Human Exposure Assessment of Pesticide Use in Developing Countries

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Doctoral Thesis
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“So divinely is the world organized that every one of us, in our place and time, is in balance with everything else”

- Johann Wolfgang von Goethe -

This doctoral thesis is especially dedicated to my mother Alba Delfina Fabián, who said to me when I was a child: "Don't give up! You have the chance to be a Doctor!"

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Summary

Problem. Pesticides play an important role in the agricultural production but their misuse affect the health of farmers and workers who manipulate such toxic substances. In the field of occupational hygiene, researches have been working in finding out the most appropriate method to estimate the human exposure in order to assess the risk and therefore to take the due decisions to improve the processes in the pesticide management and to reduce the health risk.

Goals. The goal of this research was focused in creating a model for human exposure assessment specially for farming systems in developing countries by (i) evaluating the available models for human exposure assessment developed in industrialized countries, (ii) measuring the exposure in the study areas of potato and flower farming systems in Colombia, and (iii) proposing a pesticide flow model to estimate quantitatively the human exposure.

Methods. The research was organized in three phases by using different methods, namely (i) evaluation of previous models of human exposure assessment (by means of a Multi-Criteria and Sensitivity Analysis); (ii) quantification of dermal exposures in Vereda La Hoya (by applying the Whole Body Dosimetry, Luminiscence Spectrometry and Tracer Method); and (iii) the development of a pesticide flow model for the human exposure assessment (by applying the Material Flow Analysis method). This model was built with dermal exposure measurements obtained in the study area of greenhouse flower crops in Sabana de Bogotá, Colombia.

Results. DERM, DREAM, PHED and RISKOFDERM were selected as the most appropriate models to be applied in farming systems in developing countries as their determinants are relevant for the assessment of pesticide use and all the processes involved during the pesticide management. Afterwards these four models were applied to assess the dermal exposure in the case study of Vereda La Hoya and their determinants were compared with the characteristics of the study area, DREAM and DERM were found as the most appropriate models to assess the dermal exposure in these study areas. However, because some relevant determinants are still absent, the accuracy of these models could be improved if these are included. When comparing the final model assessment of dermal exposure in the study area, DREAM was found as the model that assesses more accurately the dermal exposure in this study area.

In the study area of Vereda La Hoya, Colombia was found that the application was the activity with the highest PDE. Even though lower body parts (thighs and legs) were the most exposed, these body parts also showed the highest level of protection because of the work clothing. The ADE was high for arms and upper back due to the lack of adequate work

clothing covering the complete arm and the direct contact of the upper back with the spills on the sprayer tank. Furthermore, it was found that Metamidophos is the most toxic pesticide used in Vereda La Hoya. Farmers may reduce significantly the health risk by using adequate work clothing made of appropriate fabrics that covers the whole body including the arms, cleaning properly all the pesticide residues left on the sprayer before each application, and avoiding the modification of nozzles using only nozzles with the standard discharge.

The proposed pesticide flow model helps to identify the patterns of pesticide distribution on the body, the level of protection given by personal protective equipment and the estimates of potential and actual dermal and inhalation exposure. This information can be used to determine the health risk level by comparing the model estimates with the AEOL reference values for each pesticide. In addition, the model makes it possible to easily identify the activities or body parts that have high levels of exposure. This is useful in identifying improvements that will decrease the exposure during pesticide management. Because it is not feasible to measure directly the dermal exposure in all study areas, this model might help to obtain a quick estimation which could help stakeholders and authorities to make further decisions.

Conclusions. This research evaluated in depth the available models for human exposure assessment, so assessors can decide which model is the most appropriate according to the characteristics of the study area in which the model is going to be applied and furthermore this research suggested improvements in the models in order to increase the estimation accuracy.

This research also contributes in the proposal of a new model for human exposure based on the material flow analysis methodology studying the pesticide fractioning during the pesticide management in a certain interval of time. With this model quantitative estimations of human exposure are obtained which facilitate the risk assessment and the implementation of measures to improve the safety during the pesticide management and to decrease the risk. The proposed model also demonstrates the feasibility of applying the material flow analysis methodology in the field of human exposure, obtaining a tool that helps to understand the mechanisms of distribution of the pesticide in the farming system based on the processes involved and the flows between these processes.

Zusammenfassung

Thema. Pestizide spielen eine wichtige Rolle in der landwirtschaftlichen Produktion. Aber deren falsche Anwendung hat Auswirkungen auf die Gesundheit der Bauern und Arbeiter, die mit solchen giftigen Substanzen arbeiten. Im Bereich der Arbeitshygiene haben Wissenschaftler versucht, die bestgeeignete Methode zu finden, das Risiko durch die Exposition des Menschen abzuschätzen und zu bewerten und somit die geeigneten Entscheidungen zu treffen, die Prozesse im Pestizid-Management zu verbessern und das gesundheitliche Risiko zu verringern.

Ziel. Das Ziel dieser Forschung war es, ein Modell für die menschliche Belastung zu entwickeln, vor allem für die Landwirtschaft in Entwicklungsländern. Das Modell fokussierte auf die Exposition von Arbeitern während des manuellen und motorisierten Einsatzes von Pestiziden in Landwirtschaftssystemen wie Kartoffel-und Blumenpflanzen. Dieses Ziel wurde verfolgt durch 1. die Auswertung der verfügbaren Modelle für die menschliche Exposition in den Industrieländern, 2. die Messung der Exposition in den Untersuchungsgebieten der Kartoffel- und Blumenanbausysteme in Kolumbien und 3. die Entwicklung eines Vorschlages für ein Pestizid-Flow-Modell, um die Exposition des Menschen quantitativ abzuschätzen.

Methoden . Die Forschung wurde in drei Phasen mit unterschiedlichen Methoden gegliedert. Nämlich (i) die Bewertung der bisherigen Modelle der menschlichen Expositionsbeurteilung (mittels einer Multi-Kriterien und Sensitivitätsanalyse), (ii) die Quantifizierung der Hautexpositionen in Vereda La Hoya (mit Hilfe der Ganzkörper-Dosimetrie, Lumineszenz-Spektrometrie und Tracer-Methode) und (iii) die Entwicklung eines Pestizid-Flow-Modells für die menschliche Expositionsbeurteilung durch Anwendung der Stoffflussanalyse-Methode. Das Modell wurde erstellt mit Messungen der Hautexposition im Untersuchungsgebiet von Treibhäusern mit Blumenpflanzen in Sabana de Bogotá, Kolumbien.

Ergebnisse. DERM, DREAM, PHED und RISKOFDERM wurden als die am besten geeigneten Modelle ausgewählt, da deren Parameter relevant sind für die menschliche Expositionsbeurteilung des Einsatzes von Pestiziden und aller Prozesse beim Pestizid-Management in der Landwirtschaft in den Entwicklungsländern. Ferner wurden während der Forschung diese Modelle im Untersuchungsgebiet in Kolumbien angewendet, und nach einem Vergleich ihrer Schätzungen mit den Messungen im gleichen Untersuchungsgebiet wurde festgestellt, dass DREAM eine realistischere Abschätzung der Hautexposition ermöglicht.

Im Untersuchungsgebiet Vereda La Hoya, Kolumbien, wurde festgestellt, dass die Anwendung von Pestiziden die Aktivität mit der höchsten PDE war. Obwohl die unteren Körperteile (Oberschenkel und Beine) am stärksten exponiert waren, zeigten diese Körperteile auch den

höchsten Grad an Schutz, aufgrund der Arbeitsschutzkleidung. Die ADE war hoch an Armen und oberem Rücken wegen des Mangels an angemessener Arbeitskleidung, die den gesamten Arm bedeckt, und wegen des direkten Kontaktes des oberen Rückens mit den Verschmutzungen auf dem Sprüher Tank. Darüber hinaus wurde festgestellt, dass Metamidophos das giftigste Pestizid ist, welches in Vereda La Hoya verwendet wird. Die Bauern können das gesundheitliche Risiko deutlich reduzieren durch den Einsatz entsprechender Arbeitskleidung aus geeigneten Stoffen, die den ganzen Körper einschließlich der Arme bedeckt, korrekte Reinigung aller Rückstände von Pestiziden auf dem Sprüher Tank vor jeder Anwendung und die Vermeidung der Abänderung der Düsen, indem nur Standard-Düsen benützt werden.

Das Pestizid-Flow-Modell hilft festzustellen, wie das Pestizid auf den Körper verteilt wird, wie hoch das Niveau des Schutzes durch persönliche Schutzausrüstung ist und ermöglicht die Abschätzung von dermalen und inhalativen Expositionen. Diese Informationen können verwendet werden, um das Gesundheitsrisiko abzuschätzen, und zwar durch den Vergleich der Schätzungen der Modell-Schätzungen mit den AEOL Referenzwerten für jedes Pestizid. Darüber hinaus macht das Modell es möglich, die Aktivitäten oder Körperteile leicht zu identifizieren, die eine hohe Exposition haben. Dies ist nützlich bei der Identifizierung von Verbesserungen, welche die Exposition während des Pestizid-Managements verringert. Da es nicht möglich ist, direkt die dermale Exposition in allen Untersuchungsgebieten zu messen, könnte dieses Modell eine schnelle Einschätzung erlauben und den Interessengruppen und Behörden helfen, weitere Entscheidungen zu treffen.

Schlussfolgerungen. Diese Forschung bewertet die verfügbaren Modelle für die menschliche Expositionsbeurteilung in der Tiefe. So können Gutachter entscheiden, welches Modell, je nach den Merkmalen des Untersuchungsgebietes, am besten geeignet ist. Ferner hat diese Forschung Verbesserungen vorgeschlagen um die Schätzgenauigkeit zu erhöhen.

Diese Forschung schlägt auch ein neues Modell für die menschliche Expositionsbeurteilung vor, basierend auf der Stoffflussanalyse-Methode, mit welcher die Pestizid-Fraktionierung während des Pestizid-Managements in einem bestimmten Zeitintervall studiert wird. Mit diesem Modell erhält man eine quantitative Abschätzung der Exposition von Menschen, welche die Risikobewertung und die Umsetzung von Maßnahmen erleichtert, um die Sicherheit während des Pestizid-Managements zu verbessern und das Risiko zu verringern. Das vorgeschlagene Modell zeigt auch die Machbarkeit der Anwendung der Stoffflussanalyse- Methode im Bereich der menschlichen Expositionsbeurteilung. Es bietet ein Werkzeug, die Mechanismen der Verteilung der Pestizide im Landwirtschaftssystem zu verstehen, basierend auf den beteiligten Prozessen und den Flüssen zwischen diesen Prozessen.

Table of Contents

List of Acronyms

ADE	Actual Dermal Exposure
AOEL	Acceptable Operator Exposure Level
ASOCOFLORES	Asociación Colombiana de Exportadores de Flores
CA DPR	Californian Department of Pesticide Regulation
CAS	Chemical Abstracts Service Registration
COSHH	Control of Substances Hazardous to Health Regulations
DERM	Dermal Exposure Ranking Method
DREAM	Dermal Exposure Assessment Method
DREAM	Estimation and Assessment of Substance Expoure
EUROPOEM	European Predictive Operator Exposure Model Database
F	Flows
FAO	Food and Agricultural Organization of the United Nations
HD	Nozzle with High Discharge
LD	Noozle with Low Discharge
MADR	Ministerio de Agricultura y Desarrollo Rural de Colombia
MFA	Material Flow Analysis Methodology
P	Process
PDA	Potential Dermal Exposure
PHED	Pesticide Handlers Exposure Database
RISKOFDERM	Risk Assessment of Occupational Dermal Exposure to Chemicals
SD	Nozzle with Standard Discharge
OAT	One At the Time Sensitivity Analysis Methodolody
PUBCHEM	Database of chemical molecules and their activities against biological assays
US EPA	United States Environmental Protection Agency
US NRC	United States Nuclear Regulatory Commission
WHO	World Health Organization

Part A

Dissertation Synopsis

1. Introduction

1.1 The Pesticide Issue

The agricultural sector is under pressure to increase crop productivity in order to maintain the food security for an increasingly growing population . FAO has reported that 868 million people continue to suffer from undernourishment and the negative health consequences of micronutrient deficiencies continue to affect around 2 billion people . Pests affect productivity by causing losses in the agricultural output, storage and the distribution of products. Approximately 9,000 species of insects and mites, 50,000 species of plant pathogens, and 8,000 species of weeds damage crops, worldwide . Insect pests cause an estimated 14% of loss, plant pathogens cause a 13% loss, and weeds a 13% loss but these losses decline to 35-42% when pesticides are used . However, even though pesticides play an important role in plant protection, in many cases, overuse or inappropriate use compromise the human health of pesticide users, agricultural workers and bystanders .

Pesticides are a key element of pest management programs in modern agriculture to increase the levels of production. Their use is stimulated by the commercialization and intensification of agriculture, the difficulty in expanding cropped acreage, the increased demand for agricultural products as population rises, and the shift to cash crops for domestic and export sales . It is estimated that annually 2.5 million tons of pesticide are used worldwide and 220,000 people die because of poisoning from these substances and most of these poisonings occur in developing countries because of weak safety standards, minimal use of protective equipment, absence of washing facilities, poor labeling, and lack of information programs .

Public health has an increasing concern about the use of pesticides because epidemiological studies have found that they are associated with different types of cancers , neurologic pathologies , respiratory symptoms and hormonal and reproductive abnormalities . Regardless of the risks involved in the use of pesticides, they are considered a key input to agriculture allowing intensive production techniques . Therefore, it is crucial to assess the risk due to pesticide use by improving their management, reducing the exposure and protecting human health.

The agricultural sector in Colombia uses 3.8 million hectares of land for permanent and transitory crops. During the last decade, an average of 82,000 tons of pesticides were applied per year (17% insecticides, 47% herbicides and 35% fungicides and bactericides) . This suggests that part of the population and the environment in Colombia are likely to be exposed to the negative effects derived from pesticide use. For instance, the potato farming system occupies 128,700 ha with 230,000 production units which had a production of 2.3 million tons in 2012 and used 32.5 kg/ha of pesticide active ingredients . The case of the floriculture system in Colombia is another example where there is a cultivated area of 6,800 hectares and an average of 15 workers per hectare are directly and/or indirectly exposed to the pesticides. Studies in the 1990s showed birth defects among children as well as adverse reproductive outcomes in populations occupationally exposed to pesticides in the floriculture crop system in Colombia .

Although the floriculture industry has made significant progress in reducing pesticide exposure, and numerous studies have assessed exposure to pesticides in greenhouses worldwide , there are no recent studies of human exposure in the floriculture system in Colombia. Also, this situation occurs for the potato farming system with the additional problem that there are no regulations regarding the use of pesticides. Therefore, the quantification of human exposure to pesticide use in farming systems like potato and flowers is crucial to provide information about the level of risk faced by farmers and workers and to support the development of proper policy measures.

1.2 Risk Assessment of Pesticide Use in Developing Countries

In the agricultural field, there is an increasing concern about the health of farmers, workers and bystanders, since they might be frequently exposed to pesticides during long periods of time. Governments, especially from developed countries, have introduced new environmental policies about the adequate use of pesticides. Meanwhile, in developing countries, like Colombia, a similar attempt has been done but even though the regulation scheme is already defined, this is not efficiently implemented due to the lack of information about exposure assessment and risk characterization . The definition and implementation of these environmental policies is a further step after a risk assessment. Therefore, it is crucial to establish a method for the risk assessment of pesticide application in developing countries focusing in the exposure assessment and the risk characterization. The conclusions coming out from this method will be useful for stakeholders not only for the improvement of the risk assessment scheme, identifying the critical factors that influence the level of exposure concentrations, but also for the development of pedagogical programs about the appropriate use of pesticides.

The risk assessment of pesticide application can be defined in two essential parts: *exposure assessment* (qualitative and quantitative description of the exposure concentrations and related dose for specific pathways) and *effects assessment* (determination of the intrinsic hazards associated with the agent and quantification of the relationship between the dose with the target tissue and related harmful outcomes) . The first part is known as the initial portion of the environmental health paradigm: from sources, to environmental concentrations, to exposure, to dose. The effects assessment is aiming for the latter portion of the events continuum: from dose to adverse health effects. This research is focused in the first part, developing a model for the dermal and inhalation exposure assessment.

In the field of occupational hygiene, the attention has shifted to the research of the exposure in the agricultural workplace to improve the pesticide management and to reduce the health risk . This is of special interest in developing countries because pesticide management activities face weak safety standards . Studies in potato farming systems in Vereda La Hoya, Colombia , Mojanda, Ecuador and El Angel, Ecuador have shown that pesticide management has no a particular theoretical basis and instead it is proceeded by trial and error finding out what works out in practice. Furthermore, farmers do not wear adequate personal protective equipment, apply pesticides which are banned in industrialized countries and modify the standard discharge of nozzles to reduce the application time . Because these issues increase the health risk due to human exposure, a risk assessment of pesticide use in these areas is required in order to determine the risk level.

1.3 Modeling Human Exposure to Pesticide Use

Indirect methods to assess human exposure have been used since the early 1990s . Tools for dermal exposure, such as EASE , EUROPOEM , PHED , RISKOFDERM , COSHH STOFENMANAGER , DREAM , and the approaches proposed by the U.S. EPA are targeted at occupational situations in industrial processes in Europe and the USA, but they do not consider agricultural processes such as pesticide management countries and there might be uncertainties when they are applied in study areas in developing countries. DERM is a method focused on occupational activities in pesticide management in developing countries; nonetheless, its semi-quantitative estimations still lack reliability and validity . Because of the lack of studies about the application and further evaluation of these models in farming systems in developing countries, there is no consensus about the best method to evaluate the human exposure and the health risk in those systems. In the agricultural field, there is a major concern about the dermal exposure assessment, rather than the inhalation exposure assessment. Therefore, this research was focused on the dermal exposure assessment field and the following goals and research questions were established:

2. Goal and Research Questions

Given the drawbacks related to the necessity of a tool that facilitates the risk assessment of pesticide use in developing countries, this research had as a goal "***to develop a model for human exposure assessment of pesticide use in developing countries***" focusing on the dermal exposure assessment. The model was developed based on the case studies of manual and motorized pesticide applications in farming systems like potato and flower crops. The research goal was articulated in three groups of research questions which were organized in three research phases:

2.1 Research Phase 1: Evaluation of models for the human exposure assessment of pesticide use

Because of the lack of studies about the application and further evaluation of these models in farming systems in developing countries, up to date, there is no consensus about the best methodology to evaluate the human exposure in these study areas. Therefore, existing models for human exposure (DERM, DREAM, PHED, RISKOFDERM, COSHH, STOFENMANAGER and EASE) were evaluated in order to find out the most appropriate to be applied in case studies in developing countries. Along this evaluation the following research questions were addressed:

a) Which of the existing models are feasible to be applied in case studies in farming systems in developing countries?

b) Which parameters are considered inside the structure of the models and which are relevant for the case studies in developing countries?

c) When comparing the model outcomes with the dermal exposure measurements in the study area, which model assesses dermal exposure more accurately?

These phase and research questions were answered through the ***Publication 1*** of this dissertation.

2.2 Research Phase 2: Quantification of Dermal Exposures

The quantification of dermal exposure to pesticide use is necessary to establish the status quo of the level of risk faced by farmers in the study area and also to compare the results with the model estimations obtained from the first research phase. Therefore, the human exposure was measured in Vereda La Hoya in the highlands of Colombia and the following research questions were addressed:

a) What is the current level of potential and actual dermal exposure to pesticides under the present working conditions in the potato farming system in the highlands of Colombia?

b) What is the level of health risk due to dermal exposure faced by farmers under the present working conditions and what are the critical activities that affect it?

This phase and these research questions were answered through the ***Publication 2*** of this dissertation.

2.3 Research Phase 3: Modeling Human Exposure to Pesticide Use

Taking into account the disadvantages of the existing methodologies for human exposure assessment, a tool is required to provide a quantitative unambiguous estimation of dermal and inhalation pesticide exposure in developing countries; therefore, a human exposure model was developed based on the material flow analysis (MFA) methodology and afterwards tested with human exposure measurements made in the greenhouse flower crop system in Colombia. Accordingly, this methodology might be applied in the field of human exposure, allowing quick and early recognition of the fractioning of the pesticides in the human body during pesticide management and helping to identify activities that are crucial for improving the operational safety. In this research phase, the following research questions were addressed.

a) How can the material flow analysis methodology be adapted to study human exposure to pesticides in agricultural systems?
b) What are the advantages and disadvantages of using this methodology in the field of human exposure and risk assessment of pesticide use?

c) Based on the model outputs, what is the current situation with respect to human exposure to pesticides in the flower crop systems in Colombia, and how can the pesticide management be improved?

The conceptual framework of the model was presented in **4 international conferences**, whose summaries are included in this dissertation and the research questions were answered through the **publication 3** of this dissertation.

3. Methodology

This section will be explained according to the three research phases (Table 1): Evaluation of previous models of human exposure assessment, quantification of dermal exposures in Vereda La Hoya, and the development of a pesticide flow model for the human exposure assessment. The model was built with dermal exposure measurements obtained in the study area of greenhouse flower crops in Sabana de Bogotá, Colombia.

3.1 Research Phase 1: Evaluation of models for the human exposure assessment of pesticide use

After a literature review, seven available models were considered for the analysis: COSHH , DERM , DREAM , EASE , PHED , RISKOFDERM and STOFENMANAGER . These models were selected because of their availability, clear model description and their potential applicability for the assessment of pesticide use in farming systems in developing countries. They were analyzed according to the following group of criteria:

- *General characteristics of the model:* year of development, country of origin, model goal, conceptual basis.
- *Usability of the Model:* target group, availability, guidance, knowledge/equipment required, reliability, data required as input, type of outcome.
- *Characteristics of the assessment*: type of exposure, type of substance, physical state of evaluated the substance, dermal exposure pathway, dermal exposure descriptor, evaluated body part.

From the results of the multi-criteria analysis and based on model characteristics such as the availability, guidance, knowledge required, reliability, type of outcome, type of substance, target group and dermal exposure descriptor and dermal exposure pathway, four models (i.e. DERM, DREAM, PHED, and RISKOFDERM) were selected to be applied in the case study of potato farming systems in Vereda La Hoya in the highlands of Colombia. The data used as input comes from a previous survey made in the study area with 197 smallholder potato growers in four communities and previous studies about dermal exposure in the same study area . Furthermore, to study how the different model parameters influence the model outcome for the study area, a sensitivity analysis was performed applying the "One at the Time" (OAT) method , in which one determinant was left with the score from Vereda La Hoya and the rest of the determinants were left with the lowest score.

3.2 Research Phase 2: Quantification of Dermal Exposures

To establish the status quo of the level of risk faced by farmers in the study area and also to compare the results with the model estimations obtained from the first research phase, the exposure was measured in the study area of the potato farming system in Vereda la Hoya. The pesticide fractioning on the body was measured during the three activities of the pesticide management with the whole body dosimetry method (WHO, 1982; Chester, 1993) (Figure 1 and 2) using the tracer uranine (Fluorescein Sodium Salt; $C_{20}H_{10}Na_2O_5$; CAS Registry Number: 518-47-8; PubChem Compound ID: 10608) as surrogate for the pesticides.

Table 1: Research overview with the phases, methods, outputs and publications.

Research Goal	Phases	Methods	Outputs	Publications
Development of a Model for Human Exposure Assessment of Pesticide Use in Developing Countries	Phase 1: Evaluation of available models for human exposure assessment	Literature Review Multi-Criteria Analysis Sensitivity Analysis	Comparison of Model Estimations	Lesmes-Fabian et al., 2013b[1]
	Phase 2: Quantification of dermal exposures in a selected study area	Whole-Body-Dosimetry Tracer Method Survey	System Characterization Dermal Exposure Assessment	Lesmes-Fabian et al., 2012a[2]

	Phase 3: Modelling Pesticide flow analysis	Material Flow Analysis Survey Whole-Body-Dosimetry Tracer Method	Conceptual Framework of the Model Pesticide Flow Analysis Model	Lesmes-Fabian et al., 2010a[3] Lesmes-Fabian et al., 2010b[4] Lesmes-Fabian et al., 2010c[5] Lesmes-Fabian et al., 2012b[6] Lesmes-Fabian et al., 2013a[7]

[1]Lesmes Fabian, C., et al. (2013b). "Evaluation of Models for Dermal Exposure Assessment in Farming Systems in Developing Countries." Journal of Environmental Engineering and Ecological Science. Article in Preparation.

[2]Lesmes-Fabian, C., et al. (2012a). "Dermal Exposure Assessment of Pesticide Use: The Case of Sprayers in Potato Farms in the Colombian Highlands." Science of the Total Environment 430 (2012): 2002-2008.

[3]Lesmes-Fabian, C., et al. (2010a). “Human Exposure Assessment to Pesticides in Developing Countries: Pesticide Flow Analysis during Handed- and Motor-Pressurized Applications” 9th International Conference on Ecobalance. Presentation D3-1430, Tokyo, Japan.

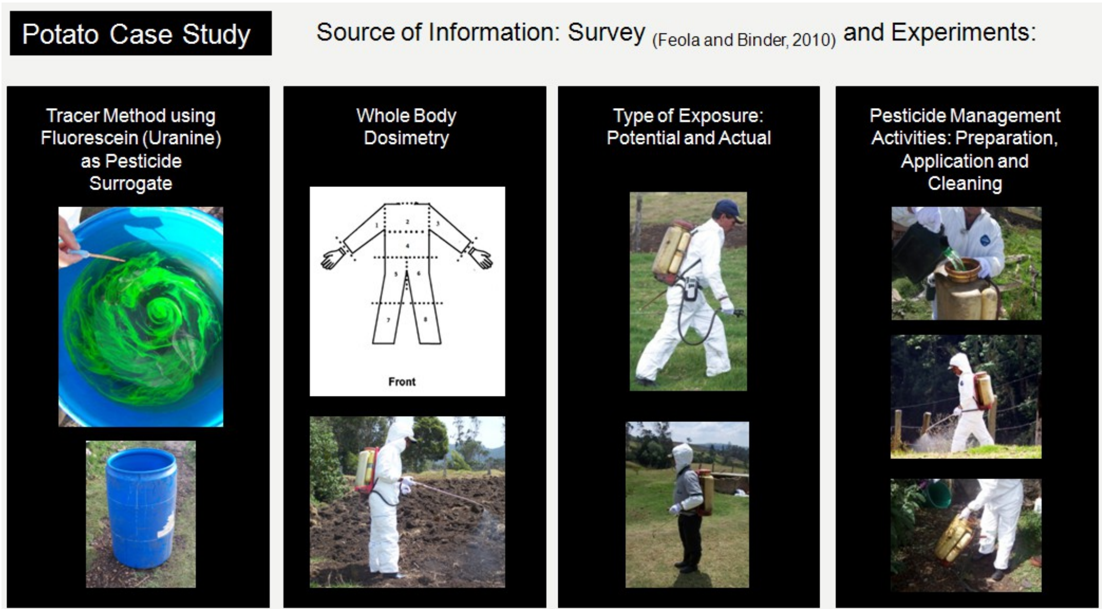
[4]Lesmes-Fabian, C., et al. (2010b). “Pesticide Flow Model for the Environmental and Human Exposure Assessment to Pesticide Use in Developing Countries”. ISIE Asia-Pacific Meeting and ISIE MFA ConAccount Meeting. Presentation A-314, Tokyo, Japan.

[5]Lesmes-Fabian, C., et al. (2010c). “Model for Dermal and Inhalation Exposure Assessment of Pesticide Applications on Agricultural Products in Colombia”. Tropentag "World Food System - A Contribution from Europe", Zurich, Switzerland.

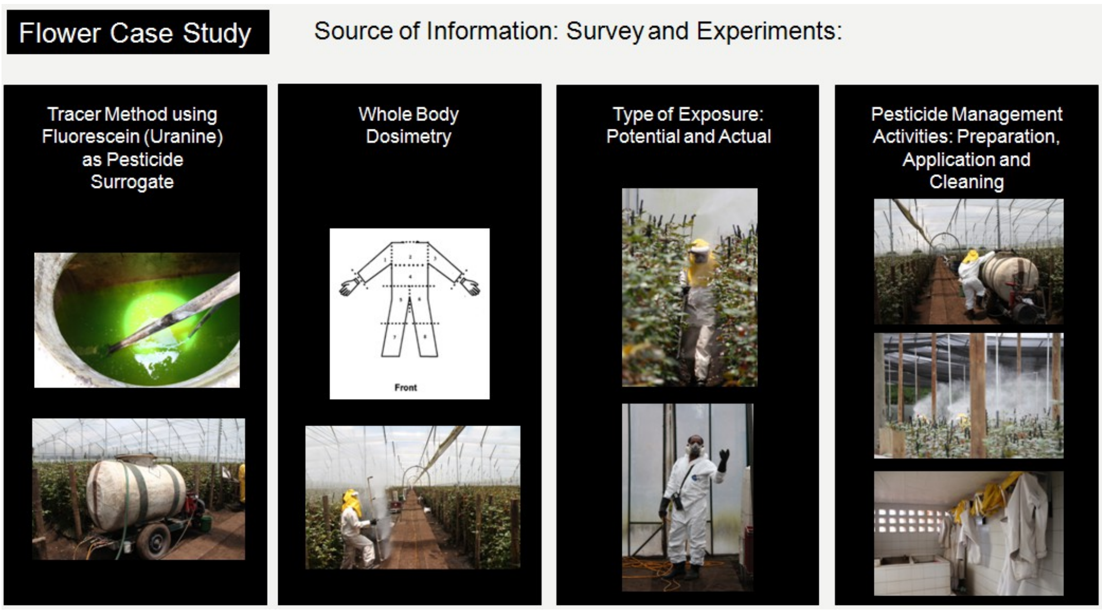
[6]Lesmes-Fabian, C., et al. (2012b). Dermal and Inhalation Exposure Assessment of Pesticide Management in Greenhouse Flower Crops in Colombia. Tropentag “Resilience of agricultural systems against crises”, Göttingen, Germany.

[7]Lesmes-Fabian, C., et al. (2013a). "Pesticide Flow Analysis to Assess Human Exposure in Greenhouse Flower Production in Colombia." International Journal of Environmental Research and Public Health 10(4): 1168-1185.

The description of all the procedure in the field and in the laboratory can be read in the second publication of this dissertation. The human exposure was measured in terms of potential dermal exposure (PDE) and actual dermal exposure (ADE). PDE is defined as the amount of contaminant landing on the outer layer of work clothing . This was measured during preparation, application and cleaning wearing the tyvek garments over the work clothing together with cotton gloves. ADE is defined as the amount of contaminant reaching the exposed skin surfaces . This was measured only during application wearing the tyvek garment under the work clothing.



a)



b)

Figure 1: Measurement of the pesticide fractioning in the potato farming system (a) and the flower crop system (b).

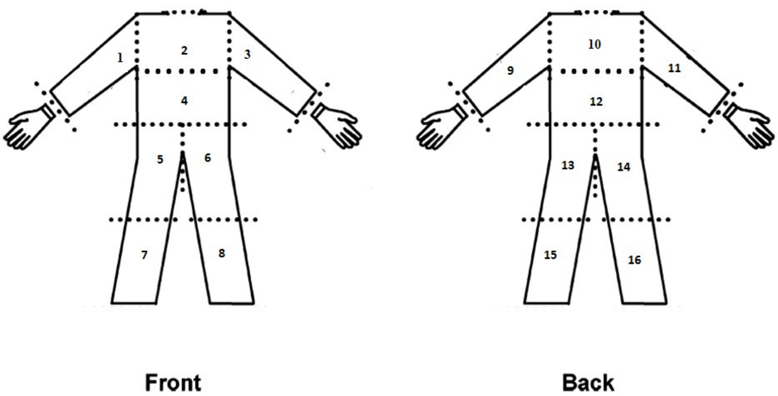


Figure 2: Whole body dosimetry with the cutting scheme (Adapted from Hughes et al., 2006).

3.3 Research Phase 3: Modeling Human Exposure to Pesticide Use

A conceptual framework (Figure 3) was proposed to study the different pathways followed by the pesticides during the pesticide management . This conceptual framework represents the flow of the pesticides according to different tasks (i.e., pesticide preparation, application and cleaning); the environmental compartment in which the pesticide is dispersed (i.e., air); the protection factors that could reduce the exposure dose (i.e., clothing, body protective equipment and respiratory protective equipment); and the human exposure dose (i.e., amount of pesticide in contact with skin and lungs which result in the exposure dose).

In order to build up the model, the human exposure to pesticide was measured in the study area of greenhouse flower production in Colombia during the different pesticide management activities such as preparation, application and cleaning of application equipment. Human exposure to pesticides was studied in terms of the fractioning of pesticides in the human body, including the dermal and inhalation exposure routes. The floriculture system was defined in terms of the pesticide management activities that are performed in the greenhouse (preparation and application of the pesticides) and the cleaning rooms (where all the application and personal protection equipment is cleaned).

3.4 Study Areas

3.4.1 Potato Farming System

This study area is located in Vereda La Hoya near Tunja, the capital city of the province of Boyacá, Colombia (Figure 4). This is a rural region devoted mainly to the cultivation of potato in production units of around 3 hectares. The crop depends on rainfall; therefore, the production is generally organized into two periods, one from March to September and another from October to February, corresponding to the two rainy seasons. Average annual productivity is 18.3 ton/ha . Potato crops in this region are vulnerable to three major pests: the soil-dwelling larvae of the Andean weevil

(*Premnotrypes vorax*), the late blight fungus (*Phytophthora infestans*) and the Guatemalan potato moth (*Tecia solanivora*) . These pests, together with the weeds present in the early phases of the crop, are controlled by the application of chlorothalonil, chlorpyrifos, cymoxanil, glyphosate, mancozeb, metamidophos and paraquat .

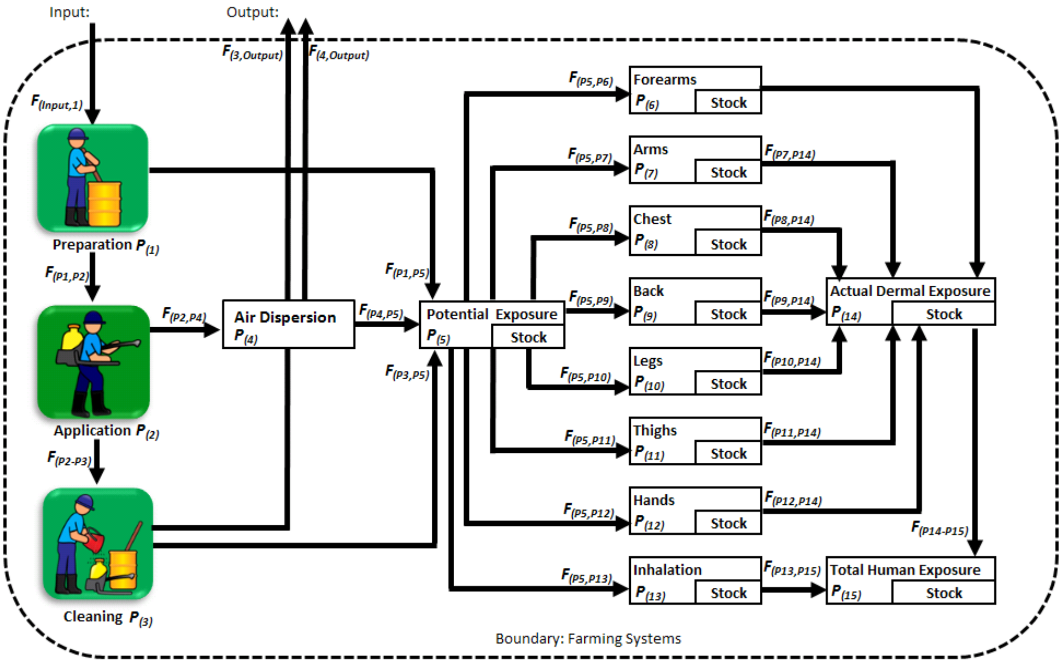


Figure 3: Conceptual framework of the pesticide flow analysis .

A survey made in the location showed that a high percentage of farmers experience various symptoms related to the use of pesticides (i.e., headaches 24%; eye irritation 20%; bronchial irritation 9%; skin irritation, 5%; dizziness, 42%; nausea, 7%) . This study area was selected because of the high intensity of pesticide use , the high health risk reported for pesticide applicators and their households and because of the available information obtained in previous studies .

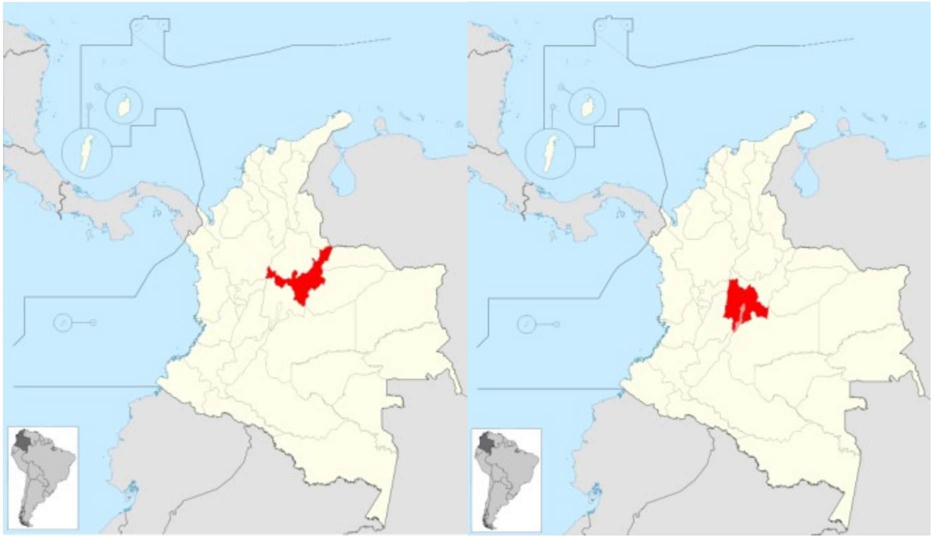


Figure 4: Map of Colombia showing the Province of Boyacá (left) where the study area of the potato farming system is located; and the Province of Cundinamarca (right), where the study area of the flower crop system is located.

3.4.2 Greenhouse Flower Production in Colombia

The study area selected for the measurement of the pesticide flows was a farm dedicated mostly to rose production, with an area of 25.5 ha, located on the Bogota Plateau at 2,685 m.a.s.l. in the province of Cundinamarca (Figure 4). The average temperature is 13 °C, and inside the greenhouses the temperature fluctuates during the day from 6 to 11 °C at 6:00 am, 21 to 31 °C at 11:00 am and 22 to 29 °C at 2:00 pm. The rose plants had a crop density of 8.2 to 8.6 plants/m^2 in rows 32 m long and 0.8 m wide, separated by 0.6 m paths. A greenhouse has between 170 and 230 rows. The main pests affecting the rose crop production are downy mildew (*Peronospora sparsa*), grey mold (*Botrytis cinerea*), thrips and spider mites (*Tethranycus spp.*). Fungicide management is performed using a rotation of products such as carbendazim (0.6 cc/L), carboxin-thiram (1 cc/L), mancozeb (2 cc/L), dimethomorph (0.7 cc/L) propamocarb chlorohydrate (1.8 cc/L) and mandipropamide (0.8 cc/L).

The pesticide preparation is made in the field mixing the commercial pesticide products with water in a 500-L container. The pesticides are applied with standard personal protection equipment used by all the farms registered as members of the Association of Colombian Flower Exporters. It consisted of a rubber level B Hazmat suit (a garment that protects against splashes from hazardous chemicals with an external breathing mask, hood, rubber gloves and waterproof boots). The cleaning activity consists of washing the personal protective equipment and the application accessories in a washing facility by using water and cleaning products like detergent and soap.

4. Results

In this section the most relevant results are presented according to the goal and the three research phases. Further details can be found in the next part of this dissertation where all the publications are available.

4.1 Research Phase 1: Evaluation of models for the human exposure assessment of pesticide use.

4.1.1 Research Question 1: Which of the existing models are feasible to be applied in case studies in farming systems in developing countries?

This answer was found after a multi-criteria analysis. Table 2 describes the evaluated models according to the different criteria and figure 5 shows the radar diagram with the multi-criteria analysis. The models DERM and DREAM were found as the most appropriate models because they include determinants that describe the working conditions and the transportation process (i.e. emission, deposition and transfer) during the pesticide management which are relevant for study areas in developing countries . However, it is important to notice that the model DERM has not been validated and the exposure outcomes might be wrongly estimated. In the case of DREAM , even though it has a more complex structure of determinants that covers most of the specific characteristics of the study areas in developing countries, the model has been criticized because its reproducibility, validity and accuracy have been partially proved . Because the models COSHH, EASE, PHED and STOFENMANAGER have been used in the last decade for the exposure assessment in industrial processes and they have been implemented by occupational hygiene institutions in their country of origin, they were considered as reliable. According to previous studies, DREAM is considered as partly validated , and DERM as a non-validated model .

Table 2: Description of the evaluated model for dermal exposure assessment according to the multi-criteria analysis

CRITERIA	MODELS						
	COSHH	DERM	DREAM	EASE	PHED	RISKOF.	STOFFEN.
Origin	UK	Nicaragua	The Netherlands	UK	USA/Canada	Europe	The Netherlands
Year	2002	2008	2003	1994	2002	2003	2003
Goal	Risk assessment in SMEs	Risk assessment in developing countries	Risk assessment of occupational exposure in any situation	Risk assessment for regulatory of new chemicals	Standardized exposure estimates	Risk assessment for regulatory and registration processes	Risk assessment in SMEs
Basis	Operational exposure levels assess exposure and R-phrases for health hazard	Transport Processes, Schneider, 1999; DREAM, 2003	Transport processes, Schneider, 1999. Airborne concentrations	Computer aided decision tree format , Schneider, 1999	Reported information on pesticides and monitoring data	Schneider, 1999; COSHH .	Schneider, 1999; COSHH . Riskofderm
Target group	SME's	Farmers in developing countries	Industrial processes and farming systems	Industrial processes	Regulatory agencies, pesticide industry	Operational and technical staff mostly in SMEs	Dutch companies
Availability	Electronic version	Publication	Publication	Software available	Software and publication	Software and publication	Website
Guidance	Website with guidelines for specific industries	Publication	Publication	Not available	Publication	Publication	Website with no guidelines about the algorithms
Knowledge/ Equipment required	No specific expertise required and electronic version available	Basic mathematics skills and easy to carry out in the field	Basic mathematics skills and easy to carry out in the field	Knowledge of the model and programming	Knowledge of the criteria and their effects on exposure. Computer required	Knowledge of the model and computer required	Internet access required
Reliability	Evaluated by the NIOSH authority	Not validated	Good inter-observer agreement	Distributed over 200 users in EU, USA, ASIA and Australia	Evaluated and approved by EPA	Developed by 15 European institutes based on a large database.	Widely used in The Netherlands
Outcome	Semi-quantitative (bands)	Semi-quantitative	Semi-quantitative	Quantifies the degree of exposure	Semi-quantitative	Quantitative	Ranking of risks in bands
Type of evaluated substances	Chemical products except pesticides	Pesticides	Metals, fluids and pesticides	Pure substances, no mixtures	Pesticides	Pure substances including pesticides	Pure substances and mixtures
Evaluated dermal exposure pathway	Deposition, indirect and direct contact	Transfer, deposition and emission	Transfer, deposition and emission	Emission to surface, air, outer clothing layers and direct to skin	No Data	Deposition and direct contact	Inhalation Exposure (near and far field). Total dermal exposure
Dermal exposure descriptor	Potential exposure	Potential and actual exposure	Potential and actual exposure	Potential exposure	Potential and actual exposure	Potential and actual exposure	Potential and actual exposure
Evaluated Body Parts	No information available	Front and back side of neck, thorax, arms, forearms, hands, thighs, legs, feet, forehead and left and right side of face	Head, upper and lower arms, hands, front torso, back, upper legs, lower legs and feet	Hands and forearms	Head, face, back and front neck, chest/stomach, back, upper arms, forearms, hands, thighs, lower legs, feet.	Hands, arms, head, front and back side of legs, front and back of torso	No information available
Reference							

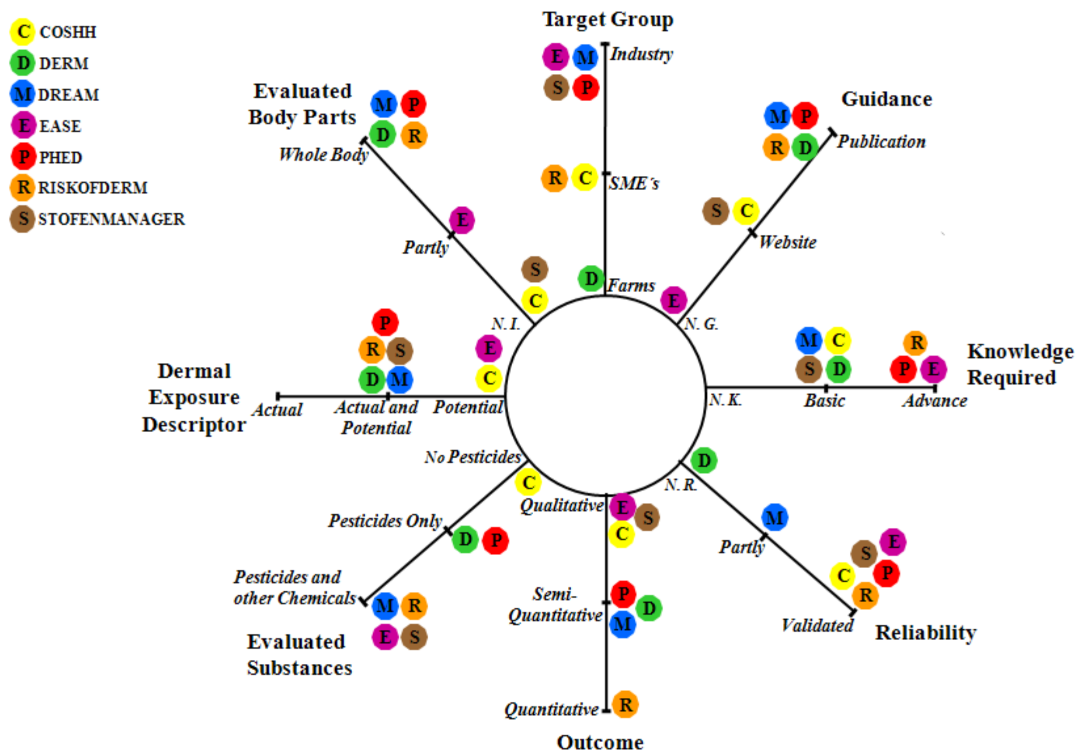
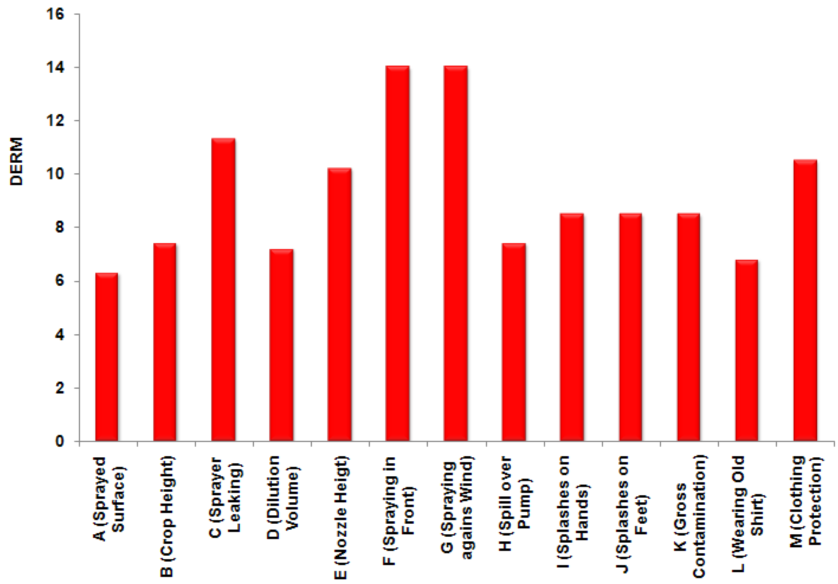


Figure 5: Radar diagram with the multi-criteria analysis for the evaluated models for dermal exposure assessment.

4.1.2 Research Question 2: Which parameters are considered inside the structure of the models and which are relevant for the case studies in developing countries?

In the case of the model DERM, the sensitivity analysis (Figure 6) shows that the modus of the pesticide application influence the model outcomes. This means, issues like spraying against the wind, height of the nozzle during the application, positioning the nozzle in the front, the possible leaking from sprayer and the protection clothing highly influence the dermal exposure estimations. In addition, according to previous studies in the study area , it was found that important determinants like washing the equipment, task duration, wearing gloves, frequency of replacement of gloves, work clothing, personal hygiene and climate conditions like wind speed and humidity, should be included to improve the assessment.

In the case of the model DREAM, according to the sensitivity analysis (Figure 7), the determinants that highly influence the exposure estimations are pesticide concentration; pesticide transportation processes like emission, deposition and transfer; and the level of protection. However, there are still some important determinants that can improve the accuracy. One is the differentiation of the level of protection for the body parts as previous studies have found that the level of protection given by the work clothing differs between each body part and the model only differentiates the protection for the body and the hands. On the other hand, the inclusion of climate conditions like wind speed and humidity which influence the dermal exposure, might improve the model accuracy as well.



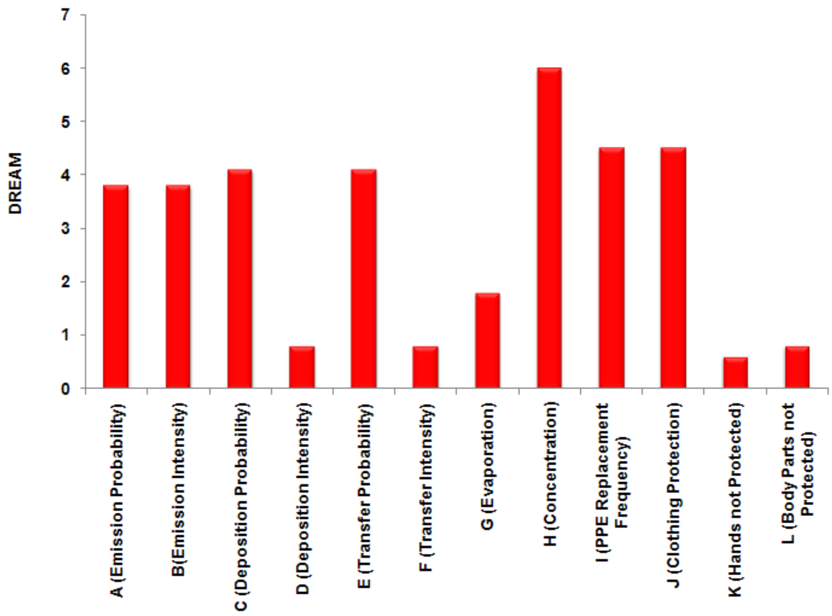


Figure 6 and 7: Dermal exposure assessment by the models DREAM and DERM after applying the sensitivity analysis, following the “One at the time” (OAT) methodology. Each scenario shows the chosen determinant with the allocated score according to the case study, assuming that the rest of the determinants have their lowest value.

4.1.3 Research Question 3: When comparing the model outcomes with the dermal exposure measurements in the study area, which model assesses dermal exposure more accurately?

Previous studies in Vereda La Hoya found that dermal exposure to pesticides is very high because of the inadequate work clothing, the modification of nozzles to increase the discharge, the inappropriate cleaning of the application equipment, the pesticide application against the wind direction and the use of pesticide with a high level of toxicity. The evaluated models (i.e. DERM, DREAM, PHED and RISKOFDERM) do not take into account these specific parameters for these type of study areas what makes their outcomes inaccurate. Furthermore, even though the evaluated dermal exposure models give an insight of the level of exposure, their outcomes are not comparable because their scoring and ranking system and their final assessments are different between each other (Table 3 and 4). Furthermore, none of them covered all the relevant determinants according to the findings in previous studies. Even though, the model DREAM assesses the dermal exposure in the study area as "very high" and taking into account that its determinants cover many characteristics of these farming systems, the accuracy of the model estimations about the dermal exposure might be improved if more specific determinants are included like work clothing, the modification of nozzles, the cleaning of the application equipment, the pesticide application against the wind direction and the level of toxicity of the pesticide. The complete performance of the models is available in the appendix of the third paper of this dissertation: "Evaluation of models for dermal exposure assessment in farming systems in developing countries".

Table 3: Actual dermal exposure assessments by the selected models for the study area.

Model	Case Study Score	Model Scoring Ranges		Unit	Qualitative Assessment
		Lowest Value	Highest Value		
DERM	44.28	0	> 150	Unitless	Moderate
DREAM	359.0	0	> 1000	Unitless	Very High
PHED	15.2	0.05	> 30	Unitless	High
RISKOFDERM	0.65	0	> 30	$mg/cm^2/h$	High

Table 4: Structure of the qualitative ranking system of the evaluated models according to their estimations. This information was taken from the description of the each model in their publications: . The qualitative assessment of dermal exposure goes from low, meaning skin irritation symptoms to extreme, meaning cancerogenesis symptoms.

Models	Qualitative Ranking System of the Models					
	Negligible	Low	Moderate	High	Very High	Extreme
DERM	<5	5-22.5	22.5 – 52.5	52.5 - 95	95 - 150	>150
DREAM	0 - 10	10 - 30	30 - 100	100 - 300	300 – 1000	> 1000
PHED	<1	1 – 4.5	4.5 – 10.5	10.5 - 19	19 - 30	> 30
RISKOFDERM	<0.003	0.003 – 0.03	0.03 – 0.3	0.3 - 3	3 - 30	> 30

4.2 Research Phase 2: Quantification of Dermal Exposures

4.2.1 Research Question 1: What is the current level of potential (PDE) and actual dermal exposure (ADE) to pesticides under the current working conditions in the potato farming system in the highlands of Colombia?

In the case study of Vereda La hoya, from the three pesticide management activities (i.e., preparation of the pesticide, application, and cleaning of the application equipment), the application was the activity with the highest PDE (Table 5). During the application, lower body parts (thighs and legs) were the most exposed (Figure 8), followed by back and arms. Even though, high PDE values were found on the lower body parts, these parts showed the highest level of protection because of the work clothing used during this activity (Figure 9). In the case of ADE, a higher value was found on the back because normally there are spills of solution on the sprayer after filling up the tank and these residues are in contact with this body part when farmers start the application without cleaning it, which is a particular situation for farmers in Vereda La Hoya. The ADE in the arms was higher than other parts due to the fact that farmers use short-sleeve shirts as a more comfortable work clothing for the applications. ADE was especially higher in the dorsal right arm because of the proximity of the sprayed droplets with this body part as this arm is in charge of handling the nozzle pipe.

In the case study of the flower production (Table 5), there is a uniform potential exposure in all the body parts, with a slight higher exposure in the front part of the body, and a low potential exposure in hands. However, the actual dermal exposure was higher for forearms and hands and slightly higher in legs and frontal body part.

Table 5: Comparison of dermal exposure values between the two case studies.

	Potato Crops				Flower Crops	
	HD	*LD*	*HD*	*LD*	*Spray Sideways with 5 Nozzles*	
% Exposure in ForeArms	0.0	0.0	0.0	0.0	15.7	19.5
% Exposure in Arms	1.1	4.6	25.7	47.2	17.7	8.3
% Exposure in Chest&Abdomen	1.6	3.2	4.1	1.7	19.5	12.2
% Exposure in Back	13.9	9.5	61.5	36.8	13.1	8.8
% Exposure in Thighs	15.3	12.9	2.0	9.1	15.2	10.9
% Exposure in Legs	67.6	69.6	6.6	5.3	15.9	15.8
% Exposure in Hands	0.5	0.3	0.0	0.0	3.0	24.5
% Exposure Total	100	100	100	100	100	100
Exposure in gr/kg pesticide applied	***1,277***	***1,80***	***0,0708***	***0,0877***	***0,173***	***0,0012***

4.2.2 Research Question 2: What is the level of health risk due to dermal exposure faced by farmers under the current working conditions and what are the critical activities that affect it?

Considering the high levels of PDE found during the application activity, the frequency of pesticide applications and the symptoms reported in the survey made in the location , there is a very high level of risk to dermal exposure under the current working conditions especially for the pesticide Metamidophos. This pesticide is the most toxic pesticide used by farmers in Vereda La Hoya and an examination of its toxicological information indicates that it is associated with adverse reproductive, teratogenic, mutagenic and carcinogenic effects . Additionally, in this case study, nozzles are modified to reduce the application time, which results in changes in the droplet size spectrum (Figure 10). This issue results in fast deposition downwards which might be one cause of high PDE in the lower parts. Previous studies have shown that an alteration of the droplet size spectrum results in a decrease in the pest management efficiency (the standard recommendation of droplet size depends on the kind of substance applied and the pest target: i.e. fungicides 150-250 µm, insecticides: 200-350 µm, contact herbicides: 200-400 µm and pre-emergence herbicides: 400-600 µm) .

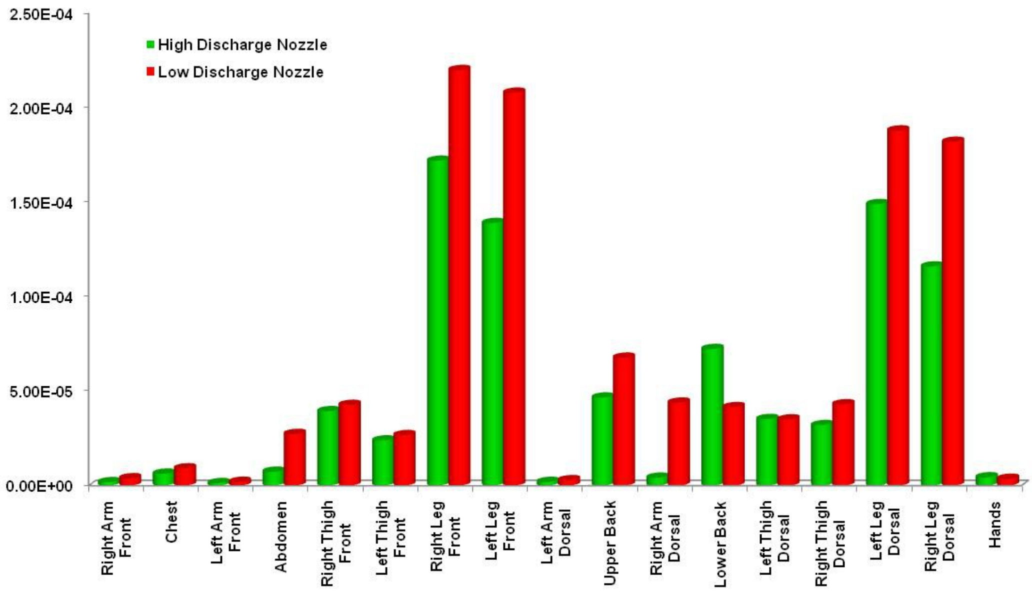


Figure 8: Potential dermal exposures for the different body parts during the application of the pesticide. Two nozzles were evaluated: One with high discharge and one with low discharge.

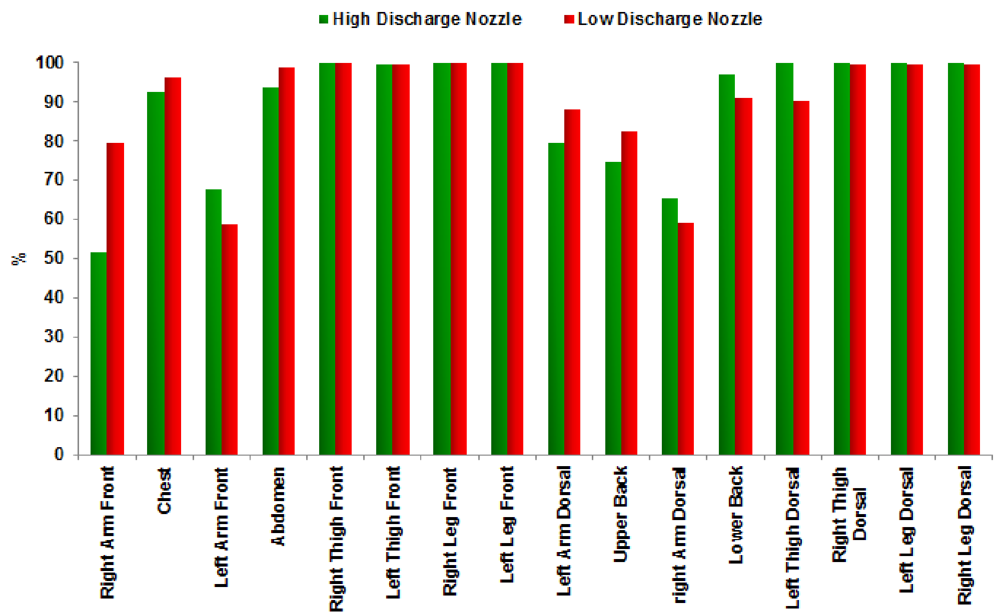


Figure 9: Level of protection given by the personal protective equipment for the different body parts during the application of the pesticide. Two nozzles were evaluated: One with high discharge and one with low discharge.

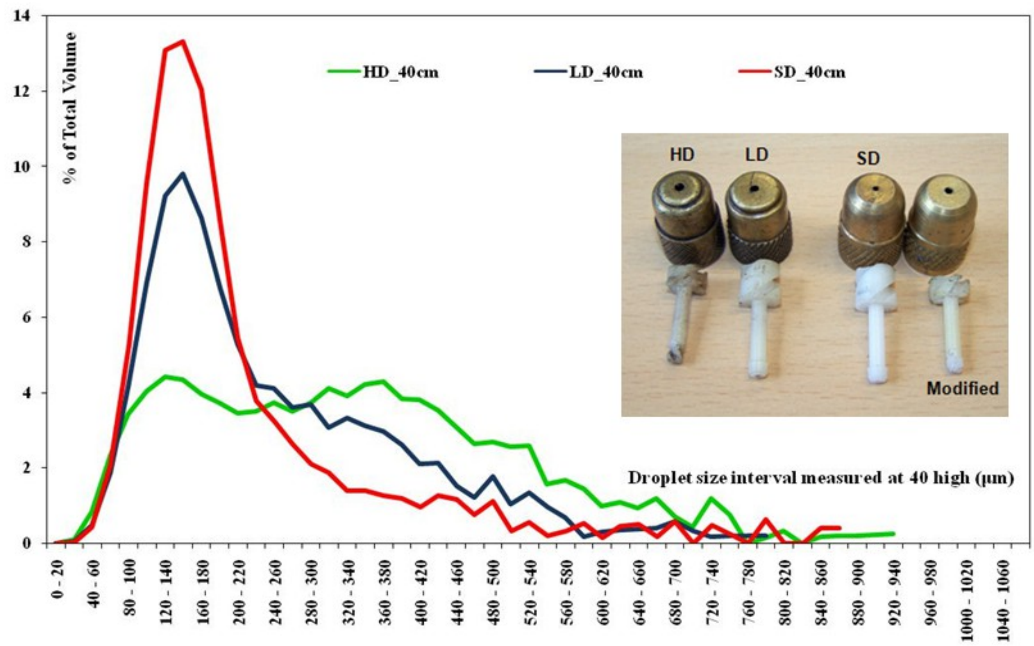


Figure 10: Volumetric droplet distribution for three nozzles: High discharge (HD), low discharge (LD), and standard nozzle (SN). The droplet size spectrum was measured at a height of 40cm.

4.3 Research Phase 3: Modeling Human Exposure to Pesticide Use

4.3.1 Research Question 1: How can the material flow analysis methodology be adapted to study human exposure to pesticides in agricultural systems?

The MFA method is based on the mass conservation law and studies the flow of a substance among the different processes involved in a system. This methodology was applied based on the conceptual framework proposed for the study of the pesticide flow in the farming system (Figure 3 and 11). This study focused only on the pesticide flow to the human body; therefore, the flow to target plants, soil and air were considered as outputs of the system. The system is composed of 15 processes and 25 fluxes (Figure 11). The pesticide enters the system as *input* and flows according to three pesticide management activities: preparation (P_1), application (P_2) and cleaning (P_3). These are considered transportation processes without a stock. From the preparation and cleaning, there is a direct transport of pesticide to the different body parts (P_5). During the application, there is a transport of the pesticide to the air (P_4) and to the different body parts (P_5). The potential dermal exposure (PDE), P_5, is the sum of the PDE from P_1, P_2, and P_3. This is defined as the fraction of contaminant landing on the outer layer of the personal protective equipment . The actual dermal exposure (ADE), P_{14}, is defined as the amount of contaminant reaching exposed skin surfaces . The level of protection given by the personal protective equipment is defined in the model separately for each body part in

P_6 to P_{13}. The pesticide flow between the potential (P_5) and actual exposure (P_{14}) depends on the level of substance retention given by the personal protective equipment. The retained amount of pesticide is defined in the model as the stock of P_6 to P_{13}. The inhalation exposure (P_{13}) is defined as the amount of contaminant arriving at the inhalation mask, and the stock is the amount retained by the filters used in the protection mask. The actual inhalation exposure is the amount of contaminant that crosses the filter in the mask.

The pesticide flow among all the processes is defined by a mass balance and is expressed by the following equations proposed by Baccini and Brunner, 2012 :

$$k_{F(P_i,P_j)} = \frac{X_{F(P_i,P_j)}}{\sum_{k \neq i}[X_{F(P_k,P_j)}]} \tag{1}$$

$$S_t = S_{t0} + \sum_{t_0}^{t}(Input_{(t)} - Output_{(t)}) \tag{2}$$

The transfer coefficient k for any flow from P_i to P_j is giving by Equation (1), where $XF(P_i, P_j)$ is the amount of pesticide flowing from P_i to P_j, $\Sigma[XF(P_k, P_i)]$is the sum of the amounts of pesticide flows coming to P_i, S_t is the stock after time step t, t_0 is the time of initial time step t, t is the current time step and S_{t0} is the existing stock at the initial time step. The time step is defined as one working day of 8 h. The transfer coefficients were obtained by means of field measurements using the whole body dosimetry, the tracer method and the button aerosol sampler. These methodologies are explained in the third publication of this dissertation.

4.3.2 Research Question 2: What are the advantages and disadvantages of using this methodology in the field of human exposure and risk assessment of pesticide use?

The pesticide flow model helps to identify the patterns of pesticide distribution on the body and the level of protection given by personal protective equipment. Furthermore, it estimates dermal and inhalation exposure to pesticides (potential and actual). This information can be used to determine the health risk level by comparing the model estimates with the acceptable operator exposure level (AOEL) reference values for each pesticide. In addition, the model makes it possible to easily identify the activities or body parts that have high levels of exposure, which is useful in identifying improvements that will decrease exposure during pesticide management. However, the model has some disadvantages because the outcomes correspond to a certain interval of time and do not consider issues such as pesticide accumulation or pesticide degradation rate. Additionally, the model considers each pesticide separately and does not take into account the fact that pesticides are usually applied in mixtures. Studies have shown that the combined toxicological effects of two or more components of a pesticide mixture can take one of three forms: independent, dose addition or interaction. Not all mixtures of pesticides with similar chemical structures produce additive effects; thus, their mixtures may produce different toxic effects .

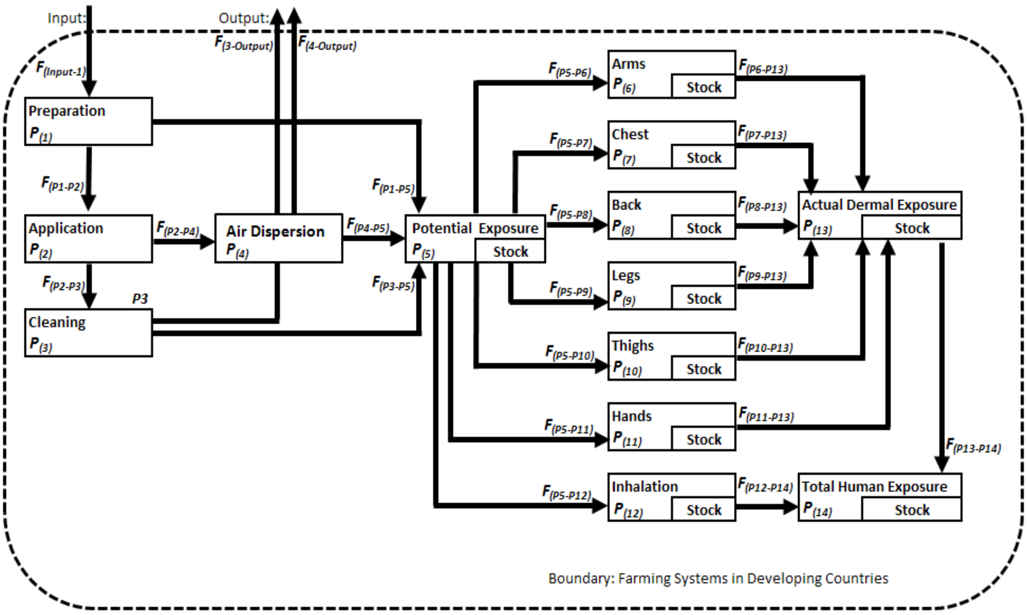


Figure 11: Pesticide flow analysis (P: Processes, F: Flows).

4.3.3 Research Question 3: Based on the model outputs, what is the current situation with respect to human exposure to pesticides in the flower crop systems in Colombia, and how can the pesticide management be improved?

Figure 12 shows the pesticide flow analysis for mancozeb when 786 cc of active ingredient were applied during a work day of 8 h. The model shows that the exposure was very high during the application, contributing with 99.9% to the total PDE, while the preparation contributed with 0.07% and the cleaning contributed with 0.03%. The exposure during preparation and cleaning is due to accidental splashes that cause minimal exposure compared with the application activity, in which most of the pesticide solution is used and during which the exposure is very high. Nevertheless, despite the high PDE (5,223±2,493 mg/d), the ADE was very low (32±23 mg/d), which indicates a level of protection of approximately 95% for the hands and between 99.2 and 99.8% for the rest of the body parts.

With respect to ADE, the model shows that the forearms and hands were the most exposed body parts (i.e., 8.0±7.3 and 6.4±4.0, respectively). This shows that despite the high level of protection given by the personal protective equipment, there is a leak of pesticide solution droplets through the overlap between gloves and sleeves. This same situation occurs for the legs, whose ADE values (5.2 ± 3.0 mg/d) might be due to a leak of pesticide solution droplets through the overlap between boots and trousers, and for the chest, whose ADE values (4.0±2.4 mg/d) might be due to a leak of pesticide solution droplets through the buttons. Despite these issues, the risk was low but improvements in the personal protective equipment could reduce even more the exposure and in consequence the risk.

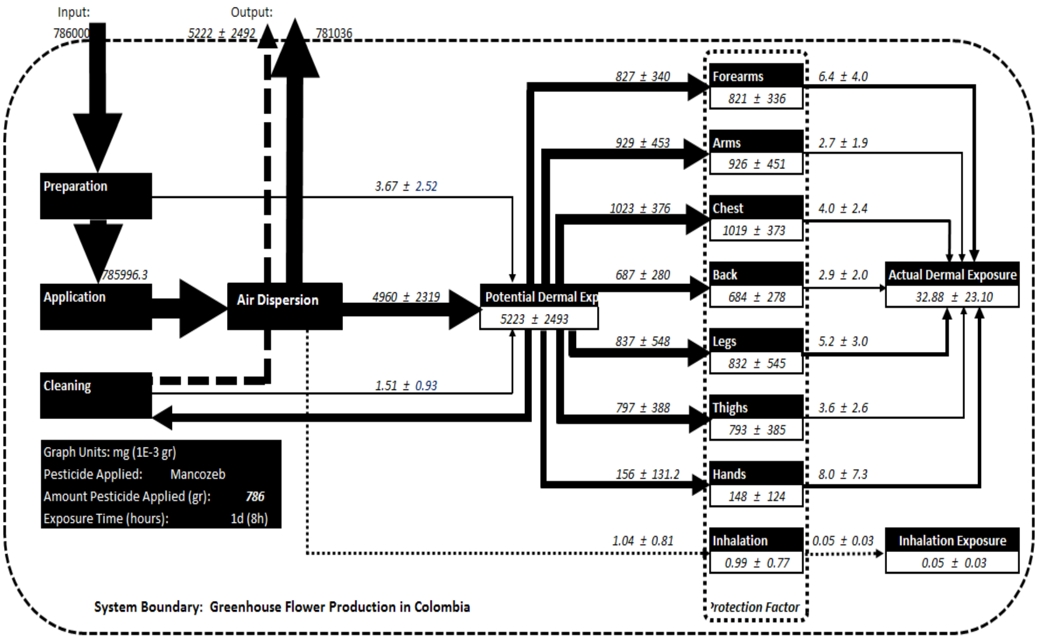


Figure 12: Pesticide flow analysis for the fungicide mancozeb. The units are in miligrams during an exposure time of 8 hours.

5. Discussion

This section describes the relevance of this research and the issues that remain open for further research. The main contribution is summarized in three aspects: the evaluation of dermal exposure models, the quantification of the dermal exposure in selected study areas, and the proposal of a model for human exposure assessment.

5.1 Evaluation of models for the human exposure assessment of pesticide use

This research contributes to find out the advantages and disadvantages of human exposure models when they are applied in study areas in developing countries. From a comparison of the models after a multi-criteria analysis, DERM, DREAM, PHED and

RISKOFDERM were selected for the further evaluation as they fulfill the required criteria for the case studies in developing countries. After these four models were applied to assess the dermal exposure in the case study of Vereda La Hoya and their determinants were compared with the characteristics of the study area, DREAM and DERM were found as the most appropriate models to assess the dermal exposure in these study areas. However, because some relevant determinants are still absent, the accuracy of these models could be improved if these are included. When comparing the final model assessment of dermal exposure in the study area, DREAM was found as the model that assesses more accurately the dermal exposure in this study area.

All the models for human exposure such as COSHH , DREAM , EASE , PHED , RISKOFDERM and STOFENMANAGER were developed after the conceptual model proposed by Schneider in 1999 . Therefore, they were developed with similarities in the structure of the determinants. However, they are built for case studies in industrialized countries and there are uncertainties about their application in developing countries. For instance COSHH is specialized in SME's in UK; DREAM, in industrialized countries and farming systems in The Netherlands were tractors and motorized pesticide applications are used; EASE, in industrialized processes in UK; PHED, in regulatory agencies and the pesticide industry in USA and Canada; RISKOFDERM, in operational and technical staff in SME's; and, STOFFENMANAGER, in Dutch companies. Some agricultural case studies in developing countries are characterized by manual pesticide applications with no regulations about the adequate pesticide use and no use of personal protection equipment. Only the model DREAM was applied in study areas in developing countries but the model has not been validated because of some issues regarding the reproducibility and accuracy of dermal exposure estimations . Furthermore, this research found that when this model is applied in case studies in developing countries, most of the determinants do not cover the specific characteristics of these study areas. Based on DREAM, Blanco made an attempt to develop a model for farming systems in developing countries with DERM ; however, this model has faced problems in the validation because of inappropriate procedures in the methodology .

The multi-criteria analysis found that only DERM, DREAM, PHED and RISKOFDERM are the most appropriate models for case studies in developing countries and they were applied in the case study of Vereda La Hoya. However, PHED was excluded because the model determinants are relevant only for farming systems in industrialized countries where tractors and sophisticated equipment is used, and furthermore because the model does not assess processes like pesticide emission and transfer. RISKOFDERM was also excluded because the model differentiates only two body parts: the hands and the rest of the body and a previous research has found a differentiation in the exposure in all the body parts . Additionally, this model does not take into account the emission and transfer processes and includes determinants only relevant for industrialized countries like automation.

DREAM was found to be the most appropriate model to assess the dermal exposure for the case study in Vereda La Hoya. However, the estimation accuracy might be improved if there is a differentiation in the protection factor according to the different body parts and other determinants are considered such as climate conditions like wind speed and humidity. If these missing determinants are included not only the model outcome will be more accurate but the model scope will be wider for not only farming systems in industrialized and developing countries but other industrial processes.

In the case of DERM, the estimation accuracy might be improved when determinants such as washing the equipment, task duration, wearing gloves, frequency and replacement of gloves, work clothing, personal hygiene and climate conditions are included in the assessment. If these missing determinants are considered a better assessment will result, especially in case studies like small farms where there is a lack of regulation surveillance.

5.2 Quantification of dermal exposure estimations

During this research phase, the main contribution was to understand the mechanisms of dermal exposure in the study area of Vereda La Hoya and the greenhouse flower crop system in Sabana de Bogota, Colombia.

In the potato crop system, it was found that the application was the activity with the highest PDE. Even though lower body parts (thighs and legs) were the most exposed, these body parts also showed the highest level of protection because of the work clothing. The ADE was high for arms and upper back because of lack of adequate work clothing covering the complete arm and the direct contact of the upper back with the spills on the sprayer tank. Furthermore, it was found that Metamidophos is the most toxic pesticide used in Vereda La Hoya and farmers may reduce significantly the health risk by using adequate work clothing made of appropriate fabrics that covers the whole body including the arms; cleaning properly all the pesticide residues left on the sprayer tank before each application; and avoiding the modification of nozzles using only nozzles with the standard discharge.

With respect to greenhouse flower crop, it was found that there is a uniform potential exposure in all the body parts with a slight higher exposure in the front part of the body and a low potential exposure in hands. However, the actual dermal exposure was higher for forearms and hands and slightly higher in legs and frontal body part. Because of the mechanisms of pesticide application within the rows of plants in the flower crop, the potential exposure is expected to be uniform in the whole body. However, the actual dermal exposure behaves differently because of the lack of adequate protection in the overlap between the sleeves of the personal protective equipment and the gloves. Therefore, the exposure might be significantly reduced by improving the protection in these two body parts.

In the case study of Vereda La Hoya, the manual application of pesticides is generally considered to represent the worst case scenario for dermal exposure due to the proximity of the nozzle to the lower body parts of operators. Dermal exposure values usually fluctuate largely because of unexpected changes in the environmental conditions and working patterns during the trials . Even though, the present results have a limited number of repetitions, they are comparable to previous studies which found similar patterns of pesticide fractioning with high percentages of PDE in the lower body part. Our results showed that PDE was higher on the lower body parts, including thighs and legs which are comparable to previously reported values: 71.5% , 70.6% and 62% . In the case of ADE, we found a higher value in the back because normally there are spills of solution on the sprayer after filling up the tank. These residues are in contact with the back when farmers start the application without cleaning it, which is a particular situation for farmers in Vereda La Hoya. Therefore, the dorsal body part was more exposed than the frontal because of the high ADE in the back together with a high ADE in the dorsal part of the arms.

The protection factor depends on the characteristics of the fabric such as the thickness, yarn twist and wicking; and the viscosity and surface tension of the pesticide mixtures (Lee and Obendorf, 2005). The obtained protection factor values of work clothing (Figure 8) differ significantly from the default data available from various statistical models and databases designed to predict exposure to pesticides. EUROPOEM suggests a value of 70% , the Pesticide Handlers Exposure Database (PHED) suggests 50% , and the Californian Department of Pesticide Regulation (CA DPR) has adopted a default protection factor of 90% . However, similar results were found in previous empirical studies in which the protection factor in cotton garments varies between 92.5 to

84.1% and in cotton/polyester varies between 91 to 99.5% . Other reports showed that protection factors are commonly 2 or 3 times higher in the lower parts of the body because of the difference in the type of material between shirts and trousers .

The differences in dermal exposures between the applications with the three nozzles may be explained by the differences in volumetric droplet size distribution. The modification of the nozzles changes the droplet size distribution and the result might be not only an increase in the dermal exposure but also a decrease in the pest control efficiency.

In the case study of greenhouse flower crops, one characteristic of the greenhouse flower crop system in Colombia is the pesticide application with five nozzles mounted on a 1.60 m long pipe. Previous studies have shown that the distribution of the PDE on the body parts depends on the spray direction of the nozzle and because the application in the study area was made sideways with five nozzles simultaneously, body parts were exposed homogenously, with the exception of the hands. This fact is reflected in the results of the PDE distributions, which range between 13 and 19% for the body parts and 3% for the hands. These results are different from those obtained in previous studies in which only one nozzle was used and the application was made downward, forward or backward, and the exposures differ, with high values generally found on the lower body parts .

Concerning the ADE distribution, previous studies have shown similar results in which the hands and forearms are the most exposed body parts, and dermal exposure is the main contributor of the total exposure . Another characteristic of this study was the size of the paths between the crop rows, which is only 60 cm wide, creating a close space in which the sprayed pesticide droplets move. This issue might contribute to the homogenous potential dermal exposure. This contrasts with the paths of greenhouse production systems in other locations , which are between 1 and 1.5 m wide.

5.3 Modeling the Human Exposure to Pesticide Use

The main contribution of this research phase was to propose a pesticide flow analysis model to obtain quantitative estimations of dermal and inhalation exposure. The pesticide flow model helps to identify the patterns of pesticide distribution on the body, the level of protection given by personal protective equipment and the estimates of potential and actual dermal and inhalation exposure and this information can be *used to determine the health risk level. In addition, the model makes it possible to easily identify the activities or body parts that have high levels of exposure, which is useful in identifying improvements that will decrease the exposure during pesticide management. Because it is not feasible to measure directly the dermal exposure in all study areas, this model might help to obtain a quick estimation which could help stakeholders and authorities to make further decisions.*

When comparing the proposed pesticide flow analysis model with the previous models for dermal exposure assessment (Table 2), this model has the following characteristics:

- *Goal:* Quick and early recognition of the fractioning of the pesticides in the human body during pesticide management activities.
- *Basis:* Material flow analysis methodology.
- *Availability:* Model published in an open access journal widely available.
- *Guidance:* The model is based on transfer coefficients and fractioning values and the model structure is explained in the published scientific article.
- *Knowledge/equipment required:* Even though, a computer facilitates the calculations by using the software Microsoft Office Excel or Stan, it is also possible to build up the fractioning scheme with pen and paper.
- *Reliability:* Because there is no option for qualitative scoring by the assessor, the reliability is very high.
- *Outcome:* The estimations are quantitative in terms of the amount of pesticide exposure per unit of time and can be estimated for a specific pesticide.
- *Type of evaluated substance:* It is specially designed for pesticide applications.
- *Evaluated dermal exposure pathway:* It takes into account the three pathways: Emission, transfer and deposition.
- *Dermal exposure descriptor:* It studies the potential and actual dermal exposure, and also the protection factor, including also the inhalation exposure.
- *Evaluated body parts:* It estimates the exposure for the all the different body parts, with the exception of head and feet.

In this way, the proposed pesticide flow model complies with all the criteria required for the assessment of pesticide use in farming systems in developing countries with manual and motorized pesticide applications. However, it is important to take into account that only one case study for each pesticide application was considered and a larger set of case studies and scenarios should be included to validate the model. Nevertheless, our pesticide flow model integrates three activities and two routes of exposure during pesticide management, which is different from other approaches in which a model was developed separately for each process or activity. Although the model can be applied to case studies in regions with similar characteristics, such as the application technique, the infrastructure and the type of personal protection equipment, the model should be calibrated when these characteristics change. Furthermore, the model provides static information about the exposure during a certain interval of time and further improvements are necessary to improve the health risk assessment by including in the model time-dependent issues such as the cumulative exposure over several days and the pesticide degradation rate. In addition, even though this research was initially thought to assess the human exposure to pesticide use, both the conceptual model (Figure 3) and the pesticide flow model (Figure 10) can be extrapolated to other application of chemicals and not only in farming systems. Because the application of any substance involves the preparation of the chemical solution, the application itself and the cleaning of the equipment, this model can assess the dermal and inhalation exposures in a wide range of case studies in different industrialized and farming processes in different regions worldwide. In order to complete the comparison of the models about their descriptions, the multi criteria analysis and the model estimations, the tables 6 and 7, and the figure 13 was completed with the information obtained with the pesticide flow analysis model (PFAM).

Table 6: Description of the evaluated model for dermal exposure assessment according to the multi-criteria analysis.

CRITERIA	Models							
	COSHH	DERM	DREAM	EASE	PHED	RISKOF.	STOFFEN.	PFAM
Origin	UK	Nicaragua	The Netherlands	UK	USA/Canada	Europe	The Netherlands	Switzerland / Colombia
Year	2002	2008	2003	1994	2002	2003	2003	2013
Goal	Risk assessment in SMEs	Risk assessment in developing countries	Risk assessment of occupational exposure in any situation	Risk assessment for regulatory of new chemicals	Standardized exposure estimates	Risk assessment for regulatory and registration processes	Risk assessment in SMEs	Risk Assessment in developing countries
Basis	Operational exposure levels assess exposure and R-phrases for health hazard	Transport Processes, Schneider, 1999; DREAM, 2003	Transport processes, Schneider, 1999. Airborne concentrations	Computer aided decision tree format , Schneider, 1999	Reported information on pesticides and monitoring data	Schneider, 1999; COSHH .	Schneider, 1999; COSHH . Riskofderm	Material Flow Analysis Methodology
Target group	SME's	Farmers in developing countries	Industrial processes and farming systems	Industrial processes	Regulatory agencies, pesticide industry	Operational and technical staff mostly in SMEs	Dutch companies	Farming Systems in Developing Countries
Availability	Electronic version	Publication	Publication	Software available	Software and publication	Software and publication	Website	Publication
Guidance	Website with	Publication	Publication	Not available	Publication	Publication	Website with no guidelines about	Publication

	guidelines for specific industries						the algorithms	
Knowledge/ Equipment required	No specific expertise required and electronic version available	Basic mathematics skills and easy to carry out in the field	Basic mathematics skills and easy to carry out in the field	Knowledge of the model and programming	Knowledge of the criteria and their effects on exposure. Computer required	Knowledge of the model and computer required	Internet access required	Basic mathematics skills
Reliability	Evaluated by the NIOSH authority	Not validated	Good inter-observer agreement	Distributed over 200 users in EU, USA, ASIA and Australia	Evaluated and approved by EPA	Developed by 15 European institutes based on a large database.	Widely used in The Netherlands	Good agreement with the dispersion scheme but still not validated
Outcome	Semi-quantitative (bands)	Semi-quantitative	Semi-quantitative	Quantifies the degree of exposure	Semi-quantitative	Quantitative	Ranking of risks in bands	Quantitative
Type of evaluated substances	Chemical products except pesticides	Pesticides	Metals, fluids and pesticides	Pure substances, no mixtures	Pesticides	Pure substances including pesticides	Pure substances and mixtures	Pesticides and other substances
Evaluated dermal exposure pathway	Deposition, indirect and direct contact	Transfer, deposition and emission	Transfer, deposition and emission	Emission to surface, air, outer clothing layers and direct to skin	No Data	Deposition and direct contact	Inhalation Exposure (near and far field). Total dermal exposure	Transfer, deposition and emission
Dermal exposure descriptor	Potential exposure	Potential and actual exposure	Potential and actual exposure	Potential exposure	Potential and actual exposure	Potential and actual exposure	Potential and actual exposure	Potential and actual exposure
Evaluated Body Parts	No information available	Front and back side of neck, thorax, arms, forearms, hands, thighs, legs, feet, forehead and left and right side of face	Head, upper and lower arms, hands, front torso, back, upper legs, lower legs and feet	Hands and forearms	Head, face, back and front neck, chest/stomach, back, upper arms, forearms, hands, thighs, lower legs, feet.	Hands, arms, head, front and back side of legs, front and back of torso	No information available	Arms, forearmes, chest, abdomen, back, legs, thighs and hands.
Reference								

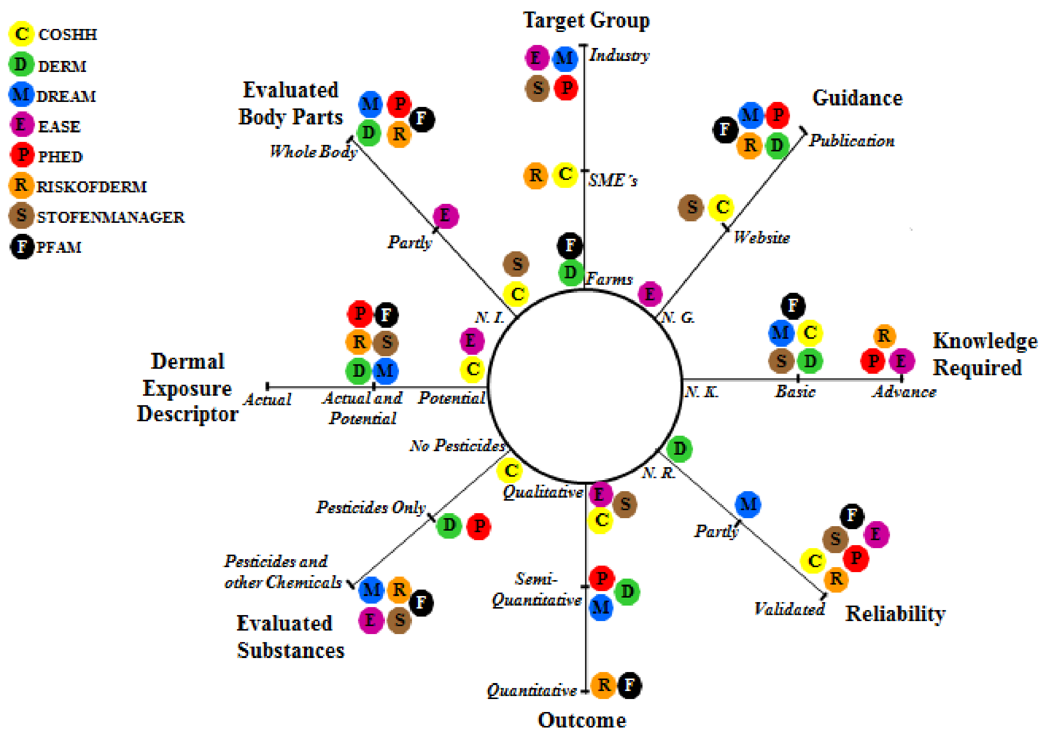


Figure 13: Radar diagram with the multi-criteria analysis for the evaluated models for dermal exposure assessment.

Table 7: Actual dermal exposure assessments by the selected models for the study area.

Model	Case Study Score	Model Scoring Ranges		Unit	Qualitative Assessment
		Lowest Value	Highest Value		
DERM	44.28	0	> 150	Unitless	Moderate
DREAM	359.0	0	> 1000	Unitless	Very High
PHED*	15.2	0.05	> 30	Unitless	High
PFAM	2.36 - 2.71	0	∞	mg/kg.day	Very High
RISKOFDERM	0.65	0	> 30	mg/cm²/h	High

*: Estimation made for the pesticide Metamidophos whose estimated value can cause carcinogenesis symtoms and according to the risk phrase, the risk is considered as very high.

5.3 Representativeness of the Case Studies

The conceptual model (Figure 3) represents the exposure mechanisms during the pesticide management and it can be extrapolated to any farming system. However, it is important to take into account that it is focused on dermal and inhalation exposure. It does not take into account the ingestion exposure and because of the mechanisms included, it does not evaluate the exposure faced by other persons like bystanders and specific characteristics of the chemicals like volatility or solubility. Furthermore, in order to evaluate other case studies, transfer coefficients must be calibrated for each case study focusing on the level of protection and the type of working clothing which might be different for each case. The results obtained during this study represent how the dermal exposure normally occurs in the potato and flower farming system. However, in the flower farming system there is a higher representativeness because the regulations about the use of pesticides are better implemented and all the activities and processes are supervised. This is not the case for the potato farming system, because there are not regulations and changes in the behavior or the work clothing might alter the mechanisms of exposure. Finally, in order to test the linearity of the model, it is necessary to test the model in other case studies and comparing the estimations with measured data. This will also validate the model and the representativeness of the transfer coefficients presented in this study.

5.4 Policy Implications

This research found that in Colombia the regulations about the use of pesticides are implemented differently according to the crop system. For instance, in the case of flower crops, there is a constant surveillance in fulfilling the regulations as the final product is exported. This is also the case for other crops with similar characteristics such as coffee, sugar cane, banana, and others. However, in the case of small crops such as potato, onion, carrot and other vegetables in the highlands of the Andean region, there is no surveillance at all and farmers apply the pesticide according to their experience or beliefs about the behavior of other farmers and the workshops organized by pesticide companies. However, one recommendation that comes out from this research is that by applying the model DREAM an overview of the level of dermal exposure can be obtained. However, both DREAM and DERM might give a more accurate dermal exposure estimation when determinants such as differentiation in the protection factor according to the different body parts and climate conditions are considered in the case of DREAM, and washing the equipment, task duration, wearing gloves, frequency and replacement of gloves, work clothing, personal hygiene and climate conditions are considered in the case of DERM. Furthermore, after the due calibration, the proposed pesticide flow model can be applied to determine both dermal and inhalation exposure of different pesticides when they are applied during a certain working time. This information will be very useful to evaluate all the pesticides included in the pesticide management and to find out which ones represent or not a risk to the health of farmers.

In order to reduce the health risks due to pesticide use, the local authorities have to organize educational programmes about the adverse health effects when pesticides are used with inappropriate personal protective equipment, insufficient cleaning of the application equipment, inadequate hygiene habits and the modification of nozzles. In the case study of potato farming system, the recommendations to reduce the health risk are: (i) to increase the protection of the lower body parts, arms and back by using a thicker personal protection clothing; (ii) to clean properly all the pesticide solution splashes on the application equipment before starting the application activity; and (iii) to avoid the modification of nozzles as the droplet size is altered and this issue not only affects the human exposure but also decreases the pest control efficiency. In the case study area of flower crop system, the recommendations are: (i) to improve the personal protective equipment in the overlapping between the gloves and forearms; (ii) to rotate the workers in order to reduce the frequency of the exposure; and (iii) to use pesticides with a low level of toxicity. In addition, the pesticide companies could sell the pesticide products including a disposable protective equipment to small farmers, an issue that will not increase much the final product price but it will reduce significantly the human exposure.

5.5 Open Issues

There are two main issues which remain open after this research: The first one concerns the evaluation of the models for human exposure assessment. DERM, DREAM, PHED and RISKOFDERM were applied in the case study of Vereda La Hoya in which the pesticide management is made by handed-pressurized sprayers. From the comparison of the models, DERM and DREAM were found to be the most appropriate models and DREAM to give the most accurate estimations. These results are valid for potato farming systems and many other crop systems with similar characteristics in different regions in Latin America and might be also be valid for other regions worldwide with similar pesticide applications in Africa or Asia. However, the results are not valid for other sophisticated pesticide applications in crops in developing countries such as flowers, banana, coffee, sugar cane, rice, etc. For these crops, the comparison of model outcomes might give a different conclusion. For instance, DREAM and PHED are models whose assessments are able to be targeted on pesticide applications with sophisticated techniques and they might be useful for the exposure assessment in these farming systems.

The second issue concerns the pesticide flow model. The conceptual model (Figure 3 and 11) is valid for all type of application techniques for pesticides and other chemicals worldwide as the model explains the movement of substances through processes and flows and this might be applied in a wide range of farming and industrial systems. However, the transfer coefficients have to be measured for each system at least one time to calibrate the model as there are differences between the case studies. In our research, for instance, the transfer coefficients for the flower crop system are uniform for most of the body parts with higher values for arms and hands and the protection factor is very high for all the body parts. Meanwhile, for the potato crop system the transfer coefficients are higher in legs, thigh and back, and the protection factor is low for arms. In addition, the model is required to include in the assessment issues like the cumulative dermal exposure during different intervals of time, the exposure when several pesticides are applied at the same time since there are possible underlying mechanisms of interactions between the chemical in a mixture, and different pesticide application frequencies along the crop cycle. Additionally, the model should consider somehow specific characteristics of the case studies. For instance, specific issues for the case studies in farming systems in developing countries such as the type of work clothing and the modification of nozzles alter the dermal exposure.

5.6 Further Research

This study contributed in the field of human exposure assessment in three topics, i.e. the evaluation of models for human exposure, the characterization of dermal exposures in the study areas and the proposal of a new model for human exposure assessment. In these three topics there are possibilities for further research:

Firstly, concerning the paper about the evaluation of models, it is suggested that the improvement of the structure of the determinants of the models DREAM and DERM might not only improve the accuracy of exposure estimations but also might result in a brand new model for human exposure with high specificity for farming systems in developing countries.

Secondly, this research found that the modification of nozzles alter the droplet size distribution affecting the exposure. It was expected that the larger the nozzle modification the larger the exposure. However, the potential exposure with low discharge nozzle was larger than the potential exposure with high discharge nozzle and the same occurs with actual exposure. Therefore, a further research is required to establish a series of potential exposure caused by different nozzle modifications in order to find out the optimum nozzle size in order to keep the pest management efficiency without increasing the exposure.

Finally, concerning the paper about the pesticide flow analysis, it is suggested to build up a dynamic pesticide flow model that includes the pesticide accumulation on the outer layer of work clothing and the exposed skin surface and the pesticide degradation rate under conditions like different temperature or sunlight. Additionally, the ingestion and the inhalation exposure should be included with data from several case studies. Also, because the conceptual framework focused only in the human exposure, there is the possibility to integrate the emission of pesticides to the soil and the air to create a model that studies the pesticide flow in all the environmental compartments, including the human exposure which also can integrate the ingestion, inhalation and dermal exposure.

6. Conclusions

Pesticides play an important role in the agricultural production but their misuse affect the health of farmers and workers that manipulate such toxic substances. In the field of occupational hygiene, researchers have been working in finding out the most appropriate method to estimate the human exposure in order to assess the risk and therefore to take the due decisions to improve the processes in the pesticide management and reduce the health risk. This was the goal of this research which was focused in developing a model for human exposure assessment specially for farming systems in developing countries by evaluating the available models for human exposure assessment developed in industrialized countries, measuring the exposure in the study areas of potato and flower farming systems in Colombia, and finally proposing a pesticide flow model to estimate quantitatively the human exposure.

This research achieved this goal by evaluating in depth the available models for human exposure assessment, so assessors can decide which model is the most appropriate according to the characteristics of the study area in which the model is going to be applied and furthermore this research suggested improvements in the models in order to increase the estimation accuracy.

This research also contributes in the proposal of a new model for human exposure based on the material flow analysis methodology studying the pesticide fractioning during the pesticide management in a certain interval of time. With this model quantitative estimations of human exposure are obtained which facilitate the risk assessment and the implementation of measures to improve the safety during the pesticide management and to decrease the risk. The proposed model also demonstrates the feasibility of applying the material flow analysis methodology in the field of human exposure, obtaining a tool that helps to understand the mechanisms of distribution of the pesticide in the farming system based on the processes involved and the flows between these processes.

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Part B

Publications

Publication 1

Evaluation of Models for Dermal Exposure Assessment in Farming Systems in Developing Countries

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Abstract

Pesticides are a key element in the agricultural sector to increase the crop productivity but their misuse compromises the human health of operators and bystanders during the pesticide management. Dermal Exposure Assessment is a crucial aspect within the risk assessment of pesticide use as it may lead to the development and improvement of measures to reduce the health risk of pesticides users. Even though, tools for dermal exposure assessment are available, their implementation in developing countries is problematic as they have been developed under working conditions in industrialized countries and most of them are not specifically focused on processes like pesticide management. This paper evaluates dermal exposure models finding out the most appropriate ones to assess dermal exposure of pesticide use in farming systems in developing countries. Seven models (i.e. COSHH, DERM, DREAM, EASE, PHED, RISKOFDERM and STOFFENMANAGER) were evaluated according to a multi-criteria analysis and four models (i.e. DERM, DREAM, PHED and RISKOFDERM) were selected for the assessment of dermal exposure in the case study of potato farming systems in Vereda La Hoya in the highlands in Colombia. The model estimations were compared with dermal exposure measurements made in the study area. The results show that the four models provide different dermal exposure estimations which are not comparable. However, because of the simplicity of the algorithms and the specificity of the determinants, the models DERM and DREAM were found to be the most appropriate ones. In addition, it was found that model outcomes would be more accurate in the

assessment if determinants like climate conditions, cleaning of the equipment, task duration, personal protective equipment and hygiene habits were included in the models.

Keywords: Dermal Exposure, Models, Developing Countries, Potato.

1. Introduction

The agricultural sector is under pressure to increase crop productivity in order to maintain the food security for an increasingly growing population (FAO, et al., 2012). FAO has reported that 868 million people continue to suffer from undernourishment and the negative health consequences of micronutrient deficiencies continue to affect around 2 billion people (FAO, et al., 2012). Pests affect agricultural productivity by causing losses in the agricultural output, storage and the distribution of products. Worldwide approximately 9,000 species of insects and mites, 50,000 species of plant pathogens, and 8,000 species of weeds damage crops (Zhang, et al., 2011). Insect pests cause an estimated 14% of loss, plant pathogens cause a 13% loss, and weeds a 13% loss (Pimentel, 2009a) but these losses decline to 35-42% when pesticides are used (Liu ZJ, et al., 1999). However, even though pesticides play an important role in plant protection, in many cases, overuse or inappropriate use compromise the health of pesticide users, agricultural workers, and bystanders (FAO, 2010).

The occupational hygiene field has turned the attention to investigate the exposure in the agricultural workplace in order to improve the pesticide management and to reduce the health risk (Fenske, 2000). In developing countries this is of special interest because pesticide management activities face weak safety standards (Blanco, et al., 2005; Feola, et al., 2010a; Feola, et al., 2010b; Hughes, et al., 2006). Studies in potato farming systems in Vereda La Hoya, Colombia (Feola, et al., 2010a; Feola, et al., 2010b; García-Santos, et al., 2011; Juraske, et al., 2010; Lesmes-Fabian, et al., 2012; Schöll, et al., 2009; Schöll, et al., 2010; Tuchschmid, 2004); Mojanda, Ecuador (Schütz, 2012); and El Angel, Ecuador (Poats, et al., 1999) have shown that pesticide management in these countries has no particular knowledge foundation and is performed by trial and error, finding out what works out in practice. Furthermore, farmers do not wear adequate personal protective equipment, apply pesticides which are banned in industrialized countries and modify the standard discharge of nozzles to reduce the application time (Lesmes-Fabian, et al., 2012). Because these issues increase the health risk, a risk assessment of pesticide use in these areas is required in order to determine the risk level faced by people.

Human exposure to pesticides occurs via three main pathways: inhalation, ingestion and dermal contact (Schneider, et al., 2000; Schneider, et al., 1999). Of these three, dermal exposure is the most complex one and there is still no consensus about the most appropriate way to evaluate it (Schneider, et al., 2000; Schneider, et al., 1999). There are different models available that might be applied to assess dermal exposure to pesticide use in developing countries like EASE (Cherrie, et al., 2003), EUROPOEM (Van Hemmen, 2001), PHED (Dosemeci, et al., 2002), RISKOFDERM (Van Hemmen, et al., 2003), COSHH (Garrod, et al., 2003) STOFENMANAGER (Marquart, et al., 2008), DREAM (Van-Wendel-De-Joode, et al., 2003), DERM (Blanco, et al., 2008) and the approaches proposed by the U.S.EPA (U.S.EPA, 2007); however, there are still uncertainties about the adequacy of these models when they are applied in developing countries as most of them have been developed in industrialized and countries, are targeted at occupational situations in industrialized processes in Europe and USA, and do not consider agricultural processes like pesticide management. In the case of the model DERM, even though it has been developed under conditions relevant for developing countries, its methodology has been criticized and the model itself has not been validated.

The goal of this paper is to evaluate the available models for dermal exposure assessment in order to find out the most adequate one to estimate the dermal exposure in farming systems in developing countries. To reach this goal the following research questions will be addressed:

a) Which of the existing models for dermal exposure are feasible to be applied in case studies in farming systems in developing countries?
b) What are the most relevant parameters to be taken into account to increase the confidence and accuracy level of the estimations?
c) When comparing the model outcomes with the dermal exposure measurements in the study area, which models assess dermal exposure more accurately?

2 Methodology

After a literature review seven available models were considered for the analysis: COSHH (Garrod, et al., 2003), DERM (Blanco, et al., 2008), DREAM (Van-Wendel-De-Joode, et al., 2003), EASE (Cherrie, et al., 2003), PHED (Dosemeci, et al., 2002), RISKOFDERM (Van Hemmen, et al., 2003) and STOFENMANAGER (Marquart, et al., 2008). These models were selected because of their availability, clear description of the algorithms, and their potential applicability in the assessment of pesticide use. They were analyzed according to the following group of criteria (Table 1):

d) *General characteristics of the model:* year of development, country of origin, model goal, conceptual basis.
e) *Usability of the Model:* target group, availability, guidance, knowledge/equipment required, reliability, data required as input, type of outcome.
f) *Characteristics of the assessment*: type of exposure, type of substance, physical state of evaluated the substance, dermal exposure pathway, dermal exposure descriptor, evaluated body part.

Table 1: Categories and related criteria considered for the analysis and comparison of dermal exposure assessment models.

Categories	Related Criteria	Categories
General Characteristics	Year of development	
	Country of origin	
Usability	Target group	Farms, SME`s, Industry
	Guidance	No Guidance, Website showing only the results, Publication showing all the calculations
	Knowledge required	No specific knowledge required, Basic knowledge about human exposure assessment required and informatics, Advance knowledge required about human exposure assessment and programming
	Reliability	No reliable, Partly reliable because it is not completely validated, Reliable because it has been validated
	Outcome	Qualitative, Semi-quantitative, Quantitative
Assessment	Evaluated substances	Other substances different from pesticides, Pesticides only, Pesticides and other chemical
	Dermal exposure descriptor	Potential, Actual and Potential, Actual
	Evaluated body parts	No body parts are evaluated, Some of the body parts are evaluated, All the body parts are evaluated

2.1 Models for Dermal Exposure Assessment

COSHH (Control of Substances Hazardous to Health Regulations): The exposure assessment model COSHH was developed in the United Kingdom (UK) by the Health and Safety Executive (HSE) and has been used since 2002. Originally, the model is targeted on large companies and safety professionals who have the equipment and the knowledge to apply the model and interpret the law (Garrod, et al., 2003). Later on, a new version of the model was developed, namely the model COSHH Essential (COSHH-E). This is an improved version that provides assistance to small and medium-sized enterprises (SMEs) that have limited resources available. The goal of this model is to provide easy-to-understand and easy-to-use assistance to SMEs, and to give advice on how to control the chemical risks (Garrod, et al., 2003).

DERM (Dermal Exposure Ranking Method): It was developed in a project called “Assessment of dermal pesticide exposure and pesticide-related skin lesions: implication for intervention”. The fieldwork of the study was conducted at the Universidad Nacional Autónoma de Nicaragua (UNAN-León) and first published in 2008 (Blanco, et al., 2008). The goal of DERM is to develop a low-cost, easy-to-use method to assess dermal exposure to pesticides in developing countries. The model concentrates on assessing dermal exposure in terms of the potential and actual exposure. The outcome can answer questions like which determinants causes the highest exposure among subsistence farmers, and/or which farmers are the most exposed while working on the field (Blanco, et al., 2008).

DREAM (Dermal Exposure Assessment Method): The model DREAM was developed in the Netherlands in 2003 (Van-Wendel-De-Joode, et al., 2003). The goal of the model was to create a method that can assess and evaluate occupational dermal exposure to chemical agents in a generic way. The model can be used in occupational hygiene and epidemiology for any given situation. It can be used for initial assessment of dermal exposure levels of liquids and solids, as a framework for measurement strategies (i.e. who, what and where to measure), or as a basis for control measures. It gives insight into the distribution of dermal exposure over the body and indicates in which routes the exposure takes place. The outcome is a numerical estimate indicating the amount of dermal exposure that workers encounter while performing a certain task. The estimate is divided into seven intervals ranging from 0 to 1,000 (no exposure to extremely high exposure) (Van-Wendel-De-Joode, et al., 2003).

EASE (Estimation and Assessment of Substance Exposure): This model was developed in the early 1990s by the UK's Health and Safety Executive (Creely, et al., 2005; Cherrie, et al., 2003). The model can assess inhalation and dermal exposure. For inhalation exposures, the model predicts a range of expected exposure levels for a given set of circumstances. For dermal exposures, the model predicts the potential exposure for hands and forearms (no other body parts are considered), expressed as a mass per unit area of exposed skin per day (mg/cm^2/day). The exposure ranges can take five different values, from very low up to 5-15 mg/cm^2/day. The model EASE was one of the first models to assess dermal exposure. Originally, this model was used as a screening tool for regulatory risk assessment for new chemicals. Nowadays, EASE is more a risk assessment tool to estimate exposure of new or existing substances in a simplified way (Creely, et al., 2005; Cherrie, et al., 2003).

PHED (Pesticide Handlers Exposure Database): The first version of this model was published in 1992 (Dosemeci, et al., 2002; U.S.EPA, 2007). The database of the model was developed by a task force, consisting of representatives from the Health Canada Pest Management Regulatory Agency (PMRA), the United States Environmental Protection Agency (EPA), the American Crop Protection Association (ACPA), and the software by an environmental consulting firm in Springfield, Virginia. The model was used by all major regulatory agencies in USA and worldwide by many other regulatory groups. Also, it was used by the pesticide industry to evaluate product safety issues (Dosemeci, et al., 2002; Krieger, 1995). Self-reported exposure information on pesticide from questionnaires, as well as pesticide monitoring data from the literature, were used to estimate the levels of exposure to pesticides. The database consists of information collected from about 100 studies submitted primarily by companies that wish to register a specific pesticide and it contains data for over 1,700 monitored exposure events (Dosemeci, et al., 2002).

RISKOFDERM (Risk Assessment of Occupational Dermal Exposure to Chemicals): RISKOFDERM was developed with the cooperation of 15 different institutes from 10 different European countries in 2003 (Auffarth, et al., 2003; Van Hemmen, et al., 2003). The aim of the project was to develop a conceptual model for dermal risk assessment and management for regulatory purposes. It was created to be a simple-to-use toolkit for SMEs. The model can be used for comparison of the skin-related hazardous properties of chemical products, general recommendations for risk control, or assessment of health risk from skin exposure for a specific working task in the field (Oppl, et al., 2003).

STOFFENMANAGER: This model was developed in the Netherlands and has been used since 2003 (Tielemans, et al., 2008a). Its goal is to assist SMEs in risk assessment and to prioritize and control risks of handling chemical products in their workplace. It was created to combine previous work published and requirements that are mandatory in the Netherlands for SMEs (Marquart, et al., 2008). The model uses information from the COSHH model for its hazard banding and the publications by Cherrie (1996) (Cherrie, et al., 1999) and Schneider (1999) (Schneider, et al., 1999) for the algorithm of the model. In addition, it uses information from the RISKOFDERM toolkit for the dermal exposure method and incorporates information from companies in the Netherlands gathered by several surveys. Sectors and companies were selected and the surveys were conducted by occupational hygienists. Also, information was used from research projects made by the Dutch government (Tielemans, et al., 2008a; Tielemans, et al., 2008b).

2.2 Selection of Models for the Evaluation in the Study Area

The multi-criteria analysis was defined based on criteria such as:

a) Target group model characteristics such as the availability, guidance, knowledge required, reliability, type of outcome, type of substance, target group and dermal exposure descriptor and dermal exposure pathway, four models (i.e. DERM, DREAM, PHED, and RISKOFDERM) were selected to be applied in the case study of Vereda La Hoya in the highlands of Colombia. COSHH, EASE and STOFENMANAGER were not selected because they did not fulfill most of the criteria, as the results will show in the section 3.1 and figure 1. The data used as input comes from a previous survey made in the study area with 197 smallholder potato growers in four communities (Feola, et al., 2010a) and previous studies about dermal exposure in the same study area (García-Santos, et al., 2011; Lesmes-Fabian, et al., 2012). The calculations and outcome of each model are provided in the supplementary information.

2.4 Sensitivity Analysis of de Models

The influence of each determinant in the model score for Vereda La Hoya was evaluated by a sensitivity analysis. Each determinant was evaluated for the models DERM, DREAM, PHED and RISKOFDERM according to the One-at a-Time sensitivity analysis methodology (Czitrom, 1999; Murphy, et al., 2004). A series of scenarios were established for each model changing the input values to the score for one specific determinant according to the scores for the study area in Vereda La Hoya, leaving the rest of the determinants at the lowest input value. The determinants of the model DERM were evaluated in 16 scenarios, DREAM in 14, PHED in 8 and RISKOFDERM in 4 scenarios, respectively. The difference in number of scenarios depended on the structure and number of determinants within each model.

2.5 Description of the Study Area

The study area selected was Vereda La Hoya which is a rural region that belongs to the city of Tunja in the highlands of Colombia. This region is devoted mainly to the cultivation of potato in production units of around 3 hectares. Potato crops in this region are vulnerable to three major pests: the soil-dwelling larvae of the Andean weevil (*Premnotrypes vorax*), the late blight fungus (*Phytophthora infestans*) and the Guatemalan potato moth (*Tecia solanivora*) (M.A.D.R., 2009). The pesticide management to control these pests is performed along three main activities: the preparation of the pesticide, the application itself, and the cleaning of the spraying equipment (Juraske, et al., 2010; Lesmes-Fabian, et al., 2012). During the whole pesticide management, farmers use work clothing consisting of trousers, short sleeve shirts and plastic boots. The pesticide management is performed along three main activities which are:

a) *Pesticide preparation,* which consists of opening the bottle containing the pure pesticide substance, mixing the solution of (different) pesticides and water, and loading the tank of the knapsack sprayer. Farmers in Vereda La Hoya prepare the pesticides in a container of 100-L capacity. The pesticide and the water (normally 80 L to obtain four applications of 20 L each) are mixed in this container with the aid of a wooden stick. During the mixing and the filling of the tank there are usually spills out of the container reaching different parts of the body including hands, arms, chest and legs.
b) *Pesticide application*, in which the knapsack sprayer is carried on the back and the pesticide application starts with the spraying process on the field. During this activity the farmers' body is exposed to the droplets emitted by the nozzles. In the study area, the spraying is performed with hand pressure sprayers with a 20-L

capacity. Farmers use two types of nozzles for pesticide application which differ in the amount of pesticide discharged: a high-discharge (HD) nozzle (1.88L/min) used during the first crop phases (sowing and emergence) and a low-discharge (LD) nozzle (1.26 L/min) used during the rest of the crop phases (growth, flowering and pre-harvest).

c) *Cleaning*, in which once the application is finished, farmers clean the sprayer and the container by pouring clean water on all the accessories in a procedure repeated three times. This procedure is included in the booklet “Good Agricultural Practices” (Fernandez, et al., 2009) which farmers use as a reference for the pesticide management. During this activity, there are numerous spills from the equipment and the accessories reaching the farmer’s body.

3. Results

3.1 Multi-Criteria Analysis of Dermal Exposure Assessment Models

Table 1 shows the description of the evaluated models according to the different criteria and characteristics of the model (i.e. origin, goal, basis, target group, availability, guidance, knowledge/equipment required, reliability, type of outcome, type of evaluated substance, dermal exposure pathway, dermal exposure descriptor, and evaluated body part). Figure 1 shows the radar diagram with the multi-criteria analysis based on the defined criteria. From the analysis, it was found that DERM, DREAM, PHED and RISKOFDERM were the most appropriate models to be applied in farming systems in developing countries because they comply best with most of the criteria. However, there are still important criteria missing in the structure of each model. For instance, DERM has not been validated and it has been criticized about the reliability and reproducibility of the outcomes as there were mistakes in the methodology when the model was developed and tested in the same study area (Kromhout, et al., 2008). DREAM has been partially validated and it has been criticized about the accuracy of their estimations and the reproducibility in several case studies with different characteristics (Van Wendel De Joode, et al., 2005b). PHED is focused on farming systems in industrialized countries, its determinants evaluate the exposure during pesticide applications made by tractor and with motorized equipment, there is no distinction of the pesticide transport processes such as emission, transfer and deposition. RISKOFDERM is focused in SME’s in industrialized countries but it does differentiate the pesticide transportation processes like emission and transfer which are very important in farming systems with manual pesticide applications.

Table 2: Description of the evaluated model for dermal exposure assessment according to the multi-criteria analysis

CRITERIA	Models						
	COSHH	DERM	DREAM	EASE	PHED	RISKOF.	STOFFEN.
Origin	UK	Nicaragua	The Netherlands	UK	USA/Canada	Europe	The Netherlands
Year	2002	2008	2003	1994	2002	2003	2003
Goal	Risk assessment in SMEs	Risk assessment in developing countries	Risk assessment of occupational exposure in any situation	Risk assessment for regulatory of new chemicals	Standardized exposure estimates	Risk assessment for regulatory and registration processes	Risk assessment in SMEs
Basis	Operational exposure levels assess exposure and R-phrases for health hazard	Transport Processes, Schneider, 1999(Schneider, et al., 1999); DREAM, 2003 (Van-Wendel-De-Joode, et al., 2003)	Transport processes, Schneider, 1999(Schneider, et al., 1999). Airborne concentrations (Cherrie, 1996)	Computer aided decision tree format (Johnston, et al., 2005), Schneider, 1999(Schneider, et al., 1999)	Reported information on pesticides and monitoring data	Schneider, 1999(Schneider, et al., 1999); COSHH (Garrod, et al., 2003).	Schneider, 1999(Schneider, et al., 1999); COSHH (Garrod, et al., 2003). Riskofderm(Oppl, et al., 2003)
Target group	SME's	Farmers in developing countries	Industrial processes and farming systems	Industrial processes	Regulatory agencies, pesticide industry	Operational and technical staff mostly in SMEs	Dutch companies
Availability	Electronic version	Publication	Publication	Software available	Software and publication	Software and publication	Website
Guidance	Website with guidelines for specific industries	Publication	Publication	Not available	Publication	Publication	Website with no guidelines about the algorithms
Knowledge/ Equipment required	No specific expertise required and electronic version available	Basic mathematics skills and easy to carry out in the field	Basic mathematics skills and easy to carry out in the field	Knowledge of the model and programming	Knowledge of the criteria and their effects on exposure. Computer required	Knowledge of the model and computer required	Internet access required
Reliability	Evaluated by the NIOSH authority	Not validated	Good inter-observer agreement	Distributed over 200 users in EU, USA, ASIA and Australia	Evaluated and approved by EPA	Developed by 15 European institutes based on a large database.	Widely used in The Netherlands
Outcome	Semi-quantitative (bands)	Semi-quantitative	Semi-quantitative	Quantifies the degree of exposure	Semi-quantitative	Quantitative	Ranking of risks in bands
Type of evaluated substances	Chemical products except pesticides	Pesticides	Metals, fluids and pesticides	Pure substances, no mixtures	Pesticides	Pure substances including pesticides	Pure substances and mixtures
Evaluated dermal exposure pathway	Deposition, indirect and direct contact	Transfer, deposition and emission	Transfer, deposition and emission	Emission to surface, air, outer clothing layers and direct to skin	No Data	Deposition and direct contact	Inhalation Exposure (near and far field). Total dermal exposure
Dermal exposure descriptor	Potential exposure	Potential and actual exposure	Potential and actual exposure	Potential exposure	Actual exposure	Potential and actual exposure	Potential and actual exposure
Evaluated Body Parts	No information available	Front and back side of neck, thorax, arms, forearms, hands, thighs, legs, feet, forehead and left and right side of face	Head, upper and lower arms, hands, front torso, back, upper legs, lower legs and feet	Hands and forearms	Head, face, back and front neck, chest/stomach, back, upper arms, forearms, hands, thighs, lower legs, feet.	Hands, arms, head, front and back side of legs, front and back of torso	No information available
Reference	(Garrod, et al., 2003)	(Blanco, et al., 2008)	(Van-Wendel-De-Joode, et al., 2003)	(Cherrie, et al., 2003)	(Dosemeci et al., 2002)	(Oppl, et al., 2003)	(Tielemans, et al., 2008a)

COSHH was excluded from the evaluation as it does not consider important criteria relevant for case studies in developing countries such as target group, as it is focused on SME´s; guidance, as it is only available in a website with a user's manual for only some specific industries; outcome, as its assessment is qualitative; evaluated substances, as it does not evaluate pesticides in farming systems; dermal exposure descriptor, as it only assesses the potential exposure; and evaluated body parts, as it does make a distinction between any body part.

EASE was also excluded from the evaluation as it does consider criteria such as target group, as it is focused on industrialized processes; guidance, as there is no a user's manual with the model description; outcome, as it is qualitative; dermal exposure descriptor, as it evaluates only the potential exposure; evaluated body parts, as it takes only arms and forearms.

STOFENMANAGER was also excluded from the evaluation as it does comply with criteria such as target group, as it is focused on industrial processes; guidance, as the website does not show the algorithms or model calculations; outcome, as the assessment is qualitative; evaluated body parts, as there is no information available.

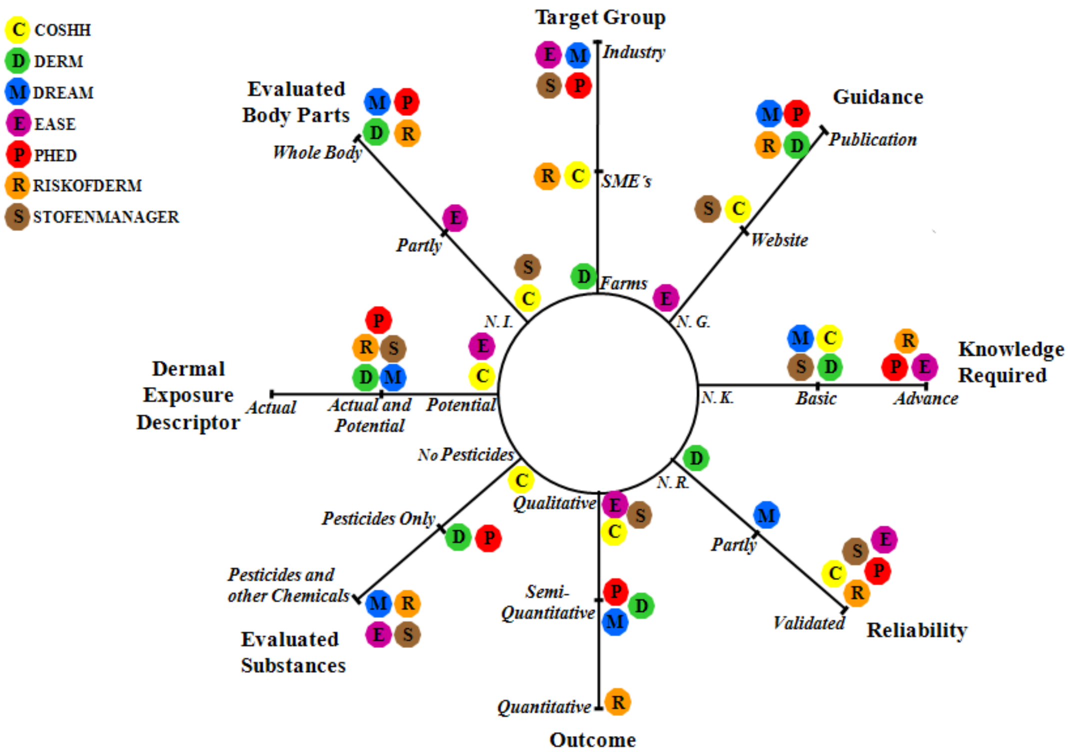

Figure 1: Radar diagram with the multi-criteria analysis for the evaluated models for dermal exposure assessment.

3.2 Model Outcomes for the Case Study of Vereda La Hoya.

Table 2 shows the actual dermal exposure assessment outcomes for the case study performed by the selected models DERM, DREAM, PHED and RISKOFDERM and Figure 2 shows the results of the sensitivity analysis of these models. The qualitative outcomes of actual dermal exposure for the four models differ significantly from each other. DERM assessed the actual dermal exposure as “moderate”; DREAM assessed the actual dermal exposure as “very high”; meanwhile both PHED and RISKOFDERM assessed the actual dermal exposure as “high”. These assessments differ between each other because of the different structure of determinants within the models and the different scoring system for each determinant. According to the sensitivity analysis each model highlights different determinants which influence greatly the model outcomes. These determinants are spraying against the wind, height of the nozzle during the application, nozzle positioning in front and possible leaking of the sprayer for the model DERM; pesticide concentrations, emission, deposition and transfer for the model DREAM; washing the equipment, wearing gloves, replacement frequency of gloves and clothes, and personal hygiene for the model PHED; and the exposed body are and protection clothing for the model RISKOFDERM. In addition, the outcomes from DERM, DREAM, and PHED are semi-quantitative and the outcome from RISKOFDERM is quantitative. This issues show that the model outcomes are not comparable and only by measuring the dermal exposure it is possible to evaluate the accuracy of the model outcomes.

Table 2: Actual Dermal Exposure Assessments by the Selected Models for the Case Study of Vereda La Hoya

Model	Case Study Score	Model Scoring Ranges		Unit	Qualitative Assessment
		Lowest Value	Highest Value		
DERM	44.28	0	> 150	Unitless	Moderate
DREAM	359.0	0	> 1000	Unitless	Very High
PHED	15.2	0.05	> 30	Unitless	High
RISKOFDERM	0.65	0	> 30	mg/cm²/h	High

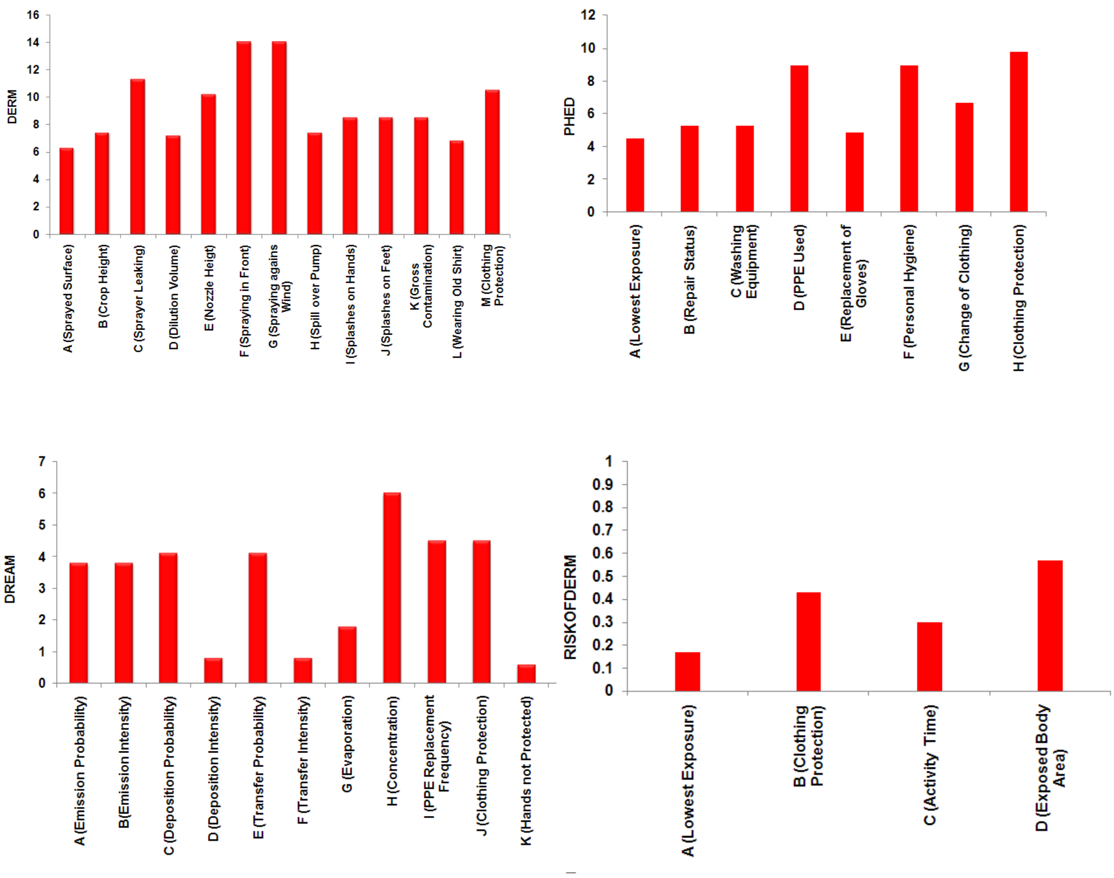

Figure 2: Actual dermal exposure assessments by the selected models according to the different scenarios established to evaluate the sensitivity of the determinants. The influence of determinants was studied establishing different scenarios. The scenarios show the chosen determinant with the allocated value according to the case study of Vereda La Hoya, assuming that the rest of the determinants have their lower value.

4. Discussion

4.1 Evaluation of models

Previous studies in Vereda La Hoya found that dermal exposure to pesticides is very high (García-Santos, et al., 2011; Lesmes-Fabian, et al., 2012) because of the inadequate work clothing, the modification of nozzles to increase the discharge, the inappropriate cleaning of the application equipment, the pesticide application against the wind direction and the use of pesticide with a high level of toxicity. Even though the evaluated dermal exposure models give an insight of the level of exposure, their outcomes are not comparable (Table

2). Furthermore, none of them covered all the relevant determinants according to the findings in previous studies. However, the model DREAM assesses the dermal exposure in the study area as “very high” and taking into account that its determinants cover many characteristics of these farming systems, this model gives the most accurate dermal exposure estimation. Even though, the validity and accuracy have been partially proved (Van Wendel De Joode, et al., 2005a; Van Wendel De Joode, et al., 2005b), these results might help to the further validation of the model.

The evaluated dermal exposure models give an insight of the level of exposure in the study area but their outcomes differ between each other. However, based on a sensitivity analysis and the results, several issues might be taken into account inside the structure of the models, which could improve the accuracy of the estimations. These issues are discussed separately for each model.

a) DERM (Dermal Exposure Ranking Method)

This is a low-cost and easy-to-use method for the assessment of exposure to pesticides in developing countries and it helps to identify the most determinants that influence the exposure; however, the validation of this model is incomplete and important determinants like washing the equipment, task duration, wearing gloves, frequency of replacement of gloves, work clothing, personal hygiene and climate conditions like wind speed and humidity, should be included to improve the assessment.

b) DREAM (Dermal Exposure Assessment Method)

This model approach has a structure in which the determinants cover most of the characteristics present in the case study. However, there are still some important determinants that can improve the accuracy. One is the differentiation of the level of protection for the body parts. Previous studies have found that the level of protection given by the work clothing differs between each body part (Lesmes-Fabian, et al., 2012) and the model only differentiates the protection for the body and the hands. On the other hand, the inclusion of climate conditions like wind speed and humidity which influence the dermal exposure, might improve the model accuracy as well. Despite this issue and comparing the model outcome with the exposure assessment previously made in the study area, the qualitative assessment of this model is the most realistic from the four evaluated models.

c) PHED (Pesticide Handlers Exposure Database)

This method is easy to use and includes determinants not included in other models, such as washing the equipment, wearing gloves, replacement frequency of gloves and clothes, and personal hygiene, which, according to the sensitivity analysis, influence strongly the scoring. However, other determinants in the model like using enclosed mixing system, tractor with enclosed cab and application with motorized sprayers, are not relevant for the working situations of farming systems in developing countries. Additionally, this model does not assess processes like emission and transfer; therefore, this model is useful for a quick assessment of dermal exposure in agricultural systems in industrialized countries but it is not appropriate for study areas in developing countries.

d) RISKOFDERM (Risk Assessment of Occupational Dermal Exposure to Chemicals)

This model assesses easily the dermal exposure, giving estimations in terms of $mg/cm^2/h$ which facilitates the comparison with direct dermal exposure measurements or reference values to assess the risk. However, this assessment does not take into account emission and transfer processes and also includes determinants only relevant for agricultural systems in industrialized countries such as automation. Therefore, this model is not appropriate for the case study of farming systems in developing countries.

DERM, DREAM, PHED and RISKOFDERM were applied in the case study of Vereda La Hoya in which pesticide management is performed by handed-pressurized sprayers. From the comparison of the models, DERM and DREAM were found to be the most appropriate models and DREAM to give the most accurate estimations. These results are valid for potato farming systems and many other crop systems with similar characteristics in different regions in Latin America and might be also be valid for other regions worldwide with similar pesticide applications in Africa or Asia. However, the results are not valid for other sophisticated pesticide applications in crops in developing countries such as flowers, banana, coffee, sugar cane, rice, etc. For these crops, the comparison of model outcomes might give a different conclusion. For instance, DREAM and PHED are models whose assessments are able to be targeted on pesticide applications with sophisticated techniques and they might be useful for the exposure assessment in these farming systems.

Improvement in the structure of the determinants of the models DREAM and DERM might not only improve the accuracy of exposure estimations but also might result in a brand new model for human exposure with high specificity for farming systems in developing countries.

5. Conclusions

This research evaluated in depth the available models for human exposure assessment, so assessors can decide which model is the most appropriate according to the characteristics of the study area in which the model is going to be applied and furthermore this research suggested improvements in the models in order to increase the estimation accuracy.

From a comparison of the models after a multi-criteria analysis, DERM, DREAM, PHED and RISKOFDERM were selected as the most appropriate models as they fulfill the required criteria for the case studies in developing countries. After these four models were applied to assess the dermal exposure in the case study of Vereda La Hoya and their determinants were compared with the characteristics of the study area, DREAM and DERM were found as the most appropriate models. However, because some relevant determinants are still absent (i.e. differentiation in the protection factor according to the different body parts and climate conditions are considered in the case of DREAM, and washing the equipment, task duration, wearing gloves, frequency and replacement of gloves, work clothing, personal hygiene and climate conditions are considered in the case of DERM), the accuracy of these models could be improved if these are included. When comparing the final model assessment of dermal exposure in the study area, DREAM was found as the model that assesses more accurately the dermal exposure in this study area.

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Publication 2

Dermal Exposure Assessment of Pesticide Use: The Case of Sprayers in Potato Farms in the Colombian Highlands

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Abstract

Quantifying dermal exposure to pesticides in farming systems in developing countries is of special interest for the estimation of potential health risks, especially when there is a lack of occupational hygiene regulations. In this paper we present the results of a dermal exposure assessment for the potato farming system in the highlands of Colombia, where farmers apply pesticides with hand pressure sprayers without any personal protective equipment. The fractioning of the pesticide, in terms of potential and actual dermal exposure, was determined via the whole-body dosimetry methodology, using the tracer uranine as pesticide surrogate, and luminescence spectrometry as analytical method. We assessed the three activities involved in pesticide management: preparation, application, and cleaning; analyzed three types of nozzles: one with a standard discharge and two modified by farmers to increase the discharge; and derived the protection factor given by work clothing. Our results suggest that to reduce the health risk, three aspects have to be considered: (i) avoiding the modification of nozzles, which affects the droplet size spectrum and increases the level of dermal exposure; (ii) using adequate work clothing

made of thick fabrics, especially on the upper body parts; and (iii) cleaning properly the tank sprayer before the application activity.

Keywords: Occupational Hygiene, Pesticides, Developing Countries, Potato, Tracer, Droplet Size, Hand Pressure Sprayer, Dermal Exposure.

1. Introduction

Pesticides are a key element of pest management programs in modern agriculture to increase the levels of production. Their use is stimulated by the commercialization and intensification of agriculture, the difficulty in expanding cropped acreage, the increased demand for agricultural products as population rises, and the shift to cash crops for domestic and export sales (Repetto, et al., 1996). It is estimated that annually 2.5 million tons of pesticide are used worldwide and 220,000 people die because of poisoning from these substances (Pimentel, et al., 1996). Most of these poisonings occur in developing countries because of weak safety standards, minimal use of protective equipment, absence of washing facilities, poor labeling, and lack of information programs (Feola, et al., 2010a; Feola, et al., 2010b; Hughes, et al., 2006; Pimentel, et al., 1996; Ramos, et al., 2010).

The agricultural sector in Colombia uses 3.8 million hectares of land for permanent and transitory crops. During the period of 1999 to 2009 an average of 82,000 tons of pesticides were applied per year (17% insecticides, 47% herbicides and 35% fungicides and bactericides) (FAO, 2013). This suggests that part of the population and the environment in Colombia are likely to be exposed to the negative effects derived from pesticide use. The potato farming system occupies 128,700 ha with 230,000 production units which in 2009 produced in total 2.3 million tons and used 32.5 kg/ha of pesticide active ingredients (M.A.D.R., 2009). For this reason the quantification of dermal exposure to pesticide use in the potato farming system in the highlands in Colombia is crucial to provide information about the level of risk faced by farmers and to support the development of proper policy measures.

Therefore the goals of this paper are:

(1) To quantify the current level of potential and actual dermal exposure to pesticides under the current working conditions (i.e. no use of personal protective equipment, and work clothing consisted of trousers and short-sleeve shirts) in the potato farming system in the highlands of Colombia, using the tracer fluorescein as pesticide surrogate.

(2) To identify the dermal exposure to pesticides on different body parts during the pesticide management activities (i.e. pesticide preparation, pesticide application and cleaning of the equipment).

(3) To determine the level of health risk due to dermal exposure faced by farmers under the current working conditions, finding out the critical activities that affect it.

2 Methodology

2.1 Study Area

The study area is located in Vereda La Hoya near Tunja, the capital city of the province of Boyacá, Colombia (Fig. 1). This is a rural region devoted mainly to the cultivation of potato in production units of around 3 hectares. The crop depends on rainfall; therefore, the production is generally organized into two periods, one from March to September and another from October to February, corresponding to the two rainy seasons. Average annual productivity is 18.3 ton/ha (M.A.D.R., 2009). Potato crops in this region are vulnerable to three major pests: the soil-dwelling larvae of the Andean weevil (*Premnotrypesvorax*), the late blight fungus (*Phytophthorainfestans*) and the Guatemalan potato moth (*Teciasolanivora*) (M.A.D.R., 2009). These pests, together with the weeds present in the early phases of the crop, are controlled by the application of chlorothalonil, chlorpyrifos, cymoxanil, glyphosate, mancozeb, metamidophos and paraquat (Feola, et al., 2010b; Juraske, et al., 2010). A survey made in the location showed that a high percentage of farmers experience various symptoms related to the use of pesticides (i.e. headaches, 24%; eye irritation 20%; bronchial irritation 9%; skin irritation, 5%; dizziness, 42%; nausea, 7%) (Feola, et al., 2010b)

Fig.1: Study Area in Vereda La Hoya, Province of Boyaca, Colombia(Oehler, 2008).

2.2 Pesticide Management in the Study Area

In the study area the pesticide management is performed along three main activities: the preparation of the pesticide, the application itself, and the cleaning of the spraying equipment. During the whole pesticide management, farmers use work clothing consisting of trousers, short-sleeve shirts and plastic boots. The three activities are explained in detail as follows:

a) Preparation: This activity includes opening the bottle containing the pure pesticide substance, mixing the solution of (different) pesticides and water, and loading the tank of the knapsack sprayer. Farmers in Vereda La Hoya prepare the pesticides in a container of 100-L capacity. The pesticide and the water (normally 80 L to obtain four applications of 20 L each) are mixed in this container with the aid of a wooden stick. During the mixing and the filling of the tank there are usually spills out of the container reaching different parts of the body including hands, arms, chest and legs.

b) Application: Once the knapsack sprayer is carried on the back, the pesticide application starts with the spraying process on the field. During this activity the farmers' body is exposed to the droplets emitted by the nozzles. In the study area the spraying is performed with hand pressure sprayers which are, on average, 9 years old (Feola, et al., 2010a; García-Santos, et al., 2011). They consist of a tank with a 20-L capacity, an injection and pressure system with an external piston pump and a pressure chamber with a capacity of 21 bar, a spraying pressure of 3 ± 0.3 bar and a pressure range between 1and 14 bar Farmers use two types of nozzles for pesticide application which differ in the amount of pesticide discharged: a high-discharge (HD) nozzle used during the first crop phases (sowing and emergence) and a low-discharge (LD) nozzle used during the rest of the crop phases (growth, flowering and pre-harvest). The discharges of the HD and LD nozzles measured in the study area were 1.88±0.12 L/min (n=24) measurements, and 1.26±0.08 L/min (n=24) respectively. Farmers purchase standard discharge nozzles and then modify the plastic and metal structures of the nozzles in order to obtain these discharges. To find out the droplet size distribution emitted by these two nozzles, the methodology developed by Nuyttens et al. (2007, 2009a) was followed, including as a reference in the measurement an unmodified nozzle with a standard discharge (SD) of 1.05±0.02 L/min (n=8).

c) Cleaning: Once the application is finished, farmers clean the sprayer and the container by pouring clean water on all the accessories in a procedure repeated three times. This procedure is included in the booklet "Good Agricultural Practices" (Fernandez, et al., 2009) which farmers use as a reference for the pesticide management. During this activity, there are numerous spills from the equipment and the accessories reaching the farmer's body.

2.3 Sampling Procedure

The pesticide fractioning on the body was measured during the three activities of the pesticide management with the whole body dosimetry method (WHO, 1982; Chester, 1993) using the tracer uranine (Fluorescein Sodium Salt; $C_{20}H_{10}Na_2O_5$; CAS Registry Number: 518-47-8; PubChem Compound ID: 10608) as surrogate for the pesticides. The selection of this tracer was based on its low detection level, rapid quantification, solubility in spray mixtures, minimum physical effect on droplet evaporation, distinctive property differentiating it from background or naturally occurring substances, stability, moderate cost, nontoxicity and acceptability under Food and Drug regulations (Akesson and Yates, 1964). Also a previous study made in Vereda La Hoya was used as a reference in which a similar procedure was carried out using patches as sampling media and the tracer uranine to study the human exposure to pesticides (García-Santos, et al., 2011). The degradation rate of uranine due to solar radiation measured in the study area was -8.9±1.2 %/hour, n=14. Tyvek garments (DuPont™Tyvek®) and cotton gloves were used as sampling media. Before the test, tyvek garments were labeled according to each body part: arms, thighs, legs (left, right, frontal and dorsal leg parts), chest, abdomen and back (upper and lower back part) (Fig. 2). When the evaluated activities were finished, the garments were cut, according to the parts previously labeled, packed together with the gloves and conserved in a dark place. The tracer solution in the 100-L container was sampled in 10-ml flasks and also conserved in a dark place until the measurement in the laboratory.

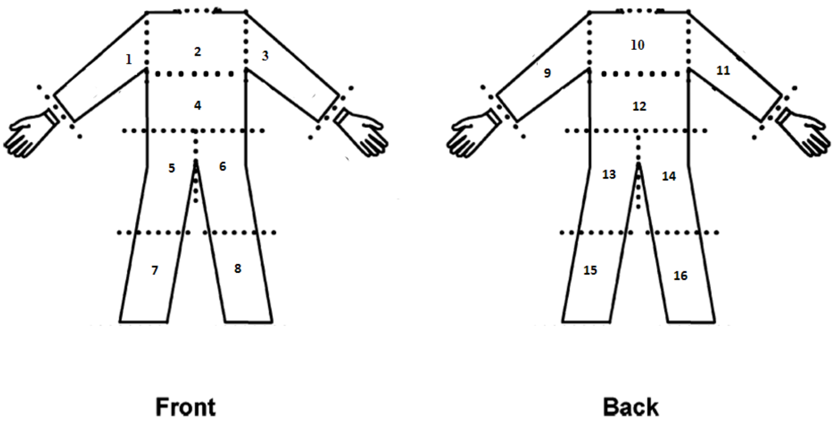

Fig. 2: Tyvek cutting scheme (Adapted from Hughes et al., 2006)

The potential dermal exposure (PDE), defined as the amount of contaminant landing on the outer layer of work clothing(Rajan-Sithamparanadarajah, et al., 2004a), was measured during preparation, application and cleaning wearing the tyvek garments over the work clothing together with the cotton gloves. The actual dermal exposure (ADE), defined as the amount of contaminant reaching the exposed skin surfaces (Rajan-Sithamparanadarajah, et al., 2004a), was measured only during application wearing the tyvek garment under the work clothing. The work clothing used by farmers during the evaluation consisted of short-sleeve shirts (made of 70% polyester and 30% cotton) and trousers (made of drill: 98% cotton and 2% spandex). A new cleaned set of work clothing was used for each test. The average age of the work clothing was 1 year. The whole evaluation of both PDE and ADE was repeated twice with the participation of two farmers using HD and LD nozzles. Farmers had 5 years of experience in pesticide spraying. Additionally, the PDE was measured during the application using the SD nozzle with one farmer.

Climatic conditions such as temperature, relative humidity, wind speed and solar radiation were measured during the whole procedure every 15 minutes with an automatic station Davis Vantage Pro-2 (Information of climate conditions measured during the evaluation is provided in the electronic supporting material).

2.4 Analytical Method

Following the proposed protocol and method by García-Santos et al., 2011, the amount of uranine in tyvek sections and gloves was firstly extracted by shaking all pieces in glass bottles with 200 or 400 ml of ultrapure water. Small tyvek sections from arms, legs, thighs and gloves were shaken in bottles with 200 ml and large tyvek sections from chest, abdomen and back in bottles with 400 ml. Afterwards, aliquots of 2 ml of the extraction solution together with aliquots from the samples taken in the tracer solution in the 100-L container were taken in cuvettes and 3 drops of 1 mol NaOH were added. Finally, the measurement of uranine was done with the Luminiscence Spectrometer PERKIN ELMER LS 50-B at an excitation wavelength of 491 nm, emission wavelength of 520 nm, excitation slit of 10 nm, emission slit of 10 nm, integration time of 1 second, and an emission filter cut-off at 515 nm. A series of standard concentrations were measured for the calibration of the equipment at 0.05, 0.1, 0.5, 1, 3,5 and 10 ppb (See calibration results in the electronic supporting material). The detection limit of the instrument is in the range of 0.05 and 30 ppb. When concentrations were above the detection limit, dilutions were made to 50x or 2500x.

2.5 Calculations

2.5.1 Dermal Exposure

Following the guideless for dermal exposure (U.S.EPA, 2007), the amount of uranine deposited on the tyvek pieces and gloves was obtained by multiplying the measurements from the luminescence spectrometer (µg/L) by the volume of extraction (0.2 or 0.4 L) and, in the same way, the total amount of uranine applied was obtained by multiplying the measurement from the luminescence spectrometer (µg/L) obtained from the samples of the solution taken in the 100-L container by the total amount of solution applied (80 L).

The PDE was calculated as the ratio of the amount of uranine measured in the tyvek garment used over the work clothing ($U_{T.O}$) plus the amount of uranine measured in the gloves (U_G), over the total amount of uranine applied measured in the 100-L container (U_A), according to Eq. 1.

$$PDE = \frac{U_{T.O} + U_G}{U_A} \qquad \text{(Eq. 1)}$$

Where $U_{T.O}$was calculated as the sum of the amount of uranine measured on the different tyvek pieces according to Eq. 2 to 4.

$$U_{T.O} = \Sigma\,(U_{T.Frontal} + U_{T.Dorsal}) \qquad \text{(Eq. 2)}$$

$$U_{T.Frontal} = \Sigma\,(U_{Front.Right.Arm} + U_{Front.Left.Arm} + U_{Front.Right.Thigh} + U_{Front.Left.Thigh} + U_{Front.Right.Leg} + U_{Front.Left.Leg} + U_{Chest} + U_{Abdomen}) \qquad \text{(Eq. 3)}$$

$$U_{T.Dorsal} = \Sigma\,(U_{Dorsal.Right.Arm} + U_{Dorsal.Left.Arm} + U_{Dorsal.Right.Thigh} + U_{Dorsal.Left.Thigh} + U_{Dorsal.Right.Leg} + U_{Dorsal.Left.Leg} + U_{Upper.Backt} + U_{Lower.Back}) \qquad \text{(Eq. 4)}$$

ADE was calculated as the ratio between the amount of uranine measured in the tyvek garment (used under the work clothing) ($U_{T.U}$) over the total amount of uranine applied measured in the 100-L container (U_A), according to Eq. 5.

$$ADE = \frac{U_{T.U}}{U_A} \qquad \text{(Eq. 5)}$$

Where $U_{T.U}$ was calculated as the sum of the amount of uranine measured in the different tyvek pieces according to Eq. 2 to 4.

2.5.2 Protection Factor

The protection factor of work clothing (PF), defined as the fraction of pesticide retained by the barrier of the work clothing layer (Lima, et al., 2011), was calculated only for the application activity as the ratio of the ADE over the PDE according to Eq.6.

$$PF = \frac{ADE}{PDE} * 100 \qquad \text{(Eq. 6)}$$

2.5.3 Health Risk

The PDE and ADE of each pesticide applied in Vereda La Hoya were calculated based on the PDE and ADE measured with the tracer and the real amount of pesticides commonly applied in Vereda La Hoya, according to Eq. 7 and 8.

$$PDE_{Pesticide} = PDE_{Uranine} * Pesticide_{Applied} \qquad \text{(Eq. 7)}$$

$$ADE_{Pesticide} = ADE_{Uranine} * Pesticide_{Applied} \qquad \text{(Eq. 8)}$$

Where, $PDE_{Uranine}$ and $ADE_{Uranine}$ are the values of PDE and ADE to the tracer obtained with Eq. 1 and 5. $Pesticide_{Applied}$ is the amount in kg of pesticide applied during one day of application (Table 3) (The pesticide application programme is provided in the electronic supporting material). Considering an average corporal weight of 70 kg and calculating the exposure for a working time of 8 hours, the PDE and ADE results were compared with the dermal median letal doses (Dermal LD_{50}) of each pesticide commonly used during the pest management in Vereda La Hoya.

3. Results

3.1 Potential Dermal Exposure

The activity presenting the highest PDE was the pesticide application (HD nozzles: 8.91E-4±3.86E-4; LD nozzles: 1.15E-3±6.50E-4; SD nozzles: 7.72E-4±9.13E-5), whereas the preparation and cleaning presented a PDE of 5.47E-5±5.52E-5 and 4.11E-5±1.98E-5, respectively. Regarding the different nozzle types, both HD and LD nozzles produced a higher PDE in the dorsal than in the frontal body part (Table 1).

Table 1. Results of potential and actual dermal exposure for the different pesticide management activities, the nozzle types and the frontal and dorsal body part.

	Type of Exposure					
	Potential Exposure			Actual Exposure		
	N	Mean	Std.Dev.	N	Mean	Std.Dev.
Activities						
Preparation	4	5.47E-5	5.52E-5			
Application with HD Nozzles	4	8.91E-4	3.86E-4	4	3.29E-5	3.79E-5
Application with LD Nozzles	4	1.15E-3	6.50E-4	4	4.23E-5	4.54E-5
Application with SD Nozzles	2	7.72E-4	9.13E-5			
Cleaning	4	4.11E-5	1.98E-5			
Body Part						
Frontal Body Part with HD Nozzle	4	3.91E-04	7.26E-05	4	3.14E-06	1.53E-06
Frontal Body Part with LD Nozzle	4	5.39E-04	1.81E-04	4	3.32E-06	2.34E-06
Dorsal Body Part with HD Nozzle	4	4.61E-04	9.10E-05	4	2.97E-05	3.17E-05
Dorsal Body Part with LD Nozzle	4	6.04E-04	3.09E-04	4	3.90E-05	3.20E-05

Table 2. Results of potential and actual dermal exposure measured in the different body parts during the application and the calculated protection factor.

Body Parts	N	Potential Dermal Exposure				Actual Dermal Exposure				Protection Factor %	
		HD Nozzles		LD Nozzles		HD Nozzles		LD Nozzles			
		Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	HD	LD
Right Arm Front	4	1.78E-06	7.61E-07	3.84E-06	2.87E-06	8.58E-07	8.23E-07	7.91E-07	6.21E-07	51.8	79.4
Chest	4	6.29E-06	3.55E-06	9.09E-06	1.61E-06	4.71E-07	3.59E-07	3.45E-07	1.43E-07	92.5	96.2
Left Arm Front	4	1.28E-06	2.49E-07	1.97E-06	6.08E-07	4.17E-07	2.88E-07	8.16E-07	1.07E-06	67.5	58.6
Abdomen	4	7.32E-06	4.51E-06	2.73E-05	1.86E-05	4.60E-07	3.33E-07	3.70E-07	3.25E-07	93.7	98.6
Right Thigh Front	4	3.94E-05	2.39E-05	4.27E-05	2.66E-05	1.32E-07	3.72E-08	9.89E-08	2.69E-08	99.7	99.8
Left Thigh Front	4	2.39E-05	1.67E-05	2.67E-05	5.36E-06	1.04E-07	1.87E-08	1.08E-07	3.20E-08	99.6	99.6
Right Leg Front	4	1.72E-04	4.29E-05	2.20E-04	7.96E-05	3.95E-07	2.88E-07	5.70E-07	6.45E-07	99.8	99.7
Left Leg Front	4	1.39E-04	6.73E-05	2.08E-04	9.21E-05	3.05E-07	2.24E-07	2.18E-07	1.25E-07	99.8	99.9
Left Arm Dorsal	4	1.91E-06	1.13E-06	2.82E-06	1.11E-06	3.89E-07	4.40E-07	3.38E-07	2.39E-07	79.6	88.0
Upper Back	4	4.66E-05	1.90E-05	6.77E-05	3.96E-05	1.17E-05	1.52E-05	1.18E-05	8.53E-06	74.8	82.6
Right Arm Dorsal	4	4.16E-06	4.28E-06	4.39E-05	6.27E-05	1.43E-05	1.66E-05	1.80E-05	2.25E-05	65.5	58.9
Lower Back	4	7.23E-05	2.73E-05	4.15E-05	2.60E-05	2.23E-06	2.52E-06	3.76E-06	3.37E-06	96.9	91.0
Left Thigh Dorsal	4	3.52E-05	3.46E-05	3.50E-05	2.65E-05	1.19E-07	6.52E-08	3.46E-06	6.02E-06	99.7	90.1
Right Thigh Dorsal	4	3.20E-05	1.90E-05	4.30E-05	2.97E-05	1.02E-07	1.23E-08	1.65E-07	1.55E-07	99.7	99.6
Left Leg Dorsal	4	1.49E-04	7.33E-05	1.88E-04	9.60E-05	4.64E-07	4.74E-07	6.61E-07	6.63E-07	99.7	99.6
Right Leg Dorsal	4	1.16E-04	4.09E-05	1.82E-04	1.39E-04	3.40E-07	2.35E-07	7.88E-07	9.28E-07	99.7	99.6
Hands	4	4.35E-06	6.94E-06	3.56E-06	2.28E-06						

The lower body part (legs and thighs) was the most exposed, representing 79.7 and 82.6% from the total PDE measured during the application for the HD and LD nozzles, respectively. Legs were the body parts with the highest PDE (65% for the HD nozzles and 69.8% for LD nozzles) (Table 2).

3.2 Actual Dermal Exposure

From the total ADE measured during the application, 48.6% was found in arms when using HD nozzles and 47.2% when using LD nozzles. Also the back represented 42.5% of the total ADE measured for HD nozzles and 36.6% for LD nozzles (Table 2). The lower body part (legs and thighs) represented 5.9% of the total ADE measured for HD nozzles and 14.3% for LD nozzles. ADE was higher in the dorsal than in the frontal body part for both types of nozzles (Table 1).

3.3 Protection Factor

The PF given by work clothing and calculated for the application activity was high for legs, thighs, chest, abdomen and lower back (>90%) when both types of nozzles (HD and LD) were used. On the contrary, the protection was low in the arms (ranging from 51.8 to 88%) and also in the upper back (ranging from 74.8 to 82.6%) (Table 2). The PF mean values for the frontal and dorsal right arm (the arm in charge of handling the nozzle pipe) ranged between 51.8 and 79%. It was observed that even though work clothing offers a high level of protection, especially in legs, thighs, abdomen and chest, this protection is lower in critical parts which are in direct contact with the sprayed droplets like the arms or with the spills residues on the application equipment like the upper back.

3.4 Effect of Nozzles on Dermal Exposure

According to the volumetric droplet size distribution for the three evaluated nozzles (Fig. 3) and following the British Crop Protection Council (BCPC) spray classification (Southcombe, et al., 1997), the categories of the HD, LD and SD nozzles are, respectively, medium, fine and fine. The smallest droplet size spectrum was found for the standard nozzle with a volume mean diameter (VMD) of 164µm, followed by the LD nozzle (VMD = 208 µm) and the HD nozzle (VMD = 324 µm). The SD nozzle shows a distribution with a peak between 70 to 230 µm and with a volume mean diameter of 160 µm. The LD nozzle shows a similar behavior but with a volume mean diameter of 208 µm. The HD nozzle had an irregular distribution with droplet sizes ranging between 70 and 670 µm and a volume mean diameter of 324 µm.

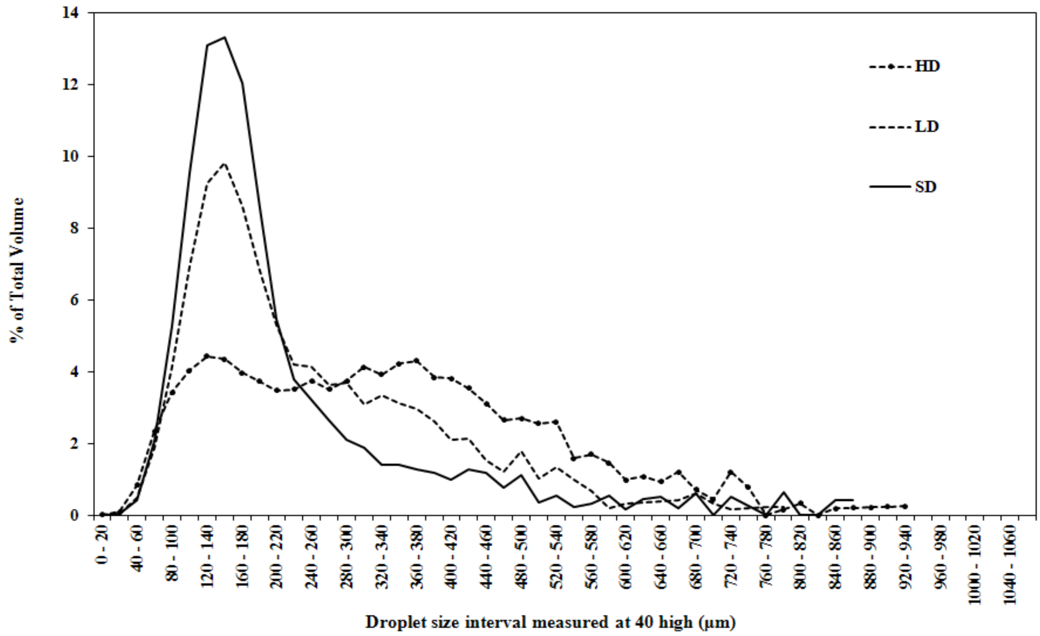

Fig.3: Volumetric droplet size distribution measured at 2.75 bar and 40 cm height for the high discharge (HD), low discharge (LD) and standard discharge (SD) nozzles.

Results of PDE and ADE between the applications with the different nozzles showed that on average, PDE was higher with the LD nozzle (1.15E-3±6.50E-4) than with the HD nozzle (8.91E-4±3.86E-4), meanwhile ADE was higher with the application with the LD nozzles (4.23E-5±4.54E-5) than with the HD nozzles(3.29E-5±3.79E-5)(Table 1). When comparing the PDE for the three nozzles, the PDE mean value for SD nozzles was lower (7.72E-4±9.13E-5) than for the HD and LD nozzles.

3.5 Health Risk

Table 3 shows the type and amount of pesticides applied during one potato crop cycle in Vereda La Hoya (Feola, et al., 2010b) with the estimated values of PDE and ADE for each of the activity during the pesticide management and for the different nozzles used during the application. The PDE and ADE was calculated for a working time of 8 hours and an average corporal weigh of 70 kg. The results were compared with the Dermal LD_{50} as a reference of the level of toxicity of each pesticide. Even though ADE values were under the Dermal LD_{50} reference values, the pesticide metamidophos presents the most toxic level with critical PDE values during the application activity for all the three nozzles.

Table 3: Results of potential and actual dermal exposures to the pesticides used in Vereda La Hoya. Amount of pesticides applied in the study area were taken from Feola and Binder, 2010a.

Pesticide Applied			PDE (mg/kg.day)					ADE (mg/kg.day)	
Name	kg/ha.day	Dermal LD_{50} (mg/kg)	Preparation	Application HD Nozzle	Application LD Nozzle	Application SD Nozzle	Cleaning	Application HD Nozzle	Application LD Nozzle
Chlorothalonil	0.54	>20,000	3.38	52.84	70.80	47.62	2.54	2.31	2.66
Chlorpyrifos	0.44	200-2000	2.75	43.06	57.69	38.80	2.07	1.88	2.17
Cymoxanil	0.08	2000-20000	0.50	7.83	10.49	7.05	0.38	0.34	0.39
Glyphosate	0.14	2000-20000	0.88	13.70	18.36	12.34	0.66	0.60	0.69
Mancozeb	0.66	>20,000	4.13	64.58	86.54	58.20	3.10	2.83	3.25
Metamidophos	0.55	≥50	3.44	53.82	72.12	48.50	2.58	2.36	2.71
Paraquat	0.08	2000-20000	0.50	7.83	10.49	7.05	0.38	0.34	0.39

4. Discussion

4.1 Potential and Actual Dermal Exposure

The hand pressure application is generally considered to represent the worst case scenario for dermal exposure due to the proximity of the nozzle to the lower body parts of operators with values usually fluctuating largely because of unexpected changes in the environmental conditions and working patterns during the trials (Castro Cano, et al., 2000a; van Hemmen, et al., 1995). Even though the present results have a limited number of repetitions, they are comparable to previous studies which found similar patterns of pesticide fractioning with high percentages of PDE in the lower body part. Our results showed that PDE was higher on the lower body parts, including thighs and legs which are comparable to previously reported values: 71.5% (Castro Cano, et al., 2000b), 70.6% (Castro Cano, et al., 2001) and 62% (Machera, et al., 2002).

In the case of ADE, we found a higher value the back because normally there are spills of solution on the sprayer after filling up the tank and these residues are in contact with the back when farmers start the application without cleaning it, which is a particular situation for farmers in Vereda La Hoya. Therefore, the dorsal body part was more exposed than the frontal because of the high ADE in the back together with a high ADE in the dorsal part of the arms as this part is in contact with the sprayed droplets during the application activity.

The ADE in the arms was higher than other parts due to the fact that farmers use short-sleeve shirts as a more comfortable work clothing for the applications. ADE was especially higher in the dorsal right arm because of the proximity of the sprayed droplets with this body part as this arm is in charge of handling the nozzle pipe. Also, a high ADE was found on the upper back because of the increasing level of humidity due to perspiration during the application and the direct contact with the residues left on the sprayer tank.

4.2 Protection Factor

Because of the differences in the fabric characteristics between trousers and shirts, different PFs were obtained for each body part, especially on legs, thighs, back and arms. In the case of legs and thighs, these parts showed on average the highest protection faction due to the fabric characteristics of the trousers, which are made of made of drill (98% cotton and 2% spandex). In the back, the protection factor was reduced in the lower back as there was an increasing rate of humidity because of the perspiration under normal working conditions, allowing the transfer of solution through the fabric which in the shirt was a thin layer composed of 70% polyester and 30% cotton. A lower PF was found on the dorsal part of the right arm as this is directly exposed to the spraying solution receiving a larger amount of spraying solution than other body parts. The PF depends on the characteristics of the fabric such as the thickness, yarn twist and wicking; and the viscosity and surface tension of the pesticide mixtures (Lee and Obendorf, 2005). The obtained PF values of work clothing (Table 2) differ significantly from the default data available from various statistical models and databases designed to predict exposure to pesticides. EUROPOEM suggests a value of 70% (Van Hemmen, 2001), the Pesticide Handlers Exposure Database (PHED) suggests 50% (Krieger, 1995), and the Californian Department of Pesticide Regulation (CA DPR) has adopted a default protection factor of 90% (Thongsinthusak, et al., 1993). However, similar results were found in previous empirical studies in which the protection factor in cotton garments varies between 92.5 to 84.1% (Protano, et al., 2009) and in cotton/polyester varies between 91 to 99.5% (Fenske, et al., 2002). Other reports showed that protection factors are commonly 2 or 3 times higher in the lower parts of the body because of the difference in the type of material between shirts and trousers (Aprea, et al., 2004; Machera, et al., 2003).

4.3 Effect of Nozzles on Dermal Exposure

In our evaluation the differences in dermal exposures between the applications with the three nozzles may be explained by the differences in volumetric droplet size distribution. The modification of the nozzles change the droplet size distribution and the result might be not only an increase in the dermal exposure but also a decrease in the pest control efficiency (the standard recommendation of droplet size depends on the kind of substance applied: i.e. fungicides 150-250 µm, insecticides: 200-350 µm, contact herbicides: 200-400 µm and pre-emergence herbicides: 400-600 µm) (Nuyttens, et al., 2007a; Nuyttens, et al., 2007b; Nuyttens, et al., 2009a).

4.4 Health Risk

Considering the high levels of PDE found during the application activity, the frequency of pesticide applications and the symptoms reported in the survey made in the location (Feola, et al., 2010b), there is a high level of risk to dermal exposure under the current working conditions especially for the pesticide Metamidophos. This pesticide is the most toxic pesticide used by farmers in Vereda La Hoya and an examination of its toxicological information indicates that it is associated with adverse reproductive, teratogenic, mutagenic and carcinogenic effects (Cochran, et al., 1995; Lima, et al., 2011). In Vereda La Hoya, dermal exposure is the most important mode of exposure as previous studies have shown a low risk of exposure by ingestion (Juraske, et al., 2010) and a preliminary test showed that when nozzles are modified, the sprayed droplet size increases which results in a fast deposition downwards, reducing the exposure by inhalation. Therefore, the reduction of the health risk from pesticide applications might be achieved in three ways at least such as using adequate work clothing made of thick materials that covers all the body parts specially the arms; cleaning properly all the spills residues on the sprayer tank before starting application; and avoiding the modification of nozzles which affects the droplet characteristics.

Conclusions

This paper presents the potential and actual exposure patterns faced by potato farmers in Vereda La Hoya, Boyaca, Colombia. During the pesticide management in Vereda La Hoya, the application was the activity with the highest PDE. Even though lower body parts (thighs and legs) were the most exposed, these body parts also showed the highest level of protection by the current work clothing. The ADE was high for arms and upper back because of lack of adequate work clothing covering the complete arm and the direct contact of the upper back with the spills on the sprayer tank.

Metamidophos is the most toxic pesticide used in Vereda La Hoya and farmers may reduce significantly the health risk by using adequate work clothing made of appropriate fabrics that covers the whole body including the arms, cleaning properly all the pesticide residues left on the sprayer tank before each application, and avoiding the modification of nozzles using only nozzles with the standard discharge.

Further research is still required to determine the cumulative dermal exposure when several pesticides are applied at the same time and with certain frequency along the crop cycle as there are possible underlying mechanisms of interactions between the chemicals in a mixture. Also, even though the patterns of dermal exposure are similar to previous studies, the particularities of the system in Vereda La Hoya suggest that risk evaluators should consider in their assessments specific characteristics of the system like the type of work clothing, the modification of nozzles and the frequency and duration of the application. Furthermore, the risk assessment might be improved by estimating the dermal exposures, taking into account parameters like pesticide degradation rates, cumulative exposures, application pesticides mixtures and the protection factor given by the work clothing.

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Publication 3

Pesticide Flow Analysis to Assess Human Exposure in Greenhouse Flower Production in Colombia

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Abstract

Human exposure assessment tools represent a means for understanding human exposure to pesticides in agricultural activities and managing possible health risks. This paper presents a pesticide flow analysis modeling approach developed to assess human exposure to pesticide use in greenhouse flower crops in Colombia, focusing on dermal and inhalation exposure. This approach is based on the material flow analysis methodology. The transfer coefficients were obtained using the whole body dosimetry method for dermal exposure and the button personal inhalable aerosol sampler for inhalation exposure, using the tracer uranine as a pesticide surrogate. The case study was a greenhouse rose farm in the Bogota Plateau in Colombia. The approach was applied to estimate the exposure to pesticides such as mancozeb, carbendazim, propamocarb hydrochloride, fosetyl, carboxin, thiram, dimethomorph and mandipropamide. We found dermal absorption estimations close to the AOEL reference values for the pesticides carbendazim, mancozeb, thiram and mandipropamide during the study period. In addition, high values of dermal exposure were found on the forearms, hands, chest and legs of study participants, indicating weaknesses in the overlapping areas of the personal protective equipment parts. These results show how the material flow analysis methodology can be applied in the field of human exposure for early recognition of the

dispersion of pesticides and support the development of measures to improve operational safety during pesticide management. Furthermore, the model makes it possible to identify the status quo of the health risk faced by workers in the study area.

Keywords: dermal exposure assessment; respiratory exposure assessment; pesticides; material flow analysis; greenhouses; developing countries; Colombia; flower crops.

1. Introduction

Pesticides are chemicals of growing public health concern because epidemiological studies have found that they are associated with different cancers(De Roos, et al., 2003; Hardell, et al., 2002), neurologic pathologies (Baldi, et al., 2003a; Baldi, et al., 2003b; Elbaz, et al., 2004), respiratory symptoms (Salameh, et al., 2003) and hormonal and reproductive abnormalities (Bell, et al., 2001; Garry, et al., 2002; Weidner, et al., 1998). Regardless of the risks involved in using pesticides, they are still considered necessary for agriculture because they allow intensive production (Glass, et al., 2009). Therefore, it is crucial to assess the risk due to pesticide use to improve their management and to reduce exposure, thereby protecting human health.

Floriculture is a growing agricultural activity in countries such as Argentina, Colombia, Ecuador, Mexico, India, Kenya and Zimbabwe, where greenhouse environment conditions are designed to optimize plant growth (Illing, 1997; Ribeiro, et al.). Colombia is the world's second largest flower exporter, with a cultivated area of 6,800 hectares and an average of 15 workers per hectare (ASOCOFLORES, 2010). Studies in the 1990s showed birth defects among children as well as adverse reproductive outcomes in populations occupationally exposed to pesticides in the floriculture crop system in Colombia (Restrepo, et al., 1990a; Restrepo, et al., 1990b). Although the floriculture industry has made significant progress in reducing pesticide exposure, and numerous studies have assessed exposure to pesticides in greenhouses worldwide (Cerrillo, et al., 2006; Costa, et al., 2007; Gerth Van Wijk, et al., 2011; Hernandez, et al., 2003; Jurewicz, et al., 2008; Machera, et al., 2003; Monsó, et al., 2002; Ribeiro, et al.; Rosano, et al., 2009) (Esechie, et al., 2011; Flores, et al., 2011; Lu, 2005; Munnia, et al., 1999; Nuyttens, et al., 2009b; Ramos, et al., 2010), there have been no recent studies of human exposure in the floriculture system in Colombia.

Tools for dermal exposure, such as EASE (Cherrie, et al., 2003), EUROPOEM (Van Hemmen, 2001), PHED (Dosemeci, et al., 2002), RISKOFDERM (Rajan-Sithamparanadarajah, et al., 2004a), COSHH (Garrod, et al., 2003)

STOFENMANAGER (Marquart, et al., 2008) and the approaches proposed by the U.S. EPA (U.S.EPA, 2007), are targeted at occupational situations in industrial processes in Europe and the USA, but they do not consider agricultural processes such as pesticide management. DREAM (Van-Wendel-De-Joode, et al., 2003) and DERM (Blanco, et al., 2008) are methods focused on occupational activities in pesticide management in developing countries; nonetheless, their semi-quantitative estimations still lack reliability and validity (Blanco, et al., 2008; Kromhout, et al., 2008). Teubl (Teubl, et al., 2012) applied the methods PHED, RISKOFDERM, DERM and DREAM to estimating dermal exposure in the potato farming system in Colombia, and the results showed that each model delivers a different dermal exposure score because of the different determinants considered in each model, resulting in uncertainties about the real risk of exposure. Therefore, taking into account the disadvantages of the existing methodologies, a tool is required to provide a quantitative unambiguous estimation of dermal and inhalation pesticide exposure in developing countries.

Material flow analysis (MFA) is a method to describe and analyze the material and energy balance of a firm, a region, or a nation. It is based on the law of matter conservation and is defined by a geographic system boundary, a time span within which the analysis is performed, processes which depict human activities, and flows of goods, matter, or energy between these processes (Binder, 2012). It has been applied to different processes such as the balance of durables in developing countries (Binder, et al., 2001), the tracing of pollutants through environmental systems such as watersheds or urban regions (Bergbäck, et al., 1994; Binder, et al., 1997; Kleijn, et al., 1994; Van der Voet, et al., 1994) and the flow of metals (Frosch, et al., 1997; Gordon, et al., 2003; Graedel, et al., 2002; Spatari, et al., 2003). Accordingly, this methodology might be applied in the field of human exposure, allowing quick and early recognition of the fractioning of the pesticides in the human body during pesticide management activities and helping to identify activities that are crucial to improving operational safety.

The goals of this study were the following: (i) to investigate the feasibility of the application of the material flow analysis methodology (MFA) to the field of human exposure to pesticides, (ii) to develop a tool that helps to estimate dermal and inhalation exposures to pesticides, and (iii) to identify pesticide management activities or processes that could be improved in the floriculture system in Colombia. To achieve these goals, the following research questions were addressed:

a) How can the material flow analysis methodology be adapted to study human exposure to pesticides in agricultural systems?

b) What are the advantages and disadvantages of using this methodology in the field of human exposure and risk assessment of pesticide use?
c) Based on the model outputs, what is the current situation with respect to human exposure to pesticides in the flower crop systems in Colombia, and how can the management of human exposure to pesticides be improved?

2. Methodology

2.1. Material Flow Analysis

The MFA method (Baccini, et al., 2012; Brunner, et al., 2004) is based on the mass conservation law and studies the flow of a substance among the different processes involved in a system. In our particular case, the method was applied to analyzing the flow of pesticides in the floriculture system during pesticide management activities such as preparation, application and cleaning of pesticide application equipment. Human exposure to pesticides was studied in terms of the fractionation of pesticides in the human body, including the dermal and inhalation exposure routes (Figure 1). The floriculture system was defined in terms of the pesticide-related activities that are performed in the greenhouse (preparation and application of the pesticides) and the cleaning rooms (where all the application and personal protection equipment is cleaned).

This study focused only on the pesticide flow to the human body; therefore, the flow to target plants, soil and air were considered outputs of the system. The system is composed of 15 processes and 25 fluxes. The pesticide enters the system as *input* and flows according to three pesticide management activities: preparation (P_1), application (P_2) and cleaning (P_3). These are considered transportation processes without a stock. From the preparation and cleaning, there is a direct transport of pesticide to the different body parts (P_5). During the application, there is a transport of the pesticide to the air (P_4) and to the different body parts (P_5). The potential dermal exposure (PDE), P_5, is the sum of the PDE from P_1, P_2, and P_3. This is defined as the fraction of contaminant landing on the outer layer of the personal protective equipment (Rajan-Sithamparanadarajah, et al., 2004b). The actual dermal exposure (ADE), P_{14}, is defined as the amount of contaminant reaching exposed skin surfaces (Rajan-Sithamparanadarajah, et al., 2004b). The level of protection given by the personal protective equipment is defined in the model separately for each body part in P_6 to P_{13}. The pesticide flow between the potential (P_5) and actual exposure (P_{14}) depends on the level of substance retention given by the personal protective equipment. The retained amount of pesticide is defined in the model as the stock of P_6 to P_{13}. The inhalation exposure (P_{13}) is defined as the amount of contaminant arriving at the inhalation mask, and the stock is the amount retained by the filters used in the protection mask. The actual inhalation exposure is the amount of contaminant that crosses the filter in the mask.

The pesticide flow among all the processes is defined by a mass balance and is expressed by the following equations proposed by Baccini and Brunner, 2012 (Baccini, et al., 2012):

$$k_{F(P_i,P_j)} = \frac{X_{F(P_i,P_j)}}{\sum_{k\neq i}[X_{F(P_k,P_j)}]} \qquad (1)$$

$$S_t = S_{t0} + \sum_{t_0}^{t}(Input_{(t)} - Output_{(t)}) \qquad (2)$$

The transfer coefficient k for any flow from P_i to P_j is giving by Equation (1), where $X_{F(Pi, Pj)}$ is the amount of pesticide flowing from P_i to P_j, $\Sigma[XF_{(Pk, Pi)}]$ is the sum of the amounts of pesticide flows coming to P_i, S_t is the stock after time step t, t_0 is the time of initial time step t, t is the current time step and S_{t0} is the existing stock at the initial time step. The time step is defined as one working day of 8 h. The transfer coefficients were obtained by means of field measurements explained in the following sections.

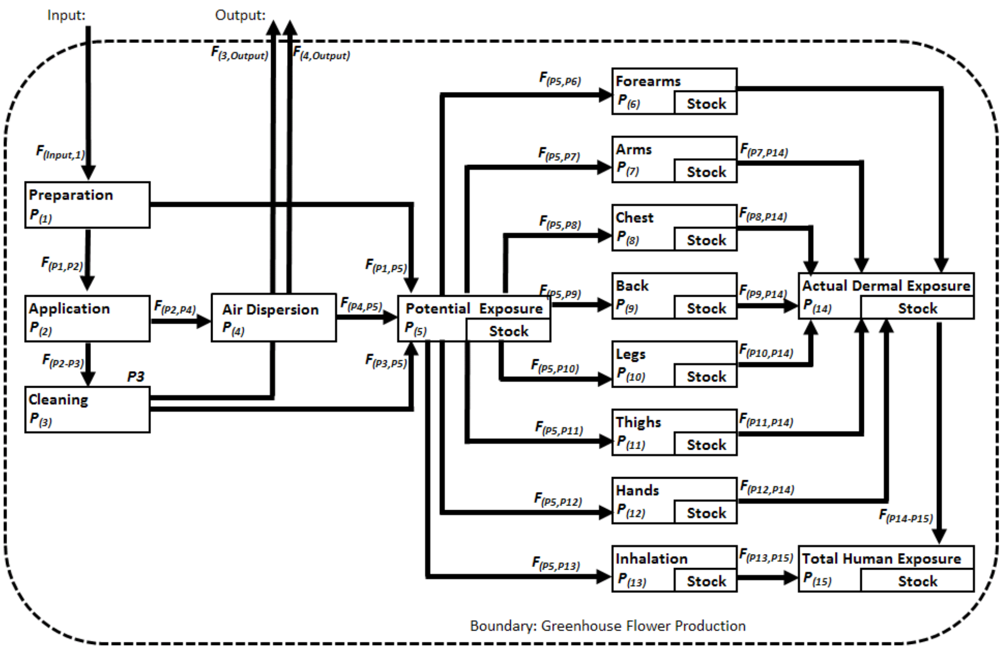


Figure 1. Pesticide flow analysis for the floriculture system (P: Processes, F: Flows).

2.2. Description of the Study Area

The study area selected for the measurement of the pesticide flows was a farm dedicated mostly to rose production, with an area of 25.5 ha, located on the Bogota Plateau at 2,685 m.a.s.l. The average temperature is 13 °C, and inside the greenhouses, the temperature fluctuates during the day from 6 to 11 °C at 6:00 am, 21 to 31 °C at 11:00 am and 22 to 29 °C at 2:00 pm. The rose plants had a crop density of 8.2 to 8.6 plants/m^2 in rows 32 m long and 0.8 m wide, separated by 0.6 m paths. A greenhouse has between 170 and 230 rows. The main pests affecting the rose crop production are downy mildew (*Peronospora sparsa*), grey mold (*Botrytis cinerea*), thrips and spider mites (*Tethranycus spp.*). Fungicide management is performed using a rotation of products such as carbendazim (0.6 cc/L), carboxin-thiram (1 cc/L), mancozeb (2 cc/L), dimethomorph (0.7 cc/L) propamocarb chlorohydrate (1.8 cc/L) and mandipropamide (0.8 cc/L). The pesticide preparation is made on the field mixing the commercial pesticide products with water in a 500-L container. The pesticides were applied using a standard personal protection equipment used by all the farms registered as members of the Association of Colombian Flower Exporters. It consisted of a rubber level B Hazmat suit (a garment that protects against splashes from hazardous chemicals with an external breathing mask, hood, rubber gloves and waterproof boots). The cleaning activity consists of washing the personal protective equipment and the application accessories in a washing facility by using water and cleaning products like detergent and soap. Figure 2 shows an example of pesticide management in greenhouse rose production and Table 1 lists the main characteristics of these pesticides.

2.3. Data Measurement

2.3.1. Dermal Exposure Measurement

The pesticide flows were measured during the three pesticide management activities: preparation, application and cleaning (P1to P3). The pesticide fractioning in the human body (P_6 to P_{12}) was measured by means of the whole body dosimetry method (Chester, 1993; Hughes, et al., 2006; WHO, 1982) using the tracer uranine (fluorescein sodium salt; $C_{20}H_{10}Na_2O_5$; CAS Registry Number: 518-47-8; PubChem Compound ID: 10608) as a surrogate for the pesticides. The selection of this tracer was based on its low detection level, rapid quantification, solubility in spray mixtures, minimal physical effects on droplet evaporation, distinctive properties differentiating it from background or naturally occurring substances, stability, moderate cost, nontoxicity and acceptability under the regulations of the US Food and Drug Administration (Akesson, et al., 1964).

Table 1. Characteristics of the fungicides used in the case study during the study period.

Commercial Name	Active Ingredient	Chemical Group	% of Active Ingredient	Dose	Total AI Applied(g/d)	Confirmed Health Effects [58]	Possible Health Effects [58]
Bavistin	Carbendazim	Benzimidazole	50%	0.6 g/L	728	Reproduction/ development effects	Endocrine disrupter
Carbovax	Carboxin	Oxathiin	20%	1 g/L	447	Eye irritant	Carcinogen, reproductive/development effects
	Thiram	Dithiocarbamate	20%	1 g/L	447	No information available	Carcinogen, mutagen, endocrine disrupter, reproduction/development effects, respiratory tract, eye and skin irritant
Dithane	Mancozeb	Dithiocarbamate	100%	2 cc/L	2400	Carcinogen, respiratory tract irritant, reproduction/development effects	Mutagen, endocrine disrupter, skin irritant
Forum	Dimethomorph	Morpholine	50%	0.7 g/L	878	Respiratory tract, eye and skin Irritant	Reproductive/development effects
Previcur	Propamocarb Hydrochloride	Carbamate	53%	1.8 g/L	2,365	Skin irritant	Acetyl cholinesterase inhibitor
	Fosetyl	Organophosphate	31%	1.8 g/L	1,383	Eye irritant, reproduction/development effects	Carcinogen, acetyl cholinesterase inhibitor, neurotoxicant
Revus	Mandipropamid	Mandelamide	25%	0.8 g/L	480	Skin irritant	No information available

Figure 2. Preparation (**left**) and application of pesticide (**central** and **right**). in a greenhouse for flower production in Colombia.

In addition, previous studies of human exposure to pesticides have demonstrated the advantages of and positive results obtained with the tracer uranine (García-Santos, et al., 2011; Lesmes-Fabian, et al., 2012). Tyvek® garments (DuPont™) and cotton gloves were used as sampling media. Before the test, Tyvek® garments were labeled by body part (Figure 3): arms, forearms, thighs, legs (left, right, frontal and dorsal leg parts), chest, abdomen and back (upper and lower back part), and when the evaluated activities were finished, the Tyvek® garments were cut according to the labeling scheme and were packed and conserved in a dark place. The same procedure was followed for the gloves. The measurement of the potential exposure was performed once a day washing the personal protective equipment in order to avoid residual contamination of uranine between the measurements. The different personal protective equipment parts were currently used by the farm whose appropriate condition is monitored by the occupational hygiene department in the farm.

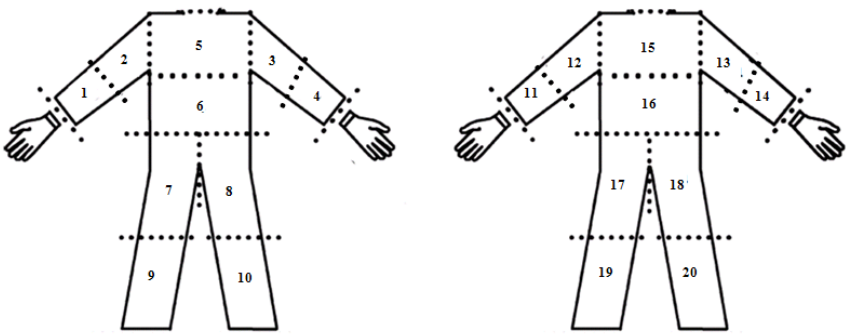


Figure 3. Tyvek® cutting scheme (adapted from (Hughes, et al., 2006).

The field measurements were carried out between 11:00 am and 2:00 pm. The duration of the preparation, application and cleaning activities were, as an average, 15, 8 and 30 min, respectively. In the model these times were extrapolated to 1 h. The application of pesticides was made by motorized equipment consisting of a Bean® Pump (Model No. R-10; Max RPM: 580; HP: 3.4; GPM: 10.0; PSI: 500; KW: 2.5; LPM: 37). The spraying was performed with 5 nozzles (Ref: C-35) with a flow rate of 3 L/min, mounted in a pipe 1.60 m long. The nozzles were spaced 40 cm apart in the pipe (See Figure 2). Following the normal pesticide application procedure, 3 workers performed the application at the same time, each holding a pipe, spraying sidewards and walking forwards.

In the laboratory, following a previously developed protocol (García-Santos, et al., 2011; Lesmes-Fabian, et al., 2012), the uranine in the Tyvek® sections and gloves was first extracted by shaking all pieces in glass bottles with 400 mL of ultrapure water. Afterwards, aliquots of 2 mL of the extraction solution, together with aliquots from the samples in the tracer solution in a 500L container, were taken in cuvettes, and three drops of 1 mol NaOH were added. Finally, the measurement of uranine was performed using a Perkin Elmer LS 50-B Luminescence Spectrometer at an excitation wavelength of 491 nm, an emission wavelength of 520 nm, an excitation slit of 10 nm, an emission slit of 10 nm, an integration time of 1 s, and an emission filter cut-off at 515 nm. A series of standard concentrations (i.e., 0.05, 0.1, 0.5, 1, 3, 5 and 10 ppb) were used for the calibration of the instrument. The detection limit of the instrument was in the range of 0.05 to 30 ppb. When concentrations were above this detection limit, dilutions were made to 50× or 2,500×.

PDE was measured on three different days during the preparation, application and cleaning processes. The PDE was calculated as the ratio of the amount of uranine measured in the Tyvek® garment ($U_{T.O}$) plus the amount of uranine measured in the gloves (U_G), divided by the total amount of uranine applied measured in the 500-L container (U_A), according to Equation (3):

$$PDE = \frac{U_{T.O} + U_G}{U_A} \tag{3}$$

where $U_{T.O}$ was calculated as the sum of the amounts of uranine measured on the different Tyvek® pieces according to Equation (4) through Equation (6):

$$U_{T.O} = \sum (U_{T.Frontal} + U_{T.Dorsal}) \tag{4}$$

$$U_{T.Frontal} = \sum \begin{matrix} (U_{Front.Right.Arm} + U_{Front.Left.Arm} + U_{Front.Left.Forearm} + U_{Front.LeftForearm} + U_{Front.Right.Thigh} + \\ U_{Front.Left.Thigh} + U_{Front.Right.Leg} + U_{Front.Left.Leg} + U_{Chest} + U_{Abdomen}) \end{matrix} \tag{5}$$

$$U_{T.Dorsal} = \sum \begin{matrix} (U_{Dorsal.Right.Arm} + U_{Dorsal.Left.Arm} + U_{Dorsal.Right.Thigh} + U_{Dorsal.Left.Thigh} + \\ U_{Dorsal.Right.Leg} + U_{Dorsal.Left.Leg} + U_{Upper.Backt} + U_{Lower.Back}) \end{matrix} \tag{6}$$

Because the application is the activity that contributes with more than 99% to the total exposure (Lesmes-Fabian, et al., 2012; U.S.EPA, 2007), ADE was measured only during the application with the three workers wearing the Tyvek® garments under the personal protective equipment. ADE was measured on three different days during the application activity, with the participation of the same three workers performing the application simultaneously and using the respective sampling media. ADE was calculated as the ratio of the amount of uranine measured in the Tyvek® garment over the total amount uranine applied measured in the 500L container.

The level of protection (PF: Protection Factor) for each body part was calculated as the fraction of pesticide retained by the barrier of the personal protective equipment. It was calculated only for the application activity as the ratio of the ADE to the PDE, according to Equation (7):

$$PF = \frac{ADE}{PDE} \times 100 \tag{7}$$

2.3.2. Inhalation Exposure Measurement

The inhalation exposure was measured using the *button personal inhalable aerosol sampler* (BPIAS). It was chosen because of its efficiency and precision, according to previous studies involving evaluation of the level of occupational exposure to inhalable airborne substances (Chen, et al., 2008; De Schampheleire, et al., 2007; Witschger, et al., 2004). The inhalation exposure measurement was performed at the same time as the dermal exposure measurement. During the application, two workers carried sets of breathing equipment consisting of one Leland Legacy® Single Pump (calibrated to sample air at a rate of 15 L/min) connected to a BPIAS that contained a filter paper with a porosity of 25 µm. The filter papers were collected, labeled and packed for analysis in the laboratory. The amount of uranine measured in the filters represented the potential inhalation exposure. In addition, filters were located in the inner structure of the inhalation masks. These filters were also collected to determine the actual inhalation exposure. The protection factor given by the mask was calculated in the same way as the protection factor for dermal exposure, according to Equation (7). The measurement was performed twice during the two applications (*i.e.*, ADE and PDE) on three different days, for a total of 12 measurements.

2.3.3. Exposure Assessment in the Study Region

Based on the transfer coefficients obtained from the field measurements and the amount of pesticide applied per person during an 8-h work day over an evaluated pesticide management period of six weeks, the pesticide flow analysis model was first used to assess the risk of exposure to the fungicide mancozeb and then to assess the risk of exposure to the fungicides carbendazim, carboxin, dimethomorph, mandipropamide, propamocarb chlorhydrate, and thiram. The dermal absorption estimates were based on the actual dermal exposures calculated with the pesticide flow model and the absorption reference values for each pesticide reported in the AERU Pesticide Properties Database (AERU, 2011). The estimated dermal absorption values were compared with acceptable operator exposure level (AOEL) values, which are health-based limits established on the basis of the full toxicological assessment required for pesticide registration and represent the quantity of pesticide that can be absorbed daily over a lifetime without manifesting toxic effects. These exposure level values allow quantification of the risk for pesticide operators (AERU, 2011).

3. Results

3.1. Pesticide Flow Analysis

Figure 4 shows the pesticide flow analysis for mancozeb when 786 cc of active ingredient were applied (the average of 25 applications for the evaluated pesticide management period of six weeks) during a work day of 8 h. The model shows that the exposure was very high during the application step, contributing 99.9% to the total PDE, while the preparation step contributed 0.07% and the cleaning step contributed 0.03. The exposure during preparation and cleaning is due to accidental splashes that cause minimal exposure compared with the application activity, in which most of the pesticide solution is used and during which the exposure is very high. Nevertheless, despite the high PDE (5,223±2,493 mg/d), the ADE was very low (32±23 mg/d), which indicates a level of protection of approximately 95% for the hands and between 99.2 and 99.8% for the rest of the body parts.

With respect to ADE, the model shows that the forearms and hands were the most exposed body parts (*i.e.*, 8.0±7.3 and 6.4±4.0, respectively). This shows that despite the high level of protection given by the personal protective equipment, there is a leak of pesticide solution droplets through the overlap between gloves and sleeves. This same situation occurs for the legs, whose ADE values (5.2 ± 3.0 mg/d) might be due to a leak of pesticide solution droplets through the overlap between boots and trousers, and for the chest, whose ADE values (4.0±2.4 mg/d) might be due to a leak of pesticide solution droplets through the buttons.

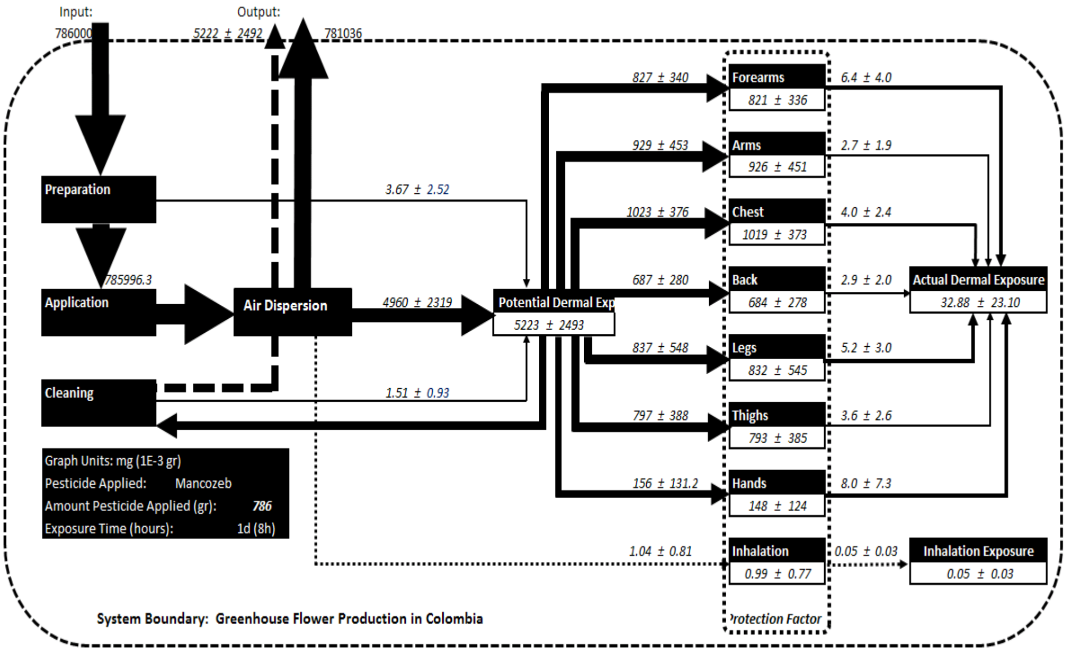


Figure 4. Pesticide flow analysis for the fungicide mancozeb. The units are in mg during an exposure time of 8 h. The transfer coefficients of the model are provided in the Appendix.

3.2. Health Risk in the Study Area

Table 2 shows the daily average dermal absorption estimates for the eight pesticides evaluated (*i.e.*, carbendazim, carboxin, mancozeb, dimethomorph, propamocarb, mandipropamide, thiram and fosetyl). The dermal absorption of mancozeb was estimated at 3.6±2.5 mg/d. This was based on the ADE results (32±23 mg/d) and the dermal absorption value of 11% for mancozeb (AERU, 2011). This value is greater than the AOEL reference value of 2.45 mg/d, which suggests that there is a health risk faced by the operator. Similar findings were found for carbendazim, thiram and mandipropamide. The inhalation exposure was found to be 0.05±0.03 mg/d, which compared with the AEOL reference value, can be considered negligible and does not represent a health risk.

Table 2. Estimated actual dermal and inhalation exposures for 8 evaluated pesticides used in greenhouse flower crops in Colombia.

Commercial Name	Active Ingredient (AI)	*Average Applied/ Operator (cc/d)	Actual Dermal Exposure (mg/d)	Inhalation Exposure	Dermal Absorption (%) [58]	Estimated Pesticide Absorbed (mg/d)	AOEL (mg/d)
Bavistin	Carbendazim	485	20.2 ± 14.2	0.03 ± 0.02	10	2.0 ± 1.4	1.4
Carbovax	Carboxin	716	29,2 ± 21.0	0.05 ± 0.03	5	1.5 ± 2.1	3.85
	Thiram	745	31.1 ± 21.9	0.05 ± 0.03	10	3.1 ± 2.1	1.4
Dithane	Mancozeb	786	32.8 ± 23.1	0.05 ± 0.03	11	3.6 ± 2.5	2.45
Forum	Dimethomorph	585	24.4 ± 17.2	0.04 ± 0.03	20	4.8 ± 3.4	10.5
Previcur	Propamocarb	1,480	61.9 ± 43.5	0.09 ± 0.06	10	6.1 ± 4.3	-
	Fosetyl	1,488	61.9 ± 43.5	0.09 ± 0.06	1	0.6 ± 0.4	350
Revus	Mandipropamide	640	26.7 ± 18.8	0.04 ± 0.03	10	2.6 ± 1.8	2.45

***** This average of the amount of active ingredient applied was obtained for the evaluated pesticide management period of six weeks (Figure 5): carbendazim, n = 10; carboxin, n = 11; thiram, n = 11; mancozeb, n = 25; dimethomorph, n = 9; propamocarb, n = 10; fosetyl, n = 10; mandipropamide, n = 8.

4. Discussion

4.1. Pesticide Flow Analysis Approach

This paper presented a pesticide flow analysis modeling approach based on the material flow analysis methodology. The pesticide flow model helps to identify the patterns of pesticide distribution on the body, the level of protection given by personal protective equipment and estimates of potential and actual dermal and inhalation exposure to pesticides. This information can be used to determine the health risk level by comparing the model estimates with the AEOL reference values for each pesticide. In addition, the model makes it possible to easily identify the activities or body parts that have high levels of exposure, which is useful in identifying improvements that will decrease exposure during pesticide management. However, the model outcomes correspond to a certain interval of time and do not consider issues such as pesticide accumulation or pesticide degradation rate. Furthermore, the model considers each pesticide separately and does not take into account the facts that pesticides are usually applied in mixtures and that this might alter the chemical nature of the pesticides.

4.2. Pesticide Management in the Case Study

One characteristic of the greenhouse flower crop system in Colombia is pesticide application with five nozzles mounted on a 1.60 m long pipe. Previous studies (Nuyttens, et al., 2009b) have shown that the distribution of the PDE on the body parts depends on the spray direction of the nozzle (Table 3), and because the application in the study area was made sideways with five nozzles simultaneously, body parts were exposed homogenously, with the exception of the hands. This fact is reflected in the results of the PDE distributions, which range between 13 and 19% for the body parts and 3% for the hands. These results are different from those obtained in previous studies in which only one nozzle was used and the application was made downward, forward or backward, and the exposures differ, with high values generally found on the lower body parts (Nuyttens, et al., 2009b).

Table 3. Comparison of the distribution of PDE for different application techniques. The values represent the percentages of the PDE distributions on the body parts. Technique 1 corresponds to the present study and techniques 2–4 correspond to experiments made in greenhouse pepper crops in Spain and Greece (Nuyttens, et al., 2009b).

Body Parts	PDE (% in Body)			
	1. Spray Sideways with 5 Nozzles	2. Spray Gun Downward	3. Spray Lance Forward	4. Spray Lance Backward
Back	13.1	0.5	0.8	1.4
Chest	19.5	0.8	1.5	1.9
Arm	17.7	18.8	10.0	6.0
Forearm	15.7	13.3	7.3	10.0
Thighs	15.2	12.6	11.3	8.1
Legs	15.9	46.7	55.1	27.0
Hands	3.0	7.3	14.0	45.6
Total	100.0	100.0	100.0	100.0

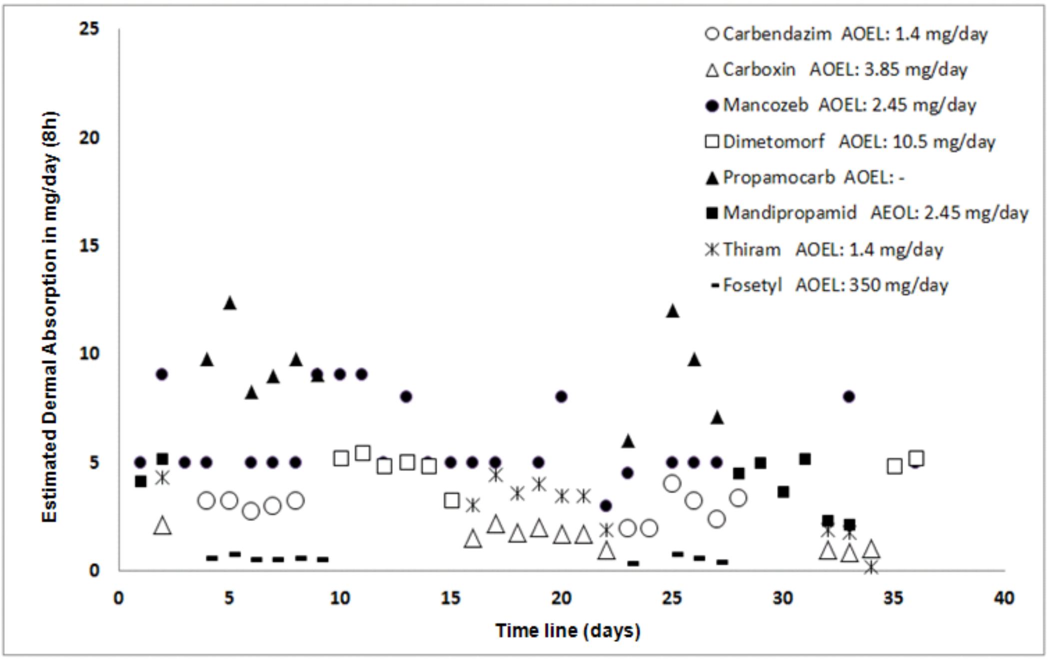
Concerning the ADE distribution, previous studies have shown similar results in which the hands and forearms are the most exposed body parts, and dermal exposure is the main contributor of the total exposure (Aprea, et al., 2005; Vitali, et al., 2009).

Another characteristic of this study was that the study area was the size of the paths between the crop rows, which is only 60 cm wide, creating a close space in which the sprayed pesticide droplets move (Figure 2). This issue might contribute to the homogenous potential dermal exposure. This contrasts with the paths of greenhouse production systems in other locations (Nuyttens, et al., 2009b), which are between 1 and 1.5 m wide.

4.3. Health Risk in the Study Area

Daily dermal absorption estimations were higher than AEOL reference values for mancozeb, carbendazim, thiram and mandipropamide. Taking into account that environmental conditions like humidity affect the level of absorption (Aprea, et al., 2005), the health risk might be higher for these pesticides during long periods of time. Figure 5 shows that during the six-week pesticide management period evaluated, carbendazim and thiram were applied 11 times, mancozeb was applied 25 times and mandipropamide was applied eight times.

Figure 5. Estimated daily dermal absorption of pesticides for the evaluated pesticide management period of six weeks. Estimations are based on the actual dermal exposures (arithmetic mean, n=9) calculated with the pesticide flow model and the absorption reference values for each pesticide reported in the AERU Pesticide Properties Database (AERU, 2011).



Because of this application frequency and the possibility of being exposed to a group of pesticides with different toxicity levels, the health risk might be higher. Furthermore, in the flower production system, additional pesticides with different toxicity levels are applied, which suggests that there might be an even greater potential health risk. For instance, in a previous survey of 84 greenhouse flower farms in Colombia, 14.3% of the pesticides were found to belong to category I, 14.4% to category II, 52% to category III and 19.2% to category IV (Varona, et al., 2005). This suggests that the health risk assessment might be different depending on the toxicity level of each pesticide and the application frequency.

5. Conclusions

The material flow analysis methodology can be applied in the field of human exposure for estimation of the patterns of pesticide distribution on the human body during different pesticide management activities. This methodology not only assesses the level of exposure but also provides information on potential measures for improving operational safety during pesticide management. Furthermore, the model outcomes, together with pesticide information such as AOEL reference values, can be used to assess the health risk associated with pesticide exposure.

Our pesticide flow model integrates three activities and two routes of exposure during pesticide management, which is different from other approaches in which a model was developed separately for each process or activity. Although the model can be applied to case studies in regions with similar characteristics, such as the application technique, the infrastructure and the type of personal protection equipment, the model should be calibrated when these characteristics change. Although the model provides static information about the exposure during one 8-h work day, further improvements are necessary to improve the health risk assessment by including in the model time-dependent issues such as the cumulative exposure over several days and the pesticide degradation rate.

With respect to the status quo of health risk in the case study, of the eight pesticides evaluated, mancozeb, carbendazim, thiram and mandipropamide were found to represent a health risk to operators because their dermal absorption estimates exceeded the AOEL reference values. However, this health risk might be reduced by using adequate personal protective equipment and improving the protection in overlapping areas such as between gloves and sleeves and between boots and trousers. There might also be a significant health risk reduction achieved by using pesticides with lower toxicity levels and by reducing the application frequency of the same pesticides, especially if their toxicity levels are very high.

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Publication 4

Model for Dermal and Inhalation Exposure Assessment of Pesticide Application on Agricultural Products in Colombia

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Abstract

In the agricultural scope, Less Developed Countries have attempted to make a risk assessment of pesticide use applying methodologies implemented in Europe or USA. Nevertheless, these methods are likely to over- or under-estimate the risk as they are developed for the specific conditions of industrialized countries. To address this problem, this paper presents a modeling approach for the dermal and inhalation exposure assessment of pesticide use in Colombia. The model studies the different routes and pathways followed by the pesticides after the application and the subsequent distribution in the different environmental compartments including the fractioning in the human body. The result is a framework that will facilitate the further mathematical development. An improved risk assessment based on a proper exposure assessment is crucial in farming systems in Colombia and other countries in the region for the protection of farmer's health without affecting the crop yields.

Keywords: Human Exposure Assessment, Risk Assessment, Life Cycle Assessment, Pesticides, Developing Countries

1. Introduction

Human Exposure to pesticides is nowadays a public health issue because people are likely to be direct or indirectly exposed to toxic active ingredients. In the Agricultural scope, there is an increasing concern about the farmers' health as they are frequently exposed to pesticides during long periods of time. Governments, especially from industrialized countries have introduced new environmental policies about the adequate use of pesticides. Meanwhile, in developing countries, like Colombia, a similar attempt has been done but even though the regulation scheme is already defined, the implementation fails because of the lack of information about exposure assessment and risk characterization, important steps in the risk assessment (Feola, et al., 2009; Schöll, et al., 2009).

Indirect methods have been used for dermal and inhalation exposure assessment since the early 1990s in industrialized countries (Paustenbach, 2000). The Estimation and Assessment of Substance Exposure (EASE Model) and the Predictive Operator Exposure Model (POEM) are two occupational exposure models used in the UK. The EASE model is designed to predict exposure levels for a broad range of occupational situations and has been incorporated as part of the European Union System for the Evaluation of Substances (EUSES) (Tickner, et al., 2005). POEM has a more limited scope as it is designed to predict exposure levels experienced by operators preparing and applying pesticides in the UK. However, it has been the base for the development of the European Predictive Operator Exposure (EUROPOEM) which is not a model but a database for reference (Van Hemmen, 2001). These methods are semi-quantitative approaches to exposure modeling. Data have been added, since EUROPOEM was set up with field assessments carried out in southern Europe. In North America, a Pesticides Handlers Exposure Database (PHED) provides generic mixer/loader/applicator exposure data (Krieger, 1995) and combined with the EUROPOEM in a new North American Model, resulted on the Applicator and Handlers Exposure Database (AHED). These models have been in constant validation; nevertheless, they have been criticized because of the uncertainties surrounding some of the exposure routes and the poor quality of the data available for them.

In the last decade some methods have been published for the dermal exposure assessment like DREAM (Van-Wendel-De-Joode, et al., 2003), DERM (Blanco, et al., 2008), RISKOFDERM (Van Hemmen, et al., 2003) and STOFFENMANAGER (Tielemans, et al., 2008a). They are semi-quantitative methodologies consisting of a ranking method that use questionnaires for describing the routes and pathways followed by the pesticides. For this description, a score is allocated according to the level of exposure observed by the assessor in the field. All these methods are in the validation process and some of them (DREAM and DERM) have been applied in LCDs. They are considered as simple, inexpensive and easy to use tools for the assessment of human exposure to pesticides. However, they have several disadvantages like high level of uncertainty, many assumptions and unavoidable errors in the allocation of the scores. Apart of these methodologies, there is not a single model that estimates dermal and inhalation exposure concentrations under the specific conditions of LCDs.

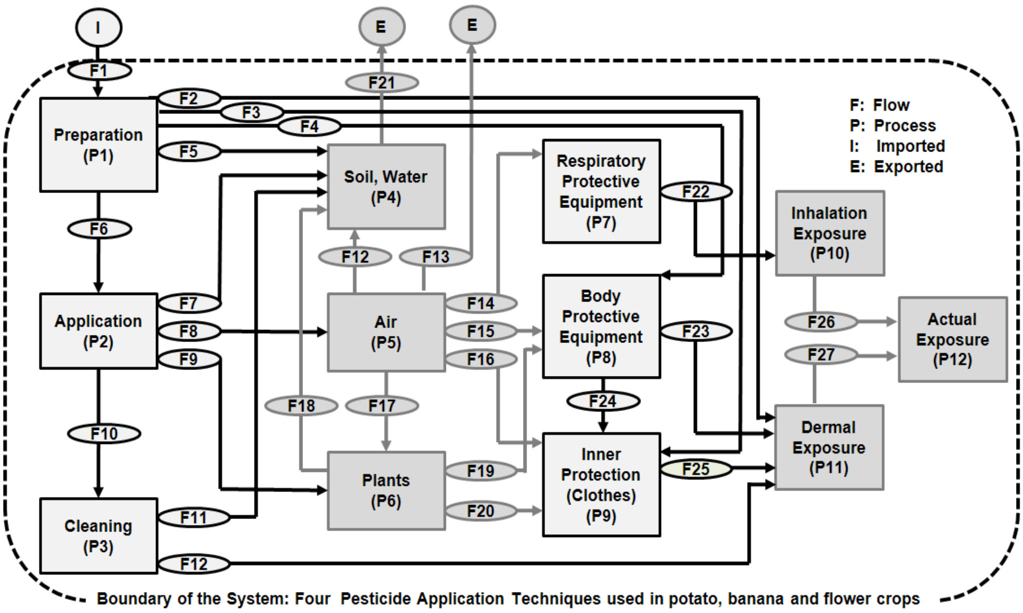

Fig. 1: Model for Dermal and Inhalation Exposure Assessment

2. Conceptual Modeling Approach

The development of a model for the human exposure assessment of pesticide application in Colombia starts with the study of the different pathways followed by the pesticides according to the different application techniques.

In Figure 1 is summarized the flow of the pesticides taking into account three tasks (i.e. pesticide preparation, application and cleaning); environmental compartments in which the pesticide is dispersed (i.e. air, water and soil); the protection factors that could reduce the exposure dose (i.e. clothing, body protective equipment and respiratory protective equipment); and finally the human exposure dose (amount of pesticide in contact with skin and lungs which result in the exposure dose). For this model only the air compartment is considered and each process will be studied separately.

2.1 Pesticide Application Activities

Because of the lack of precautions in the different activities during the preparation of the pesticide solution, there are splashes on the hands and feet and a high risk of exposition to the chemicals when hands are accidentally immersed into the pesticide solutions. According to experiments performed in Vereda La Hoya, the exposure during the preparation can be 0,0047% of the total amount applied. However, because of the manipulation of pesticides products in their original concentration, this value could be higher.

The pesticide application itself is likely the most important task in human exposure to pesticides. The exposure concentration will depend on the spray droplet dispersion that are influenced by technical and environmental features like spray characteristics (e.g. volatility and viscosity of the pesticide formulation), equipment and application techniques; weather conditions (e.g. wind speed, wind direction, temperature, relative humidity and stability of the air at the application site) and operator care, attitudes and skills forces (Gil, et al., 2005).

Droplet trajectory models estimate the movements and positions of individual drops set under external physical forces (Hiscox, et al., 2006; Richardson, et al., 2006). These models have been developed with particular environmental conditions and specific application characteristics. Thus, the movement of pesticide particles can be explained for a particular crop area and this can be connected with other parameters like the protection factor in order to quantify actual and potential dermal and inhalation exposure concentrations. The type of pesticide application will influence the behavior of the pesticide droplets in the air compartment, depending on specific characteristics of the application (i.e. nozzle type, height at which the pesticide is applied, speed of the sprayer and droplet size), meteorological conditions (i.e. temperature, wind speed and humidity) and crop characteristics (i.e. height of the plants and crop density) (Nuyttens, et al., 2007a; Nuyttens, et al., 2009a).

After applying a model for the prediction of droplet movements in the air during the spraying it is feasible to calculate the amount of pesticide that could be inhaled by the worker. Inhalation rates are known that vary directly with the amount of physical activity of the workers. The default value commonly used is 20 m3/d. When conducting occupational exposure assessments, it is assumed that workers inhale about 10 m3 in a 8-h workday and that most of the particles less than 10 µm are 100% bioavailable after they are trapped in the lower lung and likewise it is assumed that most vapors and gases are completely absorbed (100% bioavailable) if they reach the lower respiratory tract (Paustenbach, 2000; WHO, 2000).

Once the application is finished workers used to wash their hands with water and soap reducing the exposure concentration by 10-26% and when washing twice, reducing it by 46% (Van Wendel De Joode, et al., 2005a). However, contaminated working clothes and protective equipment are sources of potential exposure after work. Measurements in Vereda la Hoya have shown a potential dermal exposure of 0.0008% of the total amount applied with legs, arms and hands as the body parts with the higher exposure.

2.2 Environmental Compartments

Even though several natural resources are polluted by the pesticides in different ways, this research will be focused in the pesticide dispersion in the air. During application, up to 30-50% of the amount applied can be lost to the air (Van Den Berg, et al., 1999) and this loss may be one reason for atmospheric organic contamination (Samsonov, et al., 1998). This becomes relevant in inhalation exposure assessment because not only the exposure could be very high in the moment of the pesticide application, but also afterwards, due to the persistence of the pesticide in the atmosphere. This could be relevant in the passive human exposure by the bystanders in the surroundings of the crop and inside the greenhouses.

Workers can be exposed to pesticide particles by getting in contact with treated plants (García-Santos, et al., Unpublished). There could be a transfer of pesticide after the application directly from the plants to the clothes, the body and respiratory protective equipment and to the skin. This amount of pesticide is quantified with the whole body dosimetry methodology. The amount of pesticide in soils and water is not considered in this model.

2.3 Protection Factor

The respiratory protective equipment stops the flow of the pesticides into the lungs. However, the environmental conditions make its used uncomfortable. In production systems like potato farming in Colombia, it has been observed that 39% of the farmers do not use any protective equipment (Feola, et al., 2009) and furthermore is widely known that in the case of banana production, the aerial applications make use of human flags, with no protective equipment, in order to reach the target of the pesticide in the crop field. The use of a complete set of personal protective equipment (Tyvek coverall, rubber boots and gloves) results in pesticide penetration factors of 0,0 to 0,2%. However, because of the improper utilization (e.g. incomplete closure of the coverall, rolling up the sleeves or the transfer through seams and zips) the pesticide penetration factor can result in 0,9 to 2,1% (Protano, et al., 2009). Also conditions such as high humidity and temperature, make the use of the protective equipment very uncomfortable which results in higher penetration factors (Park, et al., 2009; Schenker, et al., 2002). The amount of pesticides that reach the body protective equipment is considered as the potential dermal exposure.

The pesticide penetration factor values from clothing worn by operators differ significantly between the default values from various statistical models: UK POEM (15,5%), EUROPOEM (30%) and PHED (50%). In a recent study (Protano, et al., 2009) it was found that penetration factor values for the different cotton garments vary significantly from 7,5 to 15,9 for all the operators involved in that research due to, perhaps, the pesticide handling methods and the characteristics of work clothing. Also it was found that the mean penetration factor value in the upper part of the body is two or three times higher than the lower part of the body, because of the difference in the type of material between shirts and trousers (Aprea, et al., 2004). Because three crop production systems are considered in this research under different environmental conditions, there is likely a wide range of different clothes used during the application. By means of a survey and an experiment with the whole body dosimetry methodology is feasible to determine the protection factor given by the different clothes used during the application and therefore establish the differences between actual and potential concentrations.

3. Model Output

The development of the model for dermal and inhalation exposure is based on qualitative data collected from the survey and quantitative information from the experiments. However, a further step can be taken by analyzing the dynamics of the pesticide exposure concentration in the human body. This can be done by including in the model information about the dermal absorption rate, the half-time of the pesticides in the body, the elimination and degradation rate. Previous researches have been done in animals and humans about all these parameters for different pesticides (Balali-Mood, et al., 2008; Timchalk, et al., 2007). Therefore, the model will not only estimate exposure concentrations but also the dynamics of the pesticide inside the human body when parameters like application duration and frequency are taking into account. The result is a mathematical tool that can predict the pesticide behavior in the human body in different intervals of time, identifying the most sensitive factors under several hypothetical particular conditions in different scenarios. Even though, blood measurements are not considered in this research, there are many reports in the literature about pesticides dermal absorption and changes in the levels of acetyl-cholinesterase and these concepts can be useful in expanding the model.

4. Conclusions

This paper proposes a model consisting of studying the routes and pathways followed by the pesticides in order to estimate exposure concentrations. Different types of application could be assessed, studying important parameters like the protection factor and several activities involved in the applications like the pesticide preparation and the hygiene habits. This first approach is a basis for the further development of the mathematical part of the model.

Acknowledgement

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Publication 5

Pesticide Flow Model for the Environmental and Human Exposure Assessment to Pesticide Use in Developing Countries

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In the agricultural sector, pesticides are applied to crops to ensure a higher production. In consequence, there is an interaction within the different environmental compartments (i.e. air, soil and water) and with the human body of farmers or workers directly or indirectly involved in the application. Depending on the duration of exposure and the level of persistence and toxicity of the pesticides, this interaction might lead to adverse health effects which must be addressed in any risk assessment procedure about the use of pesticides. This paper proposes a pesticide flow model applying concepts of material flow analysis and system dynamics in which the mobility of the pesticide is studied from the moment of the application until its deposition in the different environmental compartments and the human body (according to the three different exposure routes: dermal, inhalation and ingestion). In addition, the model includes the degradation rates of the pesticide and the frequency and duration of the application, time parameters that are not considered in previous methods or models. Thus, the model output is the description of the movement of pesticides in the environment and the estimation of their impact in the human body. This model aims to be a key tool to be included in a risk assessment framework for pesticide use with special focus in developing countries. This research is financed by the Swiss Science National Foundation.

Publication 6

Model for Dermal and Inhalation Exposure Assessment of Pesticide Application on Agricultural Products in Colombia

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This study presents a modeling approach to be included in a risk assessment framework for pesticide use in the agricultural production in developing countries. The model has two parts: the inhalation and the dermal exposure assessment. Firstly, the conceptual framework of the new proposed model is explained after a multi-criteria analysis of the existing methodologies. Then, the model itself is presented which consist of the estimation of dermal and inhalable exposure concentrations, studying the routes and pathways followed by the pesticides after they are sprayed. Four application techniques are studied in different environmental conditions: i) handed-pressurized (outdoors), ii) motor-pressurized (outdoors and greenhouses), iii) tractorized (outdoors), and iv) aerial (outdoors). The data for the model development is collected by doing surveys in three different regions in Colombia dedicated to potato, flowers and banana crops and by performing experiments quantifying the distribution of the pesticide in the human body. The experimental methodologies used to get this information are the whole body dosimetry and the button personal inhalable aerosol sampler. The tracer fluorescein is used as surrogate of pesticides. The final result is a mathematical tool that identifies the sensitive factors during the pesticide application which are suitable of being improved to mitigate the human exposure. This model is crucial for the risk assessment scheme in farming systems in Colombia and other developing countries as their current risk

assessment framework is based on models from industrialized countries. This work is part of the project “Life Cycle Human Exposure and Risk Assessment of Pesticide Application on Agricultural Products in Colombia” financed by the Swiss National Foundation.

Publication 7

Dermal and Inhalation Exposure Assessment of Pesticide Management in Greenhouse Flower Crops in Colombia

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Pesticides are chemicals of public health concern because epidemiological studies have evidenced the association between agricultural occupation activities and related health problems. Floriculture is an agricultural activity in developing countries in which the greenhouse environment conditions are designed to optimise the plant growing rather than to protect the worker's health. Colombia is the second world flower exporter with a cultivated area of 6800 hectares with an average of 15 workers per hectare. Numerous studies worldwide have assessed the exposure to pesticides in greenhouses; however, there are no available studies in the floriculture system in Colombia in which large number of workers might be at risk of exposure. In our research, we assess the dermal and inhalation exposure applying the Material Flow Analysis methodology to study the dispersion of the pesticides in the human body during pesticide management. The study area was a flower farm located in Sabana de Bogotá, Colombia. The Whole Body Dosimetry was applied to obtain the pesticide distribution on the human body parts using the tracer uranine as pesticide surrogate and tyvek garments as sampling media. The Button Personal Inhalable Aerosol Sampler was used to measure inhalation exposure. The results show high levels of potential dermal exposure in upper body parts like abdomen, chest and back; however, the level of protection given by the personal protective equipment was higher than 98.6%. Actual dermal exposure represented 0,48% of the total amount of tracer applied. From the total human exposure (i.e. actual dermal exposure and inhalation), actual dermal exposure represented 95% and inhalation exposure 5%. Even

though exposure values were very low, there is still a high health risk depending on pesticide toxicity, type of pesticide mixtures and total time of exposure. Therefore, further research is required to determine the level of human exposure and how the exposure dynamics change with the time when there is a cumulative exposure to pesticide mixtures affected by a determined degradation rate. This research was funded by the Swiss National Science Foundation and performed by a cooperation between LMU München, ETH Zürich, UniZürich, UniBoyacá and Universidad Nacional de Colombia.

Part C

Appendix

Appendix Publication 1

Scoring system of the study case for the model DERM

Determinants of the DERM model						
Nr.	**Name**	**Score of DERM**	**System characteristics**	**Body surface contamination**	**Score considered**	**Reference**
1	Sprayed surface	a) ≤0.7 ha = 1 b) >0.7 ha = 2	The mean of the parcel sizes of the four provinces was taken (mean: 0.998 ha; standev 0.751).		b) >0.7 ha = 2	
2	Height of the crop	a) 1*1 = 1 b) 1*2 = 2 c) 1*3 = 3 d) 1*4 = 4 e) 1*5 = 5 f) 3*1 = 3 g) 3*2 = 6 h) 3*3 = 9 i) 3*4 = 12 j) 3*5 = 15	During one cycle the farmer is using pesticides frequently. For this reason it can be assumed that for the transfer of pesticides the contamination is recently (T=3) rather than previously (T=1).	In general the potatoe plant is growing about 60 cm high. For this reason it is assumed that not much body surface can get contaminated, about 40% get contaminated.	g) 3*2 = 6	Rahn (2010)
3	Leaking backpack	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	In general farmers in developing countries don't pay that much attention to safety measure. In addition, the sprayers used in the study area are quite old (mean: 9.64 years; standev: 7.95). For this reason it is assumed that there are leaking accidents.	It is considered that not more than 40% of the body surface get contaminated. When the backpack is leaking the substance cannot spread out that much.	b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001); Sivyoganathan et al. (1995)
4	Volume of sprayed dilution	a) ≤30 l = 2.5 b) >30 l = 5	The mean of the amount used, by every farmer, was considered (mean: 11.51; standev: 11.58).		a) ≤30 l = 2.5	
5	Nozzle height	a) 4*1 = 4 b) 4*2 = 8 c) 4*3 = 12 d) 4*4 = 16 e) 4*5 = 25	The nozzle height (moving it up and down; from side to side) results in drift deposition. The higher the nozzle is in the air the more deposition can occur.	The body parts which are highly endangered are: head, arms, thorax, thighs, legs, and feet. Due to wind conditions the front- and the backside of the body can get contaminated. It is considered that about 60% of the body gets contaminated.	c) 4*3 = 12	Blanco et al. (2005); Blanco et al. (2008)
6	Spraying in front	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	By using a backpack sprayer it is most likely that the nozzle is used directed in front. This way it is easier to achieve a uniform coverage and a correct application rate.	The body parts which are highly endangered are: head, arms, thorax, thighs, legs and feet. Due to wind conditions the front- and the backside of the body can get contaminated. It is considered that about 60% of the body get contaminated.	d) 5*3 = 15	NRCS (2010); Lesmes, & Binder (to be published (a))
7	Spraying against wind	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Boyacá is in the Andes, where it is most likely that the wind is blowing during the day. When the wind is blowing more particles of the substance gets mixed up with the air particles and cause more contamination.	In general about 60 % of the body surface get contaminated.	d) 5*3 = 15	Tuchschmid (2004)

8	Splash/spill over the pump	a) 0 b) 1*1 = 1 c) 1*2 = 2 d) 1*3 = 3 e) 1*4 = 4 f) 1*5 = 5 g) 3*1 = 3 h) 3*2 = 6 i) 3*3 = 9 j) 3*4 = 12 k) 3*5 = 15	The possibility of the pump to get contaminated is quite high because in developing countries pesticides can be handled quite carelessly. Due to the fact that the pump is used frequently during the application cycle it is assumed that the body gets contaminated recently than previously.	Not that much body surface can get exposed to the substance. The contamination is limited to arms and hands (20%).	g) 3*1 = 3	Hoyos et al. (1996)
9	Splashes on hands	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Farmers in developing countries don't pay that much attention to safety measure, thus it is assumed that splashes on hands happen.	Due to the fact that this determinant is just concentrated on the hands not more than 20% of the body surface can get contaminated.	b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001); Sivyoganathan et al. (1995)
10	Splashes on feet	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Farmers in developing countries don't pay that much attention to safety measure, thus it is assumed that splashes on the feet happen.	Due to the fact that this determinant is just considering feet not more than 20% of the body surface can get contaminated.	b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001); Sivyoganathan et al. (1995)
11	Gross contamination of the hands	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Farmers in developing countries don't pay that much attention to safety measure. It is assumed that gross contamination of hands occurs by blocking a hose leakage, repairing nozzle, or entering hand into tank.	Due to the fact that this determinant is just concentrated on the hands not more than 20% of the body surface can get contaminated.	b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Sivyoganathan et al. (1995)
12	a. Wearing long sleeved shirt b. Wearing short sleeved shirt	a) 0 a. b) 0.20 b. c) 0.15	In general farmers wear long sleeved shirts.	Clothing Protection (CP) = 0 for not wearing such clothing protection piece, 0.15/0.20 for wearing it.	a. b) 0.20	Lesmes & Binder (to be published (b))
13	Wearing an old/ overused/torn shirt	a) 0	In general, farmers did not wear a very old/overused/torn shirt.			Lesmes & Binder (to be published (a)); Lesmes & Binder (to be published (b))
14	a. Wearing long pants b. Wearing short pants	a) 0 a. b) 0.15 b. c) 0.10	In general farmers wear long trousers with thicker fabrics.		a. b) 0.15	Lesmes & Binder (to be published (b))
15	Wearing old/ overused/torn pants	a) 0	In general, farmers didn't wear a very old/overused/torn pair of pants.			Lesmes & Binder (to be published (a)); Lesmes & Binder (to be published (b))
16	Wearing shoes	a) 0 b) 0.10	About 64% of the farmers use PPE and about 95% of the farmers believe that not using PPE can harm the health, it is assumed that farmers wear shoes.		b) 0.10	

Scoring system of the study case for the model DREAM

Determinants of the DREAM model						
Nr.	**Name**	**Score of DREAM**	**System characteristics**	**Farmers characteristics**	**Score considered**	**Reference**
1	Probability of emission on clothing and uncovered skin ($P_{E\ BP}$)	a) <1% of task duration = 0 b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	Frequency of occurrence of the concerned exposure route.	Farmers don't pay that much attention to safety measure. For this reason the probability of emission during task is considered to be very high.	d) ≥50% of task duration = 10	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001)
2	Intensity of emission ($I_{E\ BP}$)	a) <10% of body part = 1 b) 10–50% of body part = 3 c) ≥50% of body part = 10	Assess the amount of agent on clothing and uncovered skin resulting from the exposure.	Due to the fact that farmers tend to over- or misuse the products and emission can transport a high mass of substance the intensity is considered to be very high.	b) ≥50% of body part = 10	Feola & Binder (2010); van Wendel de Joode (2003)
3	Exposure route factors (ER_E, ER_D, ER_T)	a) Emission = 3 b) Deposition = 1 c) Transfer = 1	Exposure due to emission is considered to transport more mass of substance onto the skin (direct release from a source), emission gets a higher score than deposition and transfer (indirect mass transport, after interference with air or surface compartments) (van Wendel de Joode et al., 2003).	See explanation of van Wendel de Joode et al., 2003.	a) Emission = 3 b) Deposition = 1 c) Transfer = 1	
4	Probability of deposition on clothing and uncovered skin ($P_{D\ BP}$)	a) <1% of task duration = 0 b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	Frequency of occurrence of the concerned exposure route.	Farmers don't pay that much attention to safety measure. For this reason the probability of deposition during task is considered to be very high.	d) ≥50% of task duration = 10	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001)
5	Intensity of deposition on clothing and uncovered skin ($I_{D\ BP}$)	a) <10 % of body part = 1 b) 10–50% of body part = 3 c) ≥50% of body part = 10	Assess the amount of agent on clothing and uncovered skin resulting from the exposure.	Due to the fact that farmers tend to over- or misuse the products the intensity is considered to be high.	b) 10–50% of body part = 3	Feola & Binder (2010)
6	Probability of transfer to clothing and uncovered skin ($P_{T\ BP}$)	a) <1% of task duration = 0 b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	It is considered to be the contact frequency with surfaces such as floor, worktables, machines and working tools.	Farmers in developing countries don't pay that much attention to safety measure. In addition, the transfer of pesticides doesn't occur during the whole working task. For this reason the propability of transfer during task is considered to be high.	c) 10–50% of task duration = 3	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001)
7	Intensity of transfer ($I_{T\ BP}$)	a) not contaminated = 0 b) possibly contamination = 1 c) <50% of contact surface = 3 d) ≥50% of contact surface =10	It is the contamination level of the contact surface of these surfaces.	Due to the fact that farmers tend to over- or misuse the products, the intensity is considered to be high.	b) <50% of contact surface = 3	Feola & Binder (2010)
8	Body surface factor (BS_{BP})	a) Head (BS_HE) = 0.69 b) Upper arm (BS_UA) = 0.67 c) Forearm (BS_FA) = 0.53 d) Hands (BS_HA) = 0.47 e) Torso front (BS_TF) = 1.22 f) Torso back (BS_TB) = 1.22 g) Lower body part (BS_LB) = 2.43 h) Lower leg (BS_LL) = 1.15 i) Feet (BS_FE) = 0.63	The body part factor, which is used for BS_{BP}, is defined as the surface area of an individual body part divided by the mean surface area of the nine body parts (van Wendel de Joode et al., 2003).	See explanation in van Wendel de Joode et al., 2003.	For each body part the BS_{BP} is used.	
9	Physical state (PS)	a) Solid = 1 b) Liquid = 1 c) Vapour-gaseous = 0.3	Solids and liquids are supposed to result in higher exposure levels than vapours and gases.	In Vereda la Hoya 100% of the 193 farmers used pesticides in liquid form.	b) Liquid = 1	Rahn (2010)
10	Concentration (C)	a) >90% active ingredient of interest = 1 b) 1–90% active ingredient of interest = 0.3 c) <1% active ingredient of interest = 0.1	Exposure increases with concentration of active ingredient in substance.	Chemicals were diluted in water.	b) 1–90% active ingredient of interest = 0.3	
11	Evaporation (liquids): boiling temperature (EV)	a) <50°C = 3 b) 50–150°C = 1 c) >150°C = 0.3	Volatile liquids result in lower dermal exposure due to increased removal.	The pesticides are not that organic to be higher than 150 and not that salty to be lower than 50.	b) 50–150°C = 1	

12	Viscosity (V)	a) Low, like water = 1 b) Medium, like oil = 1.75 c) High, like resin/paste = 3	High viscosity results in decreased removal from skin.	The farmers used water as a solution factor.	a) Low, like water = 1	
13	Formulation (F)	a) fine particles (powder) = 3 b)granules/grain/pellets = 1 c) pack/bunch/bundle = 0.3	Adherence to skin varies inversely with particle size. Smaller particles → higher emission, increased transfer and decreased removal from skin.	The chemicals bought are fine particles (powder). For application the particles were diluted in water.		
14	Dusty (solids) (DU)	a) No = 1 b) Yes = 3	Dusty solids are emitted more easily from source than non-dusty solids.	Pesticides were in liquid form.		
15	Stickiness/wax/ moist (non-powder/ non-dusty solids) (SS)	a) No = 1 b) Yes = 1.75	Such solids result in better attachment to skin (decreased removal from skin).	Pesticides were in liquid form, not sticky no wax.	a) No = 1	
16	Glove or clothing material (M)	a) No gloves/clothing used = 1 b) Woven clothing = 0.3 c) Non-woven permeable = 0.1 d)Non-woven impermeable=0.03	Use of gloves/clothing reduces external exposure.	Due to the fact that 64% of the farmers use PPE and 95% of the farmers are aware of the importance of PPE it is assumed that farmers wear gloves or clothing material.	b) Woven clothing = 0.3	
17	Protection factor (PFM_{HA} /PFM_{BP})	a) PFMHA = 1 b) PFMBP = 0.3	Gloves experience higher pressure than clothing.		a) PFMHA = 1 b) PFMBP = 0.3	
18	Replacement frequency (RF)	a) Used once = 0.3 b) Daily = 1 c) Weekly = 3 d) Monthly = 10	Gloves/clothing that are replaced frequently reduce exposure more than when replaced infrequently.	Due to the fact that farmers in developing counties cannot spend that much money on PPE it is assumed that PPE is used until they are not useable anymore. For this reason a monthly RF is assumed.	d) Monthly = 10	Ecobichon (2001)
19	If non-woven gloves connect well to clothing of arms (GC)	a) No = 3 b) Yes = 1	If connected well exposure can be more reduced.	Farmers used woven gloves.		
20	If non-woven gloves are worn during total time of task (GD)	a) 0–25% of task duration = 10 b) 25–99% of task duration = 3 c) 100% of task duration =1	Gloves worn during total time reduce exposure more than worn during part of the time.	Farmers used woven gloves.		
21	A second pair of gloves is worn under outer gloves (UG)	a) No = 1 b) Yes = 0.3	A second pair of gloves may reduce exposure.	Farmers in Vereda la Hoya didn't use a second pair of gloves.	a) No = 1	
22	Replacement frequency of these inner gloves (URF)	a) After 1 time = 1 b) Daily = 3 c) ≥Weely = 10	Inner gloves only protect if frequently replaced.	No inner gloves were used.		
23	Barrier cream used (BC)	a) No = 1 b) Yes = 0.3	Use of cream reduces exposure.	Farmers in the study area didn't use barrier cream.	a) No = 1	
24	Relative task duration (RTD) Categorical estimate ($_{CAT}$)	a) Daily 4–8 h/weekly >20h/ monthly >80h/yearly >800h = 1 b) Daily 1–4 h/weekly 4–20 h/monthly 16–80 h/yearly 160–800 h = 0.3 c) Daily 11–60 min/weekly 1–4 h/monthly 4–16 h/yearly 40–160 h = 0.1 d) Daily <11 min/weekly 0–1 h/monthly 0–4 h/yearly 0–40 h = 0.03	Increasing task duration results in higher exposure. Relative time of task performance (RTD_{CAT}) = (frequency * duration task)/total working time	In average farmers were working daily 4–8 h/weekly >20 h/monthly >80 h/yearly >800 h.		
25-26	Worker's hygiene factor (WH)	a) Hands not washed = 1 b) Washed 2–10 times per shift with water = 0.3 c) Washed 2–5 times per shift (scrub) soap/solvents = 0.3 d) Washed >10 times per shift with water = 0.1 e) Washed >5 times per shift with (scrub) soap/solvents = 0.1	Determined by hand-wash frequency (HWF) and wash efficiency (WE). Hand washing reduces exposure.	Products like soap are not considered to be a basic element when it comes to the hygiene of the farmers.		
27-29	Continued exposure (CE)	a) Working clothes are immediately changed after work: No = 0.3, Yes = 1 b) Workers responsible for washing own working clothes: No = 1, Yes = 3 c) Workers immediately shower after work: No = 1, Yes = 0.3	Contaminated working clothes result in exposure after work. Showering reduces continued exposure. CE = working clothes immediately changed after work (a) * workers wash own working clothes (b) * workers immediately shower after work (c)			

30-33	Hygiene estimate work environment (EH)	a) Daily cleaning wet = 0.1 b) Weekly cleaning wet = 0.3 c) Cleaning dry = 1	Cleaning frequency results in cleaner work environment. Wet cleaning is more efficient than dry cleaning. Hygiene estimates of floor, worktables, machines and working tools determined by cleaning frequency and cleaning efficiency. EH = [hygiene floor (FL) + hygiene work tables (WT) + hygiene machines (MC) + hygiene working tools (TO)]/4	In general, after the application of pesticides farmers clean the equipment by rinsing it with clean water.		Lesmes & Binder (to be published (a))

Scoring system of the study case for the model

PHED

Determinants of the PHED model					
Nr.	**Name**	**Score of DERM**	**System characteristics**	**Scores considered**	**Reference**
1	Mixing status	a) Never mixed = 0 b) Mixed = 9	The solution sprayed is mixed up with different chemicals or at least diluted with water.	b) Mixed = 9	
2	Using enclosed mixing system	a) Yes = 0,5 b) No = 1.0	Pesticides are mixed in a big container. It is assumed that the mixing system is open.	b) No = 1.0	Lesmes & Binder (to be published (a))
3	Application methods	For herbicides, crop insecticides, fungicides a) Doesn't apply = 0 b) Aerial-aircraft = 1 c) In furrow/banded = 2 d) Boom on tractor = 3 e) Backpack = 8 f) Hand spray = 9 g) Mist blower/fogger = 9 h) Airblast = 9 For fumigants s) Doesn't apply = 0 t) Gas canister = 2 u) Row fumigantion = 4 For animal insecticides i) Doesn't apply = 0 j) Ear tags = 1 k) Hang pest strips = 2 l) Rope wick = 2 m) Dip animal = 5 n) Spray animal = 6 o) Spray buildings = 6 p) Dust animal = 7 q) Pour on animal = 7 r) Fog/mist animal = 9	In the study area 96% of the farmers sprayed their pesticides (insecticides, fungicides, herbicides) with a backpack sprayer.	For herbicides, crop insecticides, fungicides e) Backpack = 8	
4	Tractor with enclosed cab/charcoal filter	Boom, in furrow, hand spray, mist blower, airblast on tractor **&** a) Cab = Yes, Filter = Yes → = 0,1 b) Cab = Yes, Filter = No → = 0,5 c) Cab = No; or don't use tractor → = 1,0	In the study area a tractor is not used.	c) Cab = No; or don't use tractor → 1,0	
5	Repair status	a) No = 0 b) Yes = 2	No data was available on this matter. Thus, it is assumed that the older the backpacks the more repairs need to be made (mean: 9,64 years; standev: 7,55).	b) Repair = 2	
6	Washing equipment	a) Don't wash = 0 b) Hose down sprayer = 0,5 c) Hose down tractor = 0,5 d) Clean nozzle = 3 e) Rinse tank = 1	In general, after the application of pesticides the farmer cleans the equipment by rinsing it with clean water.	d) Clean nozzle = 3	Lesmes & Binder (to be published (a))
7	PPE used	a) PPE-0 = 1,0 b) PPE-1 = 0,8 c) PPE-2 = 0,7 d) PPE-3 = 0,6 e) PPE-1 & PPE-2 = 0,5 f) PPE-1 & PPE-3 = 0,4 g) PPE-2 & PPE-3 = 0,3 h) PPE-1 & PPE-2 & PPE-3 = 0,1	In general, farmers use fabric gloves when they are on the field.	b) PPE-1 = 0,8	
8	Replacing old gloves	Fabric/leather gloves **&** a) Change after each use = 1 b) Change once a month or 1-4 times per season = 1,1 c) Change when they are worn out = 1,2	Because of the financial limitation of the farmers it is assumed that gloves are used until they are worn out.	c) Change when they are worn out = 1,2	Ecobichon (2001)
9	Personal hygiene	a) Hyg-1 (80% protection) = 0,2 b) Hyg-2 (60% protection) = 0,4 c) Hyg-3 (40% protection) = 0,6 d) Hyg-4 (20% protection) = 0,8 e) Hyg-5 (no protection) = 1,0	Due to the fact that 64% use PPE and about 95% believe that not using PPE can harm the health, it is considered that farmers clean them-selves and also change the clothes on a regular bases.	c) Hyg-3 (40% protection) = 0,6	
10	Change clothes after a spill	a) Right away = 1,0 b) Always use disposable clothing = 1,0 c) At lunch = 1,1 d) At the end of the day = 1,2 e) At the end of the next day = 1,4 f) Later in the week = 1,8	Due to the fact that farmers in developing countries cannot spend that much money on equipment/cloths. It is considered that the farms aren't using disposable cloths nor change cloths right after the spill.	d) At the end of the day = 1,2	Ecobichon (2001)

Scoring choices for determinant "*Clothing protection*" & "*Personal hygiene*" used in the model PHED

PPE used (= Clothing protection)	PPE-0 (0% protection)	Never used PPE Hat only
	PPE-1 (20% protection)	Dust mask Full face shields Goggles Fabric/leather gloves Apron Cloth overall
	PPE-2 (30% protection)	Cartridge respirators/gas mask Chemically resistant boots Disposable outer clothing
	PPE-3 (40% protection)	Chemically resistant rubber gloves
Personal hygiene	Hyg-1 (80% protection)	Change clothing (Right away; or always use disposable clothing) **&** Wash/shower (Hands/arms washed right away; bath/shower right away; or bath/shower at lunch
	Hyg-2 (60% protection)	Change clothing (right away; or use disposable clothing) **&** Hand wash/shower (bath/shower at the end of the day) **or** Change clothing (at lunch; or at the end of the day) **&** Hand wash/shower (Hands/arms washed right away; bath/shower right away; or bath/shower at lunch)
	Hyg-3 (40% protection)	Change clothing (right away; or use disposable clothing) **&** Hand wash/shower (hand/arms only at the end of the day) **or** Change clothing (at lunch; or at the end of the day) **&** Hand wash/shower (Bath/shower at the end of the day) **or** Change clothing (at the end of the next day; or later in the week) **&** Hand wash/shower (hands/arms washed right away; bath/shower right away; or bath/shower at lunch)
	Hyg-4 (20% protection)	Change clothing (at lunch; or at the end of the day) **&** Hand wash/shower (Hands/arms washed at the end of the day) **or** Change clothing (at the end of the next day; or later in the week) **&** Hand wash/shower (bath/shower at the end of the day)
	Hyg-5 (no protection)	Change clothing (at the end of the next day; or later in the week) **&** Hand wash/shower (Hands/arms only at the end of the day)

Scoring system of the study case for the model RISKOFDERM

Determinants of the RISKOFDERM model				
Nr.	**Name**	**Score of RISKOFDERM**	**System characteristics**	**Scores considered**
1	Risk phrases	See Table 3 in Oppl et al. (2003)	See Table 3 in Oppl et al. (2003)	Chlorpyrifos, Glyphosate → low Paraquat → moderate Cymoxanil, Mancozeb → very high
2	Route weight fraction (RWF)	Hand tool dispersion Body Hand a) Direct contact (DC): 20% 30% b) surface contact (SC):50% 50% c) deposition (DEP): 30% 30% *	This DEO unit is best fitting the task group.	Hand tool dispersion Body Hand a) Direct contact (DC): 20% 30% b) surface contact (SC):50% 50% c) deposition (DEP): 30% 30%
3	Substance specific modifier	Volatility: Like water (DC 1, SC 1, DEP 1) **	This data set is best fitting the task group.	Volatility: Like water (DC 1, SC 1, DEP 1)
4	Workplace modifier	Spraying of liquids: Little pressure (DC 1, SC 0.3, DEP 0.1) **	This data set is best fitting the task group.	Spraying of liquids: Little pressure (DC 1, SC 0.3, DEP 0.1)
5	Control measure modifier	Level of automation: No automation (DC 1, SC 1, DEP 1) **	This data set is best fitting the task group.	Level of automation: No automation (DC 1, SC 1, DEP 1)
6	Default exposure Values by task group	Spray dispersion of liquids: 0.459 (Body), 1.067 (Hand) **	This default exposure value is best fitting the task group.	Spray dispersion of liquids: 0.459 (Body), 1.067 (Hand)
7	Clothing protection factor (CPF)	a) light clothing = 0.5 b) thick clothing = 0.1	Thick clothing are used more often than light onse, for this reason b) has been chosen.	b) thick clothing = 0.1
8	Activity time (AT)	a) <0.1 h = 0.1 b) 0.1 - <0,5 h = 0.1 c) 0.5 - <1 h = 0.3 d) 1 - 4 h = 1 e) >4 h = 3	The activity time of the farmers are between 1 - >4 h.	e) >4 h = 3
9	Exposed body area (EBA)	a) <10 (size of a large coin; small splashes) = 0.1 b) 10-500 (one hand or less) = 0.3 c) 501-2000 (hands and lower arms, or hands and head) = 1 d) >2001 (more than hands and head) = 3	The exposed body area is assumed bigger than just hands and bead. In general feet and thorox are exposed very often as well.	d) >2001 (more than hands and head) = 3

* For more information see Table 8 in Warren et al. (2003)
** For more information see Table 1 in Goede et al. (2003)

Scoring system of the sensitivity analysis for the model DERM

Determinants of the DERM model						
Nr.	**Name**	**Score of DERM**	**System characteristics**	**Scoring**	**Scores considered**	**Reference**
1	Sprayed surface	a) ≤0.7 ha = 1 b) >0.7 ha = 2	The mean of the parcels size is 0,998 ha, due to the fact that the standev is 0.751, both scores were considered		a) ≤0.7 ha = 1 b) >0.7 ha = 2	
2	Height of the crop	a) 1*1 = 1 b) 1*2 = 2 c) 1*3 = 3 d) 1*4 = 4 e) 1*5 = 5 f) 3*1 = 3 g) 3*2 = 6 h) 3*3 = 9 i) 3*4 = 12 j) 3*5 = 15	During one cycle the farmer is using pesticides frequently. For this reason it is assumed that for the transfer of pesticides the contamination is recently (T=3) rather than previously (T=1).	It is considered that between 0 - 40 % of the body surface get contaminated. In general the potatoe plant is growing about 60 cm high (Rahn, 2010), hence not that much body surface can get contaminated.	f) 3*1 = 3 g) 3*2 = 6	Rahn (2010)
3	Leaking backpack	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	In general farmers in developing countries don't pay that much attention to safety measure. In addition, the sprayers used in the study area are quite old (mean: 9.64 years; standev: 7.95). For this reason it is assumed that there are leaking accidents.	It is considered that between 0 - 40 % of the body surface get contaminated. When the backpack is leaking the pesticide cannot spread out that much.	a) 0 b) 5*1 = 5 c) 5*2 = 10	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001); Sivyoganathan et al. (1995)
4	Volume of sprayed dilution	a) ≤30 l = 2.5 b) >30 l = 5	The mean of the amount used, by every farmer, was considered (mean: 11.51 l). Due to the fact that the standev is 11.58 both scores were considered.		a) ≤30 l = 2.5 b) >30 l = 5	
5	Nozzle height	a) 4*1 = 4 b) 4*2 = 8 c) 4*3 = 12 d) 4*4 = 16 e) 4*5 = 25	The nozzle height (moving it up and down; from side to side) results in drift deposition. The higher the nozzle is in the air the more deposition can occur.	The body parts which are highly endangered are: head, arms, thorax, thighs, legs, and feet. Due to wind conditions the front- and the backside of the body can get contaminated. It is considered that between 0-60% of the body surface gets contaminated.	a) 4*1 = 4 b) 4*2 = 8 c) 4*3 = 12	Blanco et al. (2005); Blanco et al. (2008)
6	Spraying in front	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	By using a backpack sprayer it is most likely that the nozzle is used directed in front because this way it is easier to achieve a uniform coverage and a correct application rate (NRCS, 2010; Lesmes, & Binder, to be published (a)).	The body parts which are highly endangered are: head, arms, thorax, thighs, legs and feet. Due to wind conditions the front- and the backside of the body can get contaminated. It is considered that about 60% of the body get contaminated.	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15	NRCS (2010) Lesmes, & Binder (to be published (a))
7	Spraying against wind	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Boyacá is in the Andes, thus it is most likely that the wind is blowing in different directions. When the wind is blowing more particles of the substance gets mixed up with the air particles and cause more contamination.	In general, between 0-60 % of the body surface get contaminated.	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15	Tuchschmid (2004)

8	Splash/spill over the pump	a) 0 b) 1*1 = 1 c) 1*2 = 2 d) 1*3 = 3 e) 1*4 = 4 f) 1*5 = 5 g) 3*1 = 3 h) 3*2 = 6 i) 3*3 = 9 j) 3*4 = 12 k) 3*5 = 15	The possibility of the pump to get contaminated is quite high because in developing countries pesticides can be handled quite carelessly. Due to the fact that the pump is used frequently during the application cycle it is assumed that the body gets contaminated recently than previously.	Not that much body surface can get exposed to the substance. The contamination is limited to arms and hands (0-20%).	a) 0 b) 1*1 = 1 d) 3*1 = 3	Hoyos et al. (1996)
9	Splashes on hands	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Farmers in developing countries don't pay that much attention to safety measure, thus it is assumed that splashes on hands happen.	Due to the fact that this determinant is just concentrating on the hands not more than 20% of the body surface can get contaminated.	a) 0 b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001); Sivyoganathan et al. (1995)
10	Splashes on feet	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Farmers in developing countries don't pay that much attention to safety measure, thus it is assumed that splashes on the feet happen.	Due to the fact that this determinant is just considering feet not more than 20% of the body surface can get contaminated.	a) 0 b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001); Sivyoganathan et al. (1995)
11	Gross contamination of the hands	a) 0 b) 5*1 = 5 c) 5*2 = 10 d) 5*3 = 15 e) 5*4 = 20 f) 5*5 = 25	Farmers in developing countries don't pay that much attention to safety measure. It is assumed that gross contamination of hands occurs by blocking a hose leakage, repairing nozzle, or entering hand into tank.	Due to the fact that this determinant is just concentrating on the hands not more than 20% of the body surface can get contaminated.	a) 0 b) 5*1 = 5	van Wendel de Joode et al. (1996); Gomes et al. (1999); Sivyoganathan et al. (1995)
12	a. Wearing long sleeved shirt b. Wearing short sleeved shirt	a) 0 a. b) 0.20 b. c) 0.15	Mostly farmers wear long sleefed shirts. But depending on the temperature farmers can waer short sleeved sirts as well.	Clothing Protection (CP) = 0 for not wearing such clothing protection piece, 0.15/0.20 for wearing it.	b) 0.20 c) 0.15	Lesmes & Binder (to be published (b))
13	Wearing an old/overused/torn shirt	a) 0	In general, farmers did not wear a very old/overused/torn shirt.	Clothing Protection (CP) = 0 because an old/overused/torn clothing piece cannot protect the body that well from pesticide contamination.	a) 0	Lesmes & Binder (to be published (a)); Lesmes & Binder (to be published (b))
14	a. Wearing long pants b. Wearing short pants	a) 0 a. b) 0.15 b. c) 0.10	In general farmers wear trousers with thicker fabrics.	Clothing Protection (CP) = 0 for not wearing such a clothing protection piece, 0.15/0.10 for wearing it.	a) 0 b) 0.15	Lesmes & Binder (to be published (b))
15	Wearing old/overused/torn pants	a) 0	In general, farmers didn't wear a very old/overused/torn pair of pants.	Clothing Protection (CP) = 0 because an old/overused/torn clothing piece cannot protect the body that well from pesticide contamination.	a) 0	Lesmes & Binder (to be published (a)); Lesmes & Binder (to be published (b))
16	Wearing shoes	a) 0 b) 0.10	About 64% of the farmers use PPE and about 95% of the farmers believe that not using PPE can harm the health, it is assumed that farmers wear shoes.	Clothing Protection (CP) = 0 for not wearing shoes, 0.10 for wearing shes.	a) 0 b) 0.10	

Scoring system of the sensitivity analysis for the model DREAM

Determinants of the DREAM model						
Nr.	**Name**	**Score of DREAM**	**System characteristics**	**Farming characteristics**	**Scores considered**	**Reference**
1	Probability of emission on clothing and uncovered skin ($P_{E\,BP}$)	a) <1% of task duration = 0 b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	Frequency of occurrence of the concerned exposure route.	Farmers don't pay that much attention to safety measure. For this reason the probability of emission during task can be very high but doesn't have to be.	b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001)
2	Intensity of emission ($I_{E\,BP}$)	a) <10% of body part = 1 b) 10–50% of body part = 3 c) ≥50% of body part = 10	Assess the amount of agent on clothing and uncovered skin resulting from the exposure.	Due to the fact that farmers tend to over- or misuse the products and emission transports a high mass of substance the intensity is considered to be from low to very high.	a) <10% of body part = 1 b) 10–50% of body part = 3 b) ≥50% of body part = 10	Feola & Binder (2010); van Wendel de Joode (2003)
3	Exposure route factors (ER_E, ER_D, ER_T)	a) Emission = 3 b) Deposition = 1 c) Transfer = 1	Exposure due to emission is considered to transport more mass of substance onto the skin (direct release from a source), emission gets a higher score than deposition and transfer (indirect mass transport, after interference with air or surface compartments) (van Wendel de Joode et al., 2003).	See explanation of van Wendel de Joode et al., 2003.	a) Emission = 3 b) Deposition = 1 c) Transfer = 1	
4	Probability of deposition on clothing and uncovered skin ($P_{D\,BP}$)	a) <1% of task duration = 0 b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	Frequency of occurrence of the concerned exposure route.	Farmers don't pay that much attention to safety measure. For this reason the probability of deposition during task is considered to be from low to very high.	b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001)
5	Intensity of deposition on clothing and uncovered skin ($I_{D\,BP}$)	a) <10 % of body part = 1 b) 10–50% of body part = 3 c) ≥50% of body part = 10	Assess the amount of agent on clothing and uncovered skin resulting from the exposure.	Due to the fact that farmers tend to over- or misuse the products the intensity is considered to be from low to high.	a) <10% of body part = 1 b) 10–50% of body part = 3	Feola & Binder (2010)
6	Probability of transfer to clothing and uncovered skin ($P_{T\,BP}$)	a) <1% of task duration = 0 b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	It is considered to be the contact frequency with surfaces such as floor, worktables, machines and working tools.	Farmers don't pay that much attention to safety measures. In addition, the transfer of pesticides doesn't occur during the whole task. For this reason, the propability of transfer during the task is considered to be not <1% and ≥50%.	b) <10% of task duration = 1 c) 10–50% of task duration = 3 d) ≥50% of task duration = 10	van Wendel de Joode et al. (1996); Gomes et al. (1999); Wilson & Tisdell (2001)
7	Intensity of transfer ($I_{T\,BP}$)	a) not contaminated = 0 b) possibly contamination = 1 c) <50% of contact surface = 3 d) ≥50% of contact surface =10	It is the contamination level of the contact surface of these surfaces.	Due to the fact that a farmer tend to over- or misuse the products, the intensity is considered to be high.	b) possibly contamination = 1 c) <50% of contact surface = 3	Feola & Binder (2010)
8	Body surface factor (BS_{BP})	a) Head (BS_HE) = 0.69 b) Upper arm (BS_UA) = 0.67 c) Forearm (BS_FA) = 0.53 d) Hands (BS_HA) = 0.47 e) Torso front (BS_TF) = 1.22 f) Torso back (BS_TB) = 1.22 g) Lower body part (BS_LB) = 2.43 h) Lower leg (BS_LL) = 1.15 i) Feet (BS_FE) = 0.63	The body part factor, which is used for BS_{BP}, is defined as the surface area of an individual body part divided by the mean surface area of the nine body parts (van Wendel de Joode et al., 2003).	See explanation in van Wendel de Joode et al., 2003.	For each body part the BS_{BP} is used.	
9	Physical state (PS)	a) Solid = 1 b) Liquid = 1 c) Vapour-gaseous = 0.3	Solids and liquids are supposed to result in higher exposure levels than vapours and gases.	In Vereda la Hoya 100% of the 193 farmers used pesticides in liquid form.	b) Liquid = 1	Rahn (2010)
10	Concentration (C)	a) >90% active ingredient of interest = 1 b) 1–90% active ingredient of interest = 0.3 c) <1% active ingredient of interest = 0.1	Exposure increases with concentration of active ingredient in substance.	Chemicals were diluted in water.	b) 1–90% active ingredient of interest = 0.3	
11	Evaporation (liquids): boiling temperature (EV)	a) <50°C = 3 b) 50–150°C = 1 c) >150°C = 0.3	Volatile liquids result in lower dermal exposure due to increased removal.	The pesticides are not that organic to be higher than 150 and not that salty to be lower than 50.	b) 50–150°C = 1	

12	Viscosity (V)	a) Low, like water = 1 b) Medium, like oil = 1.75 c) High, like resin/paste = 3	High viscosity results in decreased removal from skin.	The farmers used water as a solution factor.	a) Low, like water = 1	
13	Formulation (F)	a) fine particles (powder) = 3 b)granules/grain/pellets = 1 c) pack/bunch/bundle = 0.3	Adherence to skin varies inversely with particle size. Smaller particles → higher emission, increased transfer and decreased removal from skin.	The chemicals bought are fine particles (powder). For application the particles were diluted in water.		
14	Dusty (solids) (DU)	a) No = 1 b) Yes = 3	Dusty solids are emitted more easily from source than non-dusty solids.	Pesticides were in liquid form.		
15	Stickiness/wax/ moist (non-powder/ non-dusty solids)	a) No = 1 b) Yes = 1.75	Such solids result in better attachment to skin (decreased removal from skin).	Water was used to dilute the chemicals, not sticky, no wax.	a) No = 1	
16	Glove or clothing material (M)	a) No gloves/clothing used = 1 b) Woven clothing = 0.3 c) Non-woven permeable = 0.1 d)Non-woven impermeable=0.03	Use of gloves/clothing reduces external exposure.	Due to the fact that 64% of the farmers use PPE and 95% of the farmers are aware of the importance of PPE it is assumed that farmers wear gloves or clothing material. Due to the fact that it is not 100% also scenario a) was	a) No gloves/clothing used = 1 b) Woven clothing = 0.3	
17	Protection factor (PFM_{HA} /PFM_{BP})	a) PFMHA = 1 b) PFMBP = 0.3	Gloves experience higher pressure than clothing.		a) PFMHA = 1 b) PFMBP = 0.3	
18	Replacement frequency (RF)	a) Used once = 0.3 b) Daily = 1 c) Weekly = 3 d) Monthly = 10	Gloves/clothing that are replaced frequently reduce exposure more than when replaced infrequently.	Due to the fact that farmers in developing counties cannot spend that much money on PPE, it is assumed that PPE is used until they are not useable anymore. For this reason also a monthly RF is assumed.	c) Weekly = 3 d) Monthly = 10	Ecobichon (2001)
19	If non-woven gloves connect well to clothing of arms (GC)	a) No = 3 b) Yes = 1	If connected well exposure can be more reduced.	Farmers used woven gloves.		
20	If non-woven gloves are worn during total time of task (GD)	a) 0–25% of task duration = 10 b) 25–99% of task duration = 3 c) 100% of task duration =1	Gloves worn during total time reduce exposure more than worn during part of the time.	Farmers used woven gloves.		
21	A second pair of gloves is worn under outer gloves (UG)	a) No = 1 b) Yes = 0.3	A second pair of gloves may reduce exposure.	Farmers in Vereda la Hoya didn't use a second pair of gloves.	a) No = 1	
22	Replacement frequency of these inner gloves (URF)	a) After 1 time = 1 b) Daily = 3 c) ≥Weekly = 10	Inner gloves only protect if frequently replaced.	No inner gloves were used.		
23	Barrier cream used (BC)	a) No = 1 b) Yes = 0.3	Use of cream reduces exposure.	Farmers in the study area didn't use barrier cream.	a) No = 1	
24	Relative task duration (RTD) Categorical estimate ($_{CAT}$)	a) Daily 4–8 h/weekly >20 h/ monthly >80 h/yearly >800h = 1 b) Daily 1–4 h/weekly 4–20 h/monthly 16–80 h/yearly 160–800 h = 0.3 c) Daily 11–60 min/weekly 1–4 h/monthly 4–16 h/yearly 40–160 h = 0.1 d) Daily <11 min/weekly 0–1 h/monthly 0–4 h/yearly 0–40 h = 0.03	Increasing task duration results in higher exposure. a. Relative time of task performance (RTDCAT) = (frequency * duration task)/total working time	In average farmers were working daily 4–8 h/weekly >20 h/monthly >80 h/yearly >800 h but it can also happen that it was < 4 h.		
25-26	Worker's hygiene factor (WH)	a) Hands not washed = 1 b) Washed 2–10 times per shift with water = 0.3 c) Washed 2–5 times per shift (scrub) soap/solvents = 0.3 d) Washed >10 times per shift with water = 0.1 e) Washed >5 times per shift with (scrub) soap/solvents = 0.1	Determined by hand-wash frequency (HWF) and wash efficiency (WE). Hand washing reduces exposure.	Products like soap are not considered to be a basic element when it comes to the hygiene of the farmers.		
27-29	Continued exposure (CE)	a) Working clothes are immediately changed after work: No = 0.3, Yes = 1 b) Workers responsible for washing own working clothes: No = 1, Yes = 3 c) Workers immediately shower after work: No = 1, Yes = 0.3	Contaminated working clothes result in exposure after work. Showering reduces continued exposure. CE = working clothes immediately changed after work (a) * workers wash own working clothes (b) * workers immediately shower after work (c)			

30-33	Hygiene estimate work environment (EH)	a) Daily cleaning wet = 0.1 b) Weekly cleaning wet = 0.3 c) Cleaning dry = 1	Cleaning frequency results in cleaner work environment. Wet cleaning is more efficient than dry cleaning. Hygiene estimates of floor, worktables, machines and working tools determined by cleaning frequency and cleaning efficiency. CE = [hygiene floor (FL) + hygiene work tables (WT) + hygiene machines (MC) + hygiene working tools (TO)]/4	In general, after the application of pesticides the farmer cleans the equipment by rinsing it with clean water.		Lesmes & Binder (to be published (a))

Scoring system of the sensitivity analysis for the model PHED

Determinants of the PHED model					
Nr.	**Name**	**Score of DERM**	**System characteristics**	**Scores considered**	**Reference**
1	Mixing status	a) Never mixed = 0 b) Mixed = 9	The solution sprayed is mixed up with different chemicals or at least diluted with water.	b) Mixed = 9	
2	Using enclosed mixing system	a) Yes = 0,5 b) No = 1.0	Pesticides are mixed in a big container. It is assumed that the mixing system is open.	b) No = 1.0	Lesmes & Binder (to be published (a))
3	Application methods	For herbicides, crop insecticides, fungicides a) Doesn't apply = 0 b) Aerial-aircraft = 1 c) In furrow/banded = 2 d) Boom on tractor = 3 e) Backpack = 8 f) Hand spray = 9 g) Mist blower/fogger = 9 h) Airblast = 9 For fumigants s) Doesn't apply = 0 t) Gas canister = 2 u) Row fumigantion = 4 For animal insecticides i) Doesn't apply = 0 j) Ear tags = 1 k) Hang pest strips = 2 l) Rope wick = 2 m) Dip animal = 5 n) Spray animal = 6 o) Spray buildings = 6 p) Sust animal = 7 q) Pour on animal = 7 r) Fog/mist animal = 9	In the study area 96% of the farmers sprayed their pesticides (insecticides, fungicides, herbicides) with a backpack sprayer.	For herbicides, crop insecticides, fungicides e) Backpack = 8	
4	Tractor with enclosed cab/charcoal filter	Boom, in furrow, hand spray, mist blower, airblast on tractor **&** a) Cab = Yes, Filter = Yes = 0,1 b) Cab = Yes, Filter = No = 0,5 c) Cab = No; or don't use tractor = 1,0	In the study area a tractor is not used.	c) Cab = No; or don't use tractor = 1,0	
5	Repair status	a) No = 0 b) Yes = 2	No data was available on this matter. Thus, it is assumed that the older the backpacks the more repairs need to be made (mean: 9,64 years. Due to the fact that the standev is 7,55 it is assumed that not all needed some repairment.	a) Doesn't repair = 0 b) Repair = 2	
6	Washing equipment	a) Don't wash = 0 b) Hose down sprayer = 0,5 c) Hose down tractor = 0,5 d) Clean nozzle = 3 e) Rinse tank = 1	In general, after the application of pesticides the farmer cleans the equipment by rinsing it with clean water.	a) Don't wash = 0 d) Clean nozzle = 3 e) Rinse tank = 1	Lesmes & Binder (to be published (a))
7	PPE use	a) PPE-0 = 1,0 b) PPE-1 = 0,8 c) PPE-2 = 0,7 d) PPE-3 = 0,6 e) PPE-1 & PPE-2 = 0,5 f) PPE-1 & PPE-3 = 0,4 g) PPE-2 & PPE-3 = 0,3 h) PPE-1 & PPE-2 & PPE-3 = 0,1	In general, farmers use fabric gloves when they are on the field.	a) PPE-0 = 1,0 b) PPE-1 = 0,8 e) PPE-1 & PPE-2 = 0,5	
8	Replacing old gloves	Fabric/leather gloves **&** a) Change after each use = 1 b) Change once a month or 1-4 times per season = 1,1 c) Change when they are worn out = 1,2	Because of the financial limitation of the farmers it is assumed that PPE is used for et least a month.	b) Change once a month or 1-4 times per season = 1,1 c) Change when they are worn out = 1,2	Ecobichon (2001)
9	Personal hygiene	a) Hyg-1 (80% protection) = 0,2 b) Hyg-2 (60% protection) = 0,4 c) Hyg-3 (40% protection) = 0,6 d) Hyg-4 (20% protection) = 0,8 e) Hyg-5 (no protection) = 1,0	Due to the fact that of the 193 farmers 64% use PPE and about 95% believe that not using PPE can harm the health, it is considered that the farmers clean themselves and also change the clothes regularly.	b) Hyg-2 (60% protection) = 0,4 c) Hyg-3 (40% protection) = 0,6 d) Hyg-4 (20% protection) = 0,8	
10	Change clothes after a spill	a) Right away = 1,0 b) Always use disposable clothing = 1,0 c) At lunch = 1,1 d) At the end of the day = 1,2 e) At the end of the next day = 1,4 f) Later in the week = 1,8	Due to the fact that farmers in developing countries cannot spend that much money on equipment/cloths. It is considered that the farms aren't using disposable cloths nor change cloths right after the spill, or later on.	d) At the end of the day = 1,2 e) At the end of the next day = 1,4 f) Later in the week = 1,8	Ecobichon (2001)

Scoring system of the sensitivity analysis for the model RISKOFDERM

Determinants of the RISKOFDERM model				
Nr.	**Name**	**Score of RISKOFDERM**	**System characteristics**	**Scores considered**
1	Risk phrases	See Table 3 in Oppl et al. (2003)	See Table 3 in Oppl et al. (2003)	Chlorpyrifos, Glyphosate → low Paraquat → moderate Cymoxanil, Mancozeb → very high
2	Route weight fraction (RWF)	Hand tool dispersion Body Hand a) Direct contact (DC): 20% 30% b) surface contact (SC):50% 50% c) deposition (DEP): 30% 30% *	This DEO unit is best fitting our task group.	Hand tool dispersion Body Hand a) Direct contact (DC): 20% 30% b) surface contact (SC):50% 50% c) deposition (DEP): 30% 30%
3	Substance specific modifier	Volatility: Like water (DC 1, SC 1, DEP 1) **	This data set is best fitting our task group.	Volatility: Like water (DC 1, SC 1, DEP 1)
4	Workplace modifier	Spraying of liquids: Little pressure (DC 1, SC 0.3, DEP 0.1) **	This data set is best fitting our task group.	Spraying of liquids: Little pressure (DC 1, SC 0.3, DEP 0.1)
5	Control measure modifier	Level of automation: No automation (DC 1, SC 1, DEP 1) **	This data set is best fitting our task group.	Level of automation: No automation (DC 1, SC 1, DEP 1)
6	Default exposure values by task group	Spray dispersion of liquids: 0.459 (Body), 1.067 (Hand) **	This default exposure value is best fitting the task group.	Spray dispersion of liquids: 0.459 (Body), 1.067 (Hand)
7	Clothing protection factor (CPF)	a) light clothing = 0.5 b) thick clothing = 0.1	The type of clothing depends on the climate, both are possible.	a) light clothing = 0.5 b) thick clothing = 0.1
8	Activity time (AT)	a) <0.1 h = 0.1 b) 0.1 - <0,5 h = 0.1 c) 0.5 - <1 h = 0.3 d) 1 - 4 h = 1 e) >4 h = 3	The activity time of the farmers are between 1 - >4 h.	d) 1 - 4 h = 1 e) >4 h = 3
9	Exposed body area (EBA)	a) <10 (size of a large coin; small splashes) = 0.1 b) 10-500 (one hand or less) = 0.3 c) 501-2000 (hands and lower arms, or hands and head) = 1 d) >2001 (more than hands and head) = 3	The body area is assumed to be exposure from very little to very high.	a) <10 (size of a large coin; small splashes) = 0.1 b) 10-500 (one hand or less) = 0.3 c) 501-2000 (hands and lower arms, or hands and head) = 1 d) >2001 (more than hands and head) = 3

* For more information see Table 8 in Warren et al. (2003)
** For more information see Table 1 in Goede et al. (2003)

List of Criteria of the model COSHH

COSHH

Criteria	General characteristics
Year	2002 (http://www.atl.org.uk/).
Country	Developed in the United Kingdom (Garrod & Sithamparanadarajah, 2003).
Goal	Provide assistance to SME's to manage risk assessment of chemicals for a range of common tasks, in a generic scale (Jackson, 2002).
Target group	For use in SME's & developing countries (ITG, 2009). Useable in every country, but adaptations of materials and regulatory implications are required (NIOSH, 2005).
Availability	An electronic version (on the webpage) & a paper version is supposed to be available (http://www.coshh-essentials.org.uk/;). But the paper version wasn't found.
Guidance	Homepage: general information on the model. Control guidance sheets (CGS): guidelines for specific industries (http://www.coshh-essentials.org.uk/). Fact sheets: information on technical basis of COSHH (HSE, 2009).
Conceptual basis	The framework - considers OELs to assess adequate exposure controls (Garrod & Sithamparanadarajah, 2003). The health hazard - based on R-phrases (HSE, 2009).
Reliability	It is one of the most prominent examples for chemical exposure (Tielemans et al., 2008). An evaluation, by the German authority, showed the exposure measurements being within the range predicted (NIOSH, 2005).
Knowledge required	Not that specific expertise is needed (Garrod & Sithamparanadarajah, 2003).
Equipment required	The electronic version isn't suitable for every internet browser (www.coshh-essentials.org.uk).

Criteria	Assessment characteristics
Data required as input	See subchapter 1.4.1.
Type of exposure	Assessment of inhalation & dermal exposure. The method used for the dermal exposure model is based on the inhalation one (Garrod & Sithamparanadarajah, 2003).
Dermal exp. pathway	3 pathways: deposition, direct, & indirect contact (Garrod & Sithamparanadarajah, 2003).
Dermal exp. descriptor	Assessment of the potential exposure (HSE, 2009).
Body part	Assessment of the exposure at the workplaces (ITG, 2009).
Type of substance	Useable for chemicals & products (mixtures), not for pesticides (NIOSH, 2005; http://www.coshh-essentials.org.uk/, Access 07.04.2011).
Physical state of substance	Useable for liquids & solids (HSE, 2009).
Model updates	No information was found about updates.
Expected results	Written guidance & documentation; information on risk assessment, control approaches, statements about respiratory protective equipment (Garrod & Sithamparanadarajah, 2003). A substance comparison can be made (NIOSH, 2005).
Outcome	Qualitative (which control band should be used) or semi-quantitative (information on the exposure) (ITG Review, 2009; NIOSH, 2005).

Criteria	Conclusion characteristics
Advantage/ Disadvantage (references)	- Used somewhere else than Britain adaptations of materials & reviews of legal and regulatory implications are required (NIOSH, 2005). - Not appropriate for situations with open spray applications or when pesticides are used (NIOSH, 2005). - Just useable for specific substances (Garrod & Sithamparanadarajah, 2003).
Advantage/ Disadvantage (authors' opinion)	° It is focusing on industrialized working situations. ° CGSs are not appropriate for farming environments in developing countries.
Conclusion (authors' opinion)	**The model won't be a good fit for the agricultural sector in developing countries. Furthermore, no paper version of the model was available.**

List of criteria of the model DERM

DERM

Criteria	General characteristics
Year	2008 (Blanco et al., 2008).
Country	The study was conducted at the Universided Nacional Autónoma de Nicaragua (UNAN-León) (Blanco et al., 2005).
Goal	To be a low-cost, easy-to-use method for the assessment of exposure to pesticides in developing countries, in a generic scale (Blanco et al., 2008).
Target group	An exposure assessment approach for farmers in developing countries (Blanco et al., 2008).
Availability	A paper version is available (Blanco et al., 2008).
Guidance	The method & algorithm are described in Blanco et al. (2008).
Conceptual basis	The type of transport process: based on Schneider et al. (1999) (Blanco et al., 2008). Subdivision of body parts: based on Fenske (1988) (Blanco et al., 2005).
Reliability	It is still incomplete, very few quantitative exposure studies have been completed in developing countries (Blanco et al., 2008).
Knowledge required	Understanding the description of the method in Blanco et al. (2008), & basic math skills are required.
Equipment required	It can be carried out in the field, by just using paper, pen, and calculator.

Criteria	Assessment characteristics
Data required as input	See subchapter 1.4.2.
Type of exposure	Assessment of dermal exposure (Blanco et al., 2008).
Dermal exp. pathway	3 pathways: transfer, deposition, & emission processes (Blanco et al.,
Dermal exp. descriptor	Assessment of the potential & actual exposure (Blanco et al., 2008).
Body part	19 body parts considered: front and back side of neck, thorax, arms, forearms, hands, thighs, legs, feet & forehead and left and right sides of the face (Blanco et al., 2005).
Type of substance	Useable for pesticides (Blanco et al., 2008).
Physical state of substance	Useable for liquids (Blanco et al., 2005; Blanco et al., 2008).
Model updates	No information was found about updates.
Expected results	Prioritize control measures, assess exposure, identify det. causing high exposure & farmers exposed the most (Blanco et al., 2008).
Outcome	No ranking system but a priority ranking of det. and/or farmers are possible (Blanco et al., 2008).

Criteria	Conclusion characteristics
Advantage/ Disadvantage (references)	+ The algorithm is simple & can be calculated manually & right in the field (Blanco et al., 2008). + The model was developed for farmers in developing countries (Blanco et al., 2008). + It is easy to identify det. causing the highest exposure (Blanco et al., 2008).
Advantage/ Disadvantage (authors' opinion)	° The scoring system is kept very general, for some det. more scenarios could be considered. ° It distinguishes if the subject of matter got contaminated recently or previously. None of the other models consider that aspect! ° The model doesn't consider the physical state of the substance.
Conclusion (authors' opinion)	The model is easy to be used. The determinants considered are occupational-specific. But the model still has some limitations, modifications are possible to make it more accurate/realistic.

List of criteria of the model DREAM

DREAM

Criteria	General characteristics
Year	2003 (van Wendel de Joode et al., 2003).
Country	Developed in the Netherlands (Marquart et al., 2003).
Goal	To assess occupational exposure in any given situation, in a generic scale (van Wendel de Joode et al., 2003).
Target group	A variety of sectors: e.g. automobile & chemical industries, hospitals, shoe manufacturing (van Wendel de Joode et al., 2005b) and among pesticide exposed vine yard workers in South Africa (Kromhout et al., 2008).
Availability	A paper version is available (of van Wendel de Joode et al., 2003).
Guidance	The method & algorithm are described in van Wendel de Joode et al. (2003).
Conceptual basis	DREAM follows the model of Schneider et al. (1999). The assessment of airborne concentrations: based on Cherrie et al. (1996) (van Wendel de Joode et al., 2003).
Reliability	Four studies performed (29 observers performed side-by-side observations) showed good inter-observer agreement. The accuracy of the estimates within surveys varied (van Wendel de Joode et al., 2005b).
Knowledge required	Understanding the description of the method in van Wendel de Joode et al. (2003), & basic math skills are required.
Equipment required	Paper, pen, and calculator are needed (Kromhout et al., 2005).

Criteria	Assessment characteristics
Data required as input	See subchapter 1.4.3.
Type of exposure	Assessment of dermal exposure (van Wendel de Joode et al., 2003).
Dermal exp. pathway	3 pathways: transfer, deposition, & emission processes (van Wendel de Joode et al., 2003).
Dermal exp. descriptor	Assessment of potential & actual exposure (van Wendel de Joode et al., 2005).
Body part	9 body parts considered: head, upper & lower arms, hands, torso front, back, upper legs, lower legs and feet (van Wendel de Joode et al., 2005a).
Type of substance	Useable for metal working fluids (van Wendel de Joode et al., 2005b) & pesticides (van Wendel de Joode et al., 2005a).
Physical state of substance	Useable for liquids & solids (van Wendel de Joode et al., 2003).
Model updates	No information was found about updates.
Expected results	Assessment of dermal exposure levels & control measures (van wendel de Joode et al., 2003).
Outcome	Semi-quantitative. The ranking is divided into 7 segments: 0 - 1000 (no - very high exposure) (van Wendel de Joode et al., 2003).

Criteria	Conclusion characteristics
Advantage/ Disadvantage (references)	- DREAM is more time-consuming, due to the high number of determinants used (van Wendel de Joode et al., 2003; van Wendel de Joode et al., 2005b). + The algorithm is more complex than the one of DERM (Blanco et al., 2008). + The outcome can be seen as more accurate (van Wendel de Joode et al., 2003; van Wendel de Joode et al., 2005b).
Advantage/ Disadvantage (authors' opinion)	° The consideration of the physical state of substances might be too general as to get valuable information. ° Identifying the determinants causing the highest exposure is more difficult, the algorithm is too complex. ° Not all determinants considered are needed for assessing dermal exposure to pesticides in developing countries, also important determinants are missing.
Conclusion (authors' opinion)	DREAM can be used for the agricultural sector in developing countries but alterations would be necessary to make it more suitable for developing countries.

List of criteria of the model EASE

EASE

Criteria	General characteristics
Year	1994 (Cherrie et al, 2003).
Country	Developed in the United Kingdom (Johnaston et al., 2003).
Goal	Originally: Screening tool for regulatory risk assessment for new chemicals (Creely et al., 2005). Now: To estimate exposure for new/ existing substances (Hughson & Cherrie, 2005), in a generic scale (Cherrie et al., 2003).
Target group	Distributed to over 200 users in Europe, North America, Australia and Asia (Cherrie et al., 2003).
Availability	A computer version is available (Cherrie et al., 2003).
Guidance	It is a simple-to-use model (Hughson & Cherrie, 2005), but no guideline was found.
Conceptual basis	The theoretical approach: established at the Orlando seminar. The output: based on the NEDB and personal judgment (Cherrie et al., 2003). The program: based on a computer-aided decision tree format (Johnaston et al., 2003). EASE follows the model of Schneider et al. (1999) (Creely et al., 2005).
Reliability	Further work is necessary, more elements relevant are needed to be included (Hughson & Cherrie, 2005).
Knowledge required	Knowledge about the assumptions built into EASE is needed (Johnaston et al., 2003).
Equipment required	Each version of EASE requires significant software changes and new implementations of the interface. Version 1 & 2 are available on a floppy disk. Version 3 is not in use (Cherrie et al., 2003; Tickner et al., 2005).

Criteria	Assessment characteristics
Data required as input	See subchapter 1.4.4.
Type of exposure	Assessment of inhalation & dermal exposure. The method used for the dermal exp. model is based on the inhalation one (Cherrie et al.,2003).
Dermal exp. pathway	4 emission pathways: to surfaces, air, outer clothing layers, & direct to skin (Creely et al., 2005).
Dermal exp. descriptor	Assessment of the potential exposure (Cherrie et al., 2003).
Body part	2 body parts considered: hands & forearms (Hughson & Cherrie, 2005).
Type of substance	Useable for pure substance, not mixtures (Johnaston et al., 2003).
Physical state of substance	Useable for liquids & solids (Cherrie et al., 2003).
Model updates	Changes made were not themselves major & the output ranges have not been updated since 1992 (Cherrie et al., 2003).
Expected results	Predict exposure levels at a workplace & provides data to support exposure limits (Creely et al., 2005).
Outcome	Quantifies the degree of exposure (Cherrie et al., 2003). The exposure ranges take five different values: from very low to 5-15 mg/cm/day (Hughson & Cherrie et al., 2005).

Criteria	Conclusion characteristics
Advantage/ Disadvantage (references)	- Determinants used are poorly defined, definitions of exposure are imprecise (Chreely et al., 2005) & often not related to the process (Marquart et al., 2003), leading to inconsistent use (Chreely et al., 2005) & inaccurate outcomes (Cherrie et al., 2003). - The model has not really been updated since it got developed (Cherrie et al., 2003).
Advantage/ Disadvantage (authors' opinion)	° It just considers 2 body parts (Hughson & Cherrie, 2005) → leading to a falsified outcome. ° Due to no updates, the model considers out of date working situations. ° When used now in developing countries it might be more suitable, but there are no reliable data for that assumption.
Conclusion (authors' opinion)	The model is not up to date and not developed for this specific working situation → the reliability of this model is questionable. Moreover, no paper version of the model was found.

List of criteria of the model PHED

PHED

Criteria	General characteristics
Year	2002 (Dosemeci et al., 2002)
Country	Developed by institutes from the USA & Canada (Dosemeci et al., 2002).
Goal	To standardize exposure estimates & to develop a statistical database (Krieger, 1995) for pesticides (Hamey, 2008), in a generic scale (EPA, 1995).
Target group	Regulatory agencies, regulatory groups, & the pesticide industry to evaluate product safety issues (www.epa.gov).
Availability	Computerized version: software system (EPA, 1995). Paper version: available in Dosemeci et al. (2002).
Guidance	Computerized version: user's, evaluation, reporting PHED exposure evaluations, & data entry diskette user's guidance, a handbook on how to install the software (EPA, 1995). Paper version: method & algorithm are described in Dosemeci et al. (2002).
Conceptual basis	Self-reported exposure information on pesticides (questionnaires),& monitoring data from the literature were (EPA, 1995).
Reliability	There are less reliable interpretations and extrapolations (Hamey et al., 2008).
Knowledge required	Computerized version: knowledge about the criteria and their effects on the exposure required (Hamey et al., 2008). Paper version: understanding the description in Dosemeci et al. (2002), & basic math skills are required.
Equipment required	Computerized version: an IBM-compatible computer system, certain amount of capability and memory, a math coprocessor and internet excess is required (EPA, 1995). Paper version: just paper, pen, and calculator.

Criteria	Assessment characteristics
Data required as input	See subchapter 1.4.5.
Type of exposure	Assessment of inhalation & dermal exposure (EPA, 1995).
Dermal exp. pathway	Exposure pathways are not used.
Dermal exp. descriptor	Assessment of the actual exposure (EPA, 1995; CEI, 2007).
Body part	12 body parts considered: head, face, back & front of neck, chest/ stomach, back, upper arms, forearms, hands, thighs, lower legs, feet (EPA, 1995).
Type of substance	Useable for pesticides (EPA, 1995).
Physical state of substance	Useable for liquids & solids (CEI, 2007).
Model updates	Updates were made (EPA, 1995), but modern working practices & equipments are not considered (Hamey et al., 2008). The current platform is no longer supported & has not been available for years (Hamey et al., 2008).
Expected results	The amount of pesticide deposited on clothing, skin, and in the breathing zone (CEI, 2007). Contains data for over 1700 events (Hamey et al., 2008).
Outcome	Quantitative (Krieger, 1995). PHED doesn't use an exposure level ranking (CEI, 2007).

Criteria	Conclusion
Advantage/ Disadvantage (references)	- The exposure studies are older studies (pre-1995), using older application equipment (CEI, 2007). - The current software platform for PHED is no longer supported & not available (Hamey et al., 2008).
Advantage/ Disadvantage (authors' opinion)	° Developed for the agriculture sector but for industrialized countries. ° The algorithm is easy to use, not many assumptions need to be made. ° Scores of the det. are not 100% suitable for the study area Vereda la Hoya.
Conclusion (authors' opinion)	On the one hand the model is targeted at the agricultural sector. On the other hand it is questionable if the model is a good fit for the study area Vereda la Hoya because the model is considered to be out of date and focusing on the pesticide industry rather than on the farmers themselves.

List of criteria of the model RISKOFDERM

RISKOFDERM					
Criteria	**General characteristics**	**Criteria**	**Assessment characteristics**	**Criteria**	**Conclusion characteristics**
Year	2003 (Oppl et al., 2003).	**Data required as input**	See subchapter 1.4.6.	**Advantage/ Disadvantage (references)**	- Targeted at companies of any size, particularly at SMEs (Oppl et al., 2003). - High uncertainty of the input data & the algorithms (Oppl et al., 2003). + The toolkit assumes an evidence-based approach (Goede et al., 2003).
Country	Developed by 15 institutes from 10 different European countries (Auffarth et al., 2003).	**Type of exposure**	Assessment of dermal exposure (Warren et al., 2003).		
Goal	Assessment for regulatory purposes (the registration of new chemicals) & a simple-to-use toolkit for management exposure, in a generic scale (Oppl et al., 2003).	**Dermal exp. pathway**	3 pathways: direct & surface contact, & deposition (Goede et al., 2003).		
		Dermal exp. descriptor	Assessment of potential & actual exposure (Warren et al., 2003).		
Target group	Targeted at employers, safety officers, technical staff & consultants in companies of any size, mostly SMEs (Oppl et al., 2003).	**Body part**	7 body parts considered: hands, arms, head, front and back side of the fuselage, front & back side of the legs (Auffarth et al., 2003).	**Advantage/ Disadvantage (authors' opinion)**	° It got built by praxis based information (which is good) but most of the information is from the industry sector. ° The paper version might be too rudimentary, just 8 determinants are considered. ° Uses DEO units for the task group, it makes the calculation more user friendly but the assumptions are more suitable for the industrialized sector.
Availability	Computer version: available on a CD-ROM or via download from the internet (Oppl et al., 2003). Paper version: described in Oppl et al. (2003), Goede et al. (2003), Oppl et al. (2003).	**Type of substance**	Useable for pure substances & pesticides. It provides assessments only for in-use preparations and not for specific chemicals (Warren et al., 2003).		
Guidance	Paper version: The method & algorithm are described in the above mentioned papers.				
Conceptual basis	It follows the method of Schneider et al. (1999) (Marquart et al., 2003; Goede et al., 2003). 11 existing approaches were analyzed: e.g. COSHH, AUVA work place assessment scheme, GISCODE, TRGS 440, MAL code (Oppl et al., 2003).	**Physical state of substance**	Useable for liquids & solids (Marquart et al., 2003).		
		Model updates	There is a version 1.0 and 2.0 of the model: modification of the equations, better characterization of the boundaries of valid data, & the creation of a more transparent guidance document (TNO, 2006).	**Conclusion (authors' opinion)**	The model is useable for the analysis. However, it is questionable if this method is the best fit.
Reliability	It is not 100% reliable: input data & algorithm are generalized (Oppl et al., 2003).				
Knowledge required	Computer version: the user needs to be trained (Oppl et al., 2003). Paper version: understanding the description of the method & basic math skills are required.	**Expected results**	Comparison of the skin-related hazardous properties, a general recommendation for risk control, & assessment of health risks (Oppl et al., 2003).		
Equipment required	Computerized version: a certain version of windows is needed (http://product-testing.euro ns.com). Paper version: paper, pen, & calculator are needed.	**Outcome**	The outcome is quantitative (Warren et al., 2003). The rating is from 1-10 (little exposure to very high exposure) (Oppl et al., 2003).		

List of criteria of the model STOFFENMANAGER

STOFFENMANAGER

Criteria	General characteristics
Year	2003 (Stoffenmanager, 2009)
Country	Developed in the Netherlands (Tielemans et al., 2008).
Goal	To help SMEs to prioritize potential risks & to indicate the types of exposure control (Marquart et al., 2008), in a generic scale (Tielemans et al., 2008).
Target group	Dutch companies (Marquart et al., 2008).
Availability	A computer version: on the internet (https://www.stoffenmanager.nl).
Guidance	Computer version: on its homepage there is little information. Paper version: the method of the inhalation exposure model (version 3.5) is briefly described in Marquart et al. (2008) but there is no information about the dermal exposure model.
Conceptual basis	The 'hazard banding': based on COSHH. The structure: derived from ChemAudid. The core of the risk banding module is RISKOFDERM. The regulatory requirements of The Netherlands are considered (Marquart et al., 2008). The algorithm: based on Cherrie et al. (1996) and Cherrie and Schneider (1999). The health hazard: based on the health risk phrases (R-phrases) (Schneider, 2009).
Reliability	There is a scope for improvement (Tielemans et al., 2008).
Knowledge required	No information has been found.
Equipment required	For the web-based tool computer and internet excess is needed.

Criteria	Assessment characteristics
Data required as input	See subchapter 1.4.7.
Type of exposure	Assessment of inhalation & dermal exp.. The method used for the dermal exposure model is based on the inhalation one (Schneider, 2009; Marquart et al., 2008).
Dermal exp. pathway	The inhalation exposure method considers the total concentration (near-field + far-field source + background concentration) (Marquart et al., 2008). For the dermal exposure model no information was found on this matter.
Dermal exp. descriptor	Assessment of the potential & actual exposure (Schneider, 2009).
Body part	Assessment of the exposure at the workplace (Marquart et al., 2008).
Type of substance	Useable for pure substances & mixtures (Marquart et al., 2008).
Physical state of substance	Useable for liquid & solids (Tielemans et al., 2008).
Model updates	Computer version: the model was last updated in 2010 (version 4.0) to comply with recent legislations like REACH and EU-GHS (https://www.stoffenmanager.nl/Public/NewsItem.aspx?id=1071).
Expected results	Computer version: hazard, exposure, & risk ranking (Schneider, 2009). It offers risk banding, control scenarios, action plans, workplace instruction cards, information for the storage of substances & explosion safety information (Tielemans et al., 2008).
Outcome	Relative ranking of risks: classification in one of four exposure (priority) bands (Marquart et al., 2008).

Criteria	Conclusion characteristics
Advantage/ Disadvantage (references)	- A branch specific version might be more accurate/reliable than the generic version (Tielemans et al., 2008). - It inherently assumes that exposure is linearly dependent on the fraction of a substance in a mixture (Tielemans et al., 2008). + It is a new instrument but based on previous models. It represents a combination of useful elements from different sources (Marquart et al., 2008).
Advantage/ Disadvantage (authors' opinion)	° It is very industrialized. ° For the agriculture sector a model version is still need to be developed. ° No paper version of the model was found. In Marquart et al. (2008) the method of the inhalation exposure assessment is mentioned.
Conclusion (authors' opinion)	This model is not the best fit to assess dermal exposure in developing countries. It is too specifically developed for the industry sector for the Netherlands. Moreover the electronic version of the model cannot be used.

Appendix Publication 2

PDE results in the different body parts

Descriptives

Potential_Exposure

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Right_Arm_Front	8	2.8088E-6	2.23472E-6	7.90094E-7	9.4048E-7	4.6770E-6	7.73E-7	7.90E-6
Chest	8	7.6894E-6	2.95812E-6	1.04585E-6	5.2164E-6	1.0162E-5	3.16E-6	1.06E-5
Left_Arm_Front	8	1.6265E-6	5.66228E-7	2.00192E-7	1.1531E-6	2.0999E-6	1.06E-6	2.88E-6
Abdomen	8	1.7292E-5	1.64715E-5	5.82357E-6	3.5213E-6	3.1062E-5	3.82E-6	5.29E-5
Right_Thigh_Front	8	4.1075E-5	2.34440E-5	8.28872E-6	2.1475E-5	6.0675E-5	1.33E-5	7.86E-5
Left_Thigh_Front	8	2.5309E-5	1.15972E-5	4.10021E-6	1.5613E-5	3.5004E-5	7.14E-6	4.56E-5
Right_Leg_Front	8	1.9603E-4	6.43690E-5	2.27579E-5	1.4222E-4	2.4985E-4	1.28E-4	2.91E-4
Left_Leg_Front	8	1.7347E-4	8.33817E-5	2.94799E-5	1.0377E-4	2.4318E-4	5.44E-5	3.10E-4
Left_Arm_Dorsal	8	2.3644E-6	1.14419E-6	4.04533E-7	1.4078E-6	3.3209E-6	9.39E-7	4.40E-6
Upper_Back	8	5.7121E-5	3.08805E-5	1.09179E-5	3.1304E-5	8.2938E-5	1.61E-5	1.11E-4
Right_Arm_Dorsal	8	2.5511E-5	4.56037E-5	1.61233E-5	-1.2614E-5	6.3637E-5	3.94E-6	1.38E-4
Lower_Back	8	5.6929E-5	2.96472E-5	1.04819E-5	3.2143E-5	8.1714E-5	6.42E-6	9.11E-5
Left_Thigh_Dorsal	8	3.5075E-5	2.85306E-5	1.00871E-5	1.1223E-5	5.8927E-5	3.30E-6	7.37E-5
Right_Thigh_Dorsal	8	3.7493E-5	2.38120E-5	8.41882E-6	1.7586E-5	5.7400E-5	3.99E-6	7.36E-5
Left_Leg_Dorsal	8	1.6882E-4	8.18036E-5	2.89219E-5	1.0043E-4	2.3721E-4	7.95E-5	2.88E-4
Right_Leg_Dorsal	8	1.4918E-4	1.01032E-4	3.57203E-5	6.4710E-5	2.3364E-4	4.11E-5	3.08E-4
Hands	8	3.9530E-6	4.80252E-6	1.69795E-6	-6.1983E-8	7.9680E-6	2.34E-7	1.47E-5
Total	136	5.8926E-5	7.80319E-5	6.69118E-6	4.5693E-5	7.2160E-5	2.34E-7	3.10E-4

ADE results in the different body parts.

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Right_Arm_Front	8	8.2448E-7	6.76316E-7	2.39114E-7	2.5907E-7	1.3899E-6	5.36E-8	2.03E-6
Chest	8	4.0818E-7	2.61816E-7	9.25660E-8	1.8930E-7	6.2707E-7	1.67E-7	9.92E-7
Left_Arm_Front	8	6.1681E-7	7.56411E-7	2.67432E-7	-1.5566E-8	1.2492E-6	9.12E-8	2.39E-6
Abdomen	8	4.1501E-7	3.08014E-7	1.08899E-7	1.5751E-7	6.7252E-7	1.54E-7	9.46E-7
Right_Thigh_Front	8	1.1555E-7	3.48887E-8	1.23350E-8	8.6378E-8	1.4471E-7	6.69E-8	1.82E-7
Left_Thigh_Front	8	1.0636E-7	2.43351E-8	8.60375E-9	8.6014E-8	1.2670E-7	6.27E-8	1.37E-7
Right_Leg_Front	8	4.8250E-7	4.71599E-7	1.66736E-7	8.8237E-8	8.7677E-7	1.11E-7	1.51E-6
Left_Leg_Front	8	2.6158E-7	1.74258E-7	6.16094E-8	1.1590E-7	4.0726E-7	1.23E-7	6.32E-7
Left_Arm_Dorsal	8	3.6385E-7	3.28852E-7	1.16267E-7	8.8919E-8	6.3877E-7	5.04E-8	1.02E-6
Upper_Back	8	1.1755E-5	1.14280E-5	4.04040E-6	2.2007E-6	2.1309E-5	1.58E-7	3.41E-5
Right_Arm_Dorsal	8	1.6191E-5	1.83902E-5	6.50191E-6	8.1617E-7	3.1565E-5	1.28E-7	4.83E-5
Lower_Back	8	2.9953E-6	2.86903E-6	1.01435E-6	5.9674E-7	5.3939E-6	2.52E-7	8.77E-6
Left_Thigh_Dorsal	8	1.7907E-6	4.32570E-6	1.52937E-6	-1.8257E-6	5.4071E-6	6.55E-8	1.25E-5
Right_Thigh_Dorsal	8	1.3349E-7	1.07221E-7	3.79083E-8	4.3846E-8	2.2312E-7	5.27E-8	3.94E-7
Left_Leg_Dorsal	8	5.6258E-7	5.43627E-7	1.92201E-7	1.0809E-7	1.0171E-6	1.40E-7	1.59E-6
Right_Leg_Dorsal	8	5.6412E-7	6.70904E-7	2.37201E-7	3.2269E-9	1.1250E-6	1.10E-7	2.11E-6
Total	128	2.3491E-6	6.93050E-6	6.12576E-7	1.1370E-6	3.5613E-6	5.04E-8	4.83E-5

PF results in the different body parts

Descriptives

Protection_Factor

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Right_Arm_Front	8	57.0752	34.86839	12.32784	27.9245	86.2259	1.00	99.32
Chest	8	93.6465	4.39887	1.55523	89.9690	97.3240	87.21	98.43
Left_Arm_Front	8	65.0583	32.89800	11.63120	37.5549	92.5617	1.00	94.38
Abdomen	8	95.9153	3.48934	1.23367	92.9981	98.8324	89.44	99.43
Right_Thigh_Front	8	99.5923	.30784	.10884	99.3349	99.8497	99.01	99.91
Left_Thigh_Front	8	99.4228	.46409	.16408	99.0348	99.8108	98.35	99.82
Right_Leg_Front	8	99.7172	.31436	.11114	99.4544	99.9800	99.02	99.96
Left_Leg_Front	8	99.7483	.37177	.13144	99.4375	100.0591	98.84	99.96
Left_Arm_Dorsal	8	86.2489	8.39949	2.96967	79.2267	93.2710	69.82	97.57
Upper_Back	8	71.1804	29.85430	10.55509	46.2216	96.1392	21.40	99.66
Right_Arm_Dorsal	8	43.6285	47.65742	16.84944	3.7859	83.4711	1.00	99.91
Lower_Back	8	91.9141	9.92094	3.50758	83.6200	100.2082	70.44	99.69
Left_Thigh_Dorsal	8	89.8612	24.92875	8.81364	69.0202	110.7021	28.26	99.91
Right_Thigh_Dorsal	8	98.4940	3.38589	1.19709	95.6634	101.3247	90.13	99.93
Left_Leg_Dorsal	8	99.5060	.63678	.22514	98.9736	100.0383	98.42	99.94
Right_Leg_Dorsal	8	99.0896	1.74371	.61650	97.6318	100.5473	94.86	99.96
Total	128	86.8812	25.40650	2.24564	82.4374	91.3249	1.00	99.96

Appendix Publication 3

Transfer coefficients used for the pesticide flow analysis model according to the field measurements of the tracer uranine.

	PDE			ADE			Stock		
Body Parts									
Forearms (n=9)	1.84E-05	±	7.57E-06	1.43E-07	±	8.83E-08	1.83E-05	±	7.48E-06
Arms (n=9)	2.07E-05	±	1.01E-05	6.10E-08	±	4.19E-08	2.06E-05	±	1.00E-05
Chest & Abdomen (n=9)	2.28E-05	±	8.37E-06	8.94E-08	±	5.30E-08	2.27E-05	±	8.32E-06
Back (n=9)	1.53E-05	±	6.24E-06	6.47E-08	±	4.37E-08	1.52E-05	±	6.20E-06
Thighs (n=9)	1.77E-05	±	8.63E-06	7.95E-08	±	5.81E-08	1.77E-05	±	8.57E-06
Legs (n=9)	1.86E-05	±	1.22E-05	1.16E-07	±	6.72E-08	1.85E-05	±	1.21E-05
Hands (n=9)	3.48E-06	±	2.92E-06	1.79E-07	±	1.62E-07	3.30E-06	±	2.76E-06
Total Dermal (n=9)	1.17E-04	±	5.60E-05	7.32E-07	±	5.14E-07	1.16E-04	±	5.55E-05
Inhalation (n=12)	2.31E-08	±	1.80E-08	1.10E-09	±	8.50E-10	2.20E-08	±	1.72E-08
Pesticide Management Activities									
Preparation (n=3)	4.67E-06	±	3.21E-06						
Application (n=9)	1.10E-04	±	5.16E-05						
Cleaning (n=3)	1.92E-06	±	1.18E-06						