000. https://www3.epa.gov/pesticides/chem\_search/cleared\_reviews/csr\_PC-111401\_16- Jun-99\_051.pdf
- [37] Gammon D. Califronia department of pesticide regulation. Acephate risk characterization document. 2008. Available from: http://www.cdpr.ca.gov/docs/risk/rcd/acephate.pdf
- [38] Nuyttens D, Braekman P, Windey S, Sonck B. Potential dermal pesticide exposure affected by greenhouse spray application technique. Pest Management Science. 2009;**65**(7):781-790
- [39] Lake R. Health risk assessment: Glyphosate: Prepared as part of a Ministry of Health contract for scientific services. 2014. https://www.esr.cri.nz/assets/HEALTH-CONTENT/ MoH-reports/FW14022-Glyphosate-FINAL-28-Oct-2014.pdf
- [40] Wong HL, Garthwaite DG, Ramwell CT, Brown CD. Assessment of exposure of professional agricultural operators to pesticides. Science of the Total Environment. 2018;**619-620**:874-882
- [41] Barreto C, Chen JP, Desai I, Finegold S, George A, Hu M, Nan K, Otake R, Rao A, Smolen C, Yin L, Zhao D. Improving the hydrophobicity of fabrics with the use of phosphonic acids. 2013. Available from: http://www.drew.edu/wp-content/uploads/sites/99/Team2. pdf
- [42] Espanhol-Soares M, Nociti LAS, Gonçalves Machado-Neto J. Procedures to evaluate the efficiency of protective clothing worn by operators applying pesticide. Annals of Occupational Hygiene. 2013;**57**(8):1041-1053
- [43] Shaw A, Cohen E, Hinz T, Herzig B. Laboratory test methods to measure repellency, retention, and penetration of liquid pesticides through protective clothing part I: Comparison of three test methods. Textile Research Journal. 2001;**71**(10):879-884
- [44] Leonas KK. The mechanism of pesticide transmission through apparel fabrics: A comparison of drop and spray exposure methodologies. Archives of Environmental Contamination and Toxicology. 1991;**20**(3):427-431
- [45] Espanhol-Soares M, Teodoro de Oliveira M, Machado-Neto JG. Loss of effectiveness of protective clothing after its use in pesticide sprays and its multiple washes. Journal of Occupational and Environmental Hygiene. 2017;**14**(2):113-123
- [46] Taylor SM, Kim CJ, Lombadi J, Lea SM. Pesticide residue distribution on protective clothing fabrics as determined by SEM micrographs and their image analyses, performance of Protective Clothing: Issues and priorities for the 2t. In: Nelson CN, Henry NW. Century: Seventh Volume, ASTM STP 1386. West Conshohocken, PA: American Society for Testing and Materials; 2000
- [47] Nelson C, Laughlin J, Kim C, Rigakis K, Raheel M, Scholten L. Laundering as decontamination of apparel fabrics: Residues of pesticides from six chemical classes. Archives of Environmental Contamination and Toxicology. 1992;**23**(1):85-90
- [48] Faulde MK, Nehring O. Synergistic insecticidal and repellent effects of combined pyrethroid and repellent-impregnated bed nets using a novel long-lasting polymer-coating multi-layer technique. Parasitology Research. 2012;**111**(2):755-765
- [49] Alpern JD, Dunlop SJ, Dolan BJ, Stauffer WM, Boulware DR. Personal protection measures against mosquitoes, ticks, and other arthropods. Medical Clinics of North America. 2016;**100**(2):303-316
- [50] Most B, Pommier de Santi V, Pagès F, Mura M, Uedelhoven WM, Faulde MK. Erratum to: Long-lasting permethrin-impregnated clothing: Protective efficacy against malaria in hyperendemic foci, and laundering, wearing, and weathering effects on residual bioactivity after worst-case use in the rain forests of French Guiana. Parasitology Research. 2017;**116**(2):677-684. DOI: 10.1007/s00436-016-5333-6
- [51] Liu H, Wang Y, Gong RH, Zeng J, Ding X. The relationships between washing parameters, fabric movement, and wrinkling in a top-loading washer. Textile Research Journal [Internet]:40517517700197. Available from: https://doi.org/10.1177/0040517517700197
- [52] Mortazavi V, Khonsari MM. On the degradation of superhydrophobic surfaces: A review. Wear. 2017;**372-373**:145-157
- [53] Obendorf SK, Dixit V, Woo DJ. Microscopy study of distribution of laundry fabric softner on cotton fabric. Journal Surfactant Detergent. 2009;**12**:225-230
- [54] Aprea C, Terenzoni B, De Angelis V, Sciarra G, Lunghini L, Borzacchi G, et al. Evaluation of skin and respiratory doses and urinary excretion of alkylphosphates in workers exposed to dimethoate during treatment of olive trees. Archives of Environmental Contamination and Toxicology. 2004;**48**(1):127-134
- [55] de Oliveira ML, Machado Neto JG. Segurança na aplicação de agrotóxicos em cultura de batata em regiões montahosas TT—Safety of pesticides application on potato crop on sloped areas. Revista Brasileira de Saúde Ocupacional. 2005;**30**:15-25. DOI: 10.1590/ S0303-76572005000200003
- [56] Holmér I. The role of performance tests, manikins and test houses in defining clothing characteristics relevant to risk assessment. Annals of occupational hygiene [Internet]. 1999;**43**(5):353-356. Available from: http://www.ncbi.nlm.nih.gov/pubmed/10481635
- [57] Oliveira ML, Machado-Neto JG. Permeability of two types of cotton fabric used in personal protective clothing to the insecticide methamidophos. Bulletin of Environmental Contamination and Toxicology. 2005;**75**:1156-1162



