ADVANCES IN LIFE CYCLE IMPACT ASSESSMENT OF PESTICIDES: METHODOLOGICAL IMPROVEMENTS AND EXPERIMENTAL STUDIES

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presented by

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FAN CONSTAR:

Que el present trebell que porta per títol:

ADVANCES IN LIFE CYCLE IMPACT ASSESSMENT OF PESTICIDES: METHODOLOGICAL IMPROVEMENTS AND EXPERIMENTAL STUDIES

i que presenta el sr **Ronnie Juraske** per optar al grau de Doctor per la Universitat Rovira i Virgili, ha estat realitzat sota la seva direcció I que tots els resultants presentats I la seva anälisi són fruit de la investigació realitzada per l'esmentat doctorand.

I perque se'n prengui coneixement I tingui els efectes corresponents, signen aquenst certificat

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Abstract

The overall goal of this dissertation is to contribute to the development of best available practice in fate and the exposure assessment of pesticides for evaluating their impacts on human health and ecosystems. Environmental models used in Life Cycle Impact Assessment (LCIA) and Environmental Risk Assessment (ERA) relate emissions to impacts by combining fate and exposure estimates with toxicological assessment data. Pesticides released to air, water, soil and plants enter the human body through food commodities, particularly through the ingestion of edible parts of plants. Therefore, specific methods to assess the presence of residues in agricultural products are of importance for human exposure assessment. This raises the following questions:

1. How can the fate (from air and soil) of pesticides in/on plants cultivated in greenhouses be measured and modelled? How does dynamic behaviour affect the final residues in edible parts of plants?
2. How can the degradation of pesticides on plant surfaces and within plants be measured and modelled?
3. How can a substance specific half-life in/on plants be estimated from soil degradation data?
4. How can a risk indicator for comparative assessment of pesticides be developed using fate, exposure, and toxicity characteristics?

After a short introduction to environmental assessment approaches and the specific problems related to the application of pesticides and their characteristics in *Chapter 1*, *Chapter 2* proposes an approach for modelling pesticide residues in greenhouse tomato plants. This fate and exposure model considers the time between pesticide application and harvest, the time between harvest and consumption, the absorption of spray deposit on plant surfaces, transfer properties through the cuticle, degradation inside the plant and loss due to food processing. The model is validated with experimental data which was obtained from field trials. Human intake fractions of pesticides due to ingestion of tomatoes representing a realistic scenario of human exposure to pesticide residues in foods are presented.

In *Chapter 3*, two generic estimation routines for substance specific half-lives of pesticides (i) on plant surfaces and (ii) within plants to be used in fate and exposure models are presented. First, an extrapolation routine for the estimation of pesticide half-lives on plant surfaces based on a conversion factor from half-lives of pesticides in soil is proposed. Furthermore, a tentative estimation method for the calculation of metabolism half-lives of pesticides in inner parts of plants based on experimental data is presented.

Chapter 4 presents a follow-up of *Chapter 2* and *Chapter 3*. Previous results are combined with new experimental assessment to measure the uptake, translocation and persistence behaviour of pesticides in tomato fruits treated by (i) standard foliar spray application and (ii) soil application using direct localised drip irrigation into root zone. A dynamic root uptake model for pesticides aiming at the estimation of time dependent contaminant concentrations in fruits is proposed. Finally, experimental results are compared with model estimates in terms of human population intake fractions of pesticides. These investigations aim to evaluate the environmental performance of pesticides when the same active ingredient is applied to crops by different application techniques.

Chapter 5 illustrates the development of a new method entitled PestScreen, to calculate the relative risk level of pesticides with the aim of ranking them from lowest to highest degree of concern. The approach is an estimation method of relative risk levels and allows comparing environmental and human health risks of specific pesticide types through their ranking. The method is developed to serve as an analytical tool in screening and identification of pesticides of environmental concern used in agriculture. PestScreen incorporates both the toxic effects of pesticides and their fate and exposure characteristics in different compartments of the environment. This is done by combining measures of chemical toxicity pertaining to both human health and the environment with chemical release amounts and information on overall environmental persistence, long-range transport potential and human population intake fractions. In *Chapter 6* the most important results are summarized and recommendations for further research are discussed.

Resumen

El objetivo principal de esta tesis doctoral es el de contribuir al desarollo y evaluación en la aplicación y exposición de pesticidas en plantas y su impacto sobre la salud humana y los ecosistemas. Los modelos ambientales usados para la evaluación de impacto en el análisis de ciclo de vida y en analisis de riesgo ambiental relacionan las emisiones con su impacto, combinando el destino y la exposición estimada y relacionandolo con información toxicológica. Los pesticidas liberados en aire, agua y suelos llegan al cuerpo humano a través de los alimentos, principalmente por la ingestión de las partes comestibles de los vegetales. Por dicha razón, es de gran importacia el desarollo de métodos para el análisis de residuos tóxicos en productos agrícolas. De aquí emergen las siguientes preguntas:

1. ¿Como puede ser modelada la cantidad residual y el lugar de destino de los pesticidas aplicados por aire en los invernaderos? ¿Cual es su compotamiento dinámico y como afecta la concentración residual en las partes comestibles de los vegetales?
2. ¿Como puede medirse y modelarse la degradación de los pesticidas tanto en superficie como en el interior de vegetación?
3. ¿Como puede hacerse una estimación de la vida media específica tanto en superficie como en el interior de vegetales partiendo de la información de degradación en el suelo?
4. ¿Como puede desarollarse un indicador de riesgo con el cual se puedan analizar comparativamente pesticidas basado en el lugar de aplicación, tiempo de exposición y características toxicológicas?

Después de una breve introdución al análisis medioambiental y los problemas específicamente relacionados con la aplicación de pesticidas y sus características en el capítulo uno, en el capítulo dos se propone un acercamiento a través del modelado de residuos de pesticidas en tomates cultivados en invernadero. Este modelo de destino y exposición tiene en consideración el tiempo transcurrido entre la aplicación, la cosecha y el consumo, la absorción del spray depositado en la superficie de las plantas, las

propiedades de transporte a través de la cutícula, la degradación en el interior de la misma planta y perdidas debido al procesado del alimento. El modelo fue validado usando datos experimentales obtenidos a partir de ensayos de campo. También se presenta la fracción de pesticida ingerido por humanos debido al consumo de tomate mostrando un escenario realista de la exposición humana a estos productos.

En el capítulo tercero se presentan dos algoritmos genéricos para la estimación de (i) la vida media específica de pesticidas en superficie y (ii) en el interior de las plantas, usados en el modelo de destino y exposición. También se propone una rutina de extrapolación para estimar la vida media de plaguicidas en superficie, basándose en un factor de conversión cuya base de cálculo parte de la vida media de estos en suelos. Más adelante se presenta un método de estimación tentativa para el cálculo de la vida media de pesticidas en el interior de las plantas, básandose en datos experimentales.

El capítulo cuatro es una prolongación de los capítulos dos y tres. Los resultados antes obtenidos, se combinan aquí con un nuevo método de análisis experimental para medir absorción, transporte y persistencia de pesticidas en tomates tratados por (i) spray foliar estándar y (ii) aplicación en raíces por riego por goteo. Un modelo dinámico de absorción de pesticidas por raíz trata de estimar la dependencia temporal de la concentración del contaminante en los frutos. Finalmente, los resultados experimentales son comparados con el modelo en terminos de ingestión de fracción de pesticida por parte de la población humana. En esta investigación se intenta evaluar el comportamiento medioambiental de los pesticidas comparando los diferentes métodos de aplicación de un mismo ingrediente activo.

El capítulo cinco ilustra el desarollo de un nuevo método llamado PestScreen, el cual calcula el nivel relativo de riesgo de pesticidas con el fin de clasificarlos ascendentemente dependiendo de su impacto. Esta aproximación es un método de estimación del nivel relativo de riesgo y permite comparar la peligrosidad tanto a nivel de salud humana como de impacto medioambiental, de diferentes tipos de pesticidas, a través de una categorización. Este método se desarolla como una herramienta para la evaluación e identificación de pesticidas con peligrosidad medioambiental usados en la agricultura. PestScreen incorpora tanto su efecto tóxico como su destino y exposición en varios compartimentos medioambientales. Esto se realiza combinando medidas de toxicidad química con la cantidad liberada, la persistencia medioambiental, el potencial de transporte en un radio amplio y la fracción ingerida por la población humana. En el capítulo seis los principales resultados son presentados y resumidos, finalmente se sugieren recomendaciones para investigaciones futuras.

Chapter 1

General Introduction

1. Introduction

Pesticides are applied to agricultural land to protect crops and plantation from probable pests, diseases, and weeds that might decrease productivity. It is well known that pesticides, having become indispensable elements of modern agriculture, are considered significant sources of diffuse pollutants that cause health implications upon living organisms including humans. Plant protection products are an integral part of cropping systems, helping to realize the full yield potential of crops and thus contributing to food supply (Geisler et al., 2004). Around 90% of all plant protection products sold in the European Union are used in agriculture in the production of various types of products such as fruits, vegetables, and cereals. The use of pesticides in agriculture is subject to steady observation due to the risk for human toxicity and environmental ecotoxicity. This thesis is focused on agricultural use of pesticides in the production of temporary crops such as greenhouse tomatoes, it is a contribution to the development of methods to assess the fate and exposure of plant protection products, in particular the presence of residues in agricultural commodities, according to the frame of Life Cycle Assessment methodology.

1.1 Characteristics and history of pesticides

A pesticide is "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest" (FIFRA 1947). Pesticides are used in various economic sectors, such as agriculture, forestry, transport (railroads), industrial zones, parks and households (gardens). Among these sectors, however, agriculture is by far the main user (approx. 90% of all pesticides sold) (Brouwer et al. 1994). Based on the target-organism group, pesticides of agricultural importance can be broadly categorised as:

- Herbicides (for weed control),
- Insecticides (for insect control),
- Fungicides (for fungal pathogen control),
- Others (such as nematicides, bactericides, rodenticides).

Other compounds such as plant growth regulators do not kill any organisms, but are used in agriculture in the same way as pesticides. Pesticides may be organic or inorganic compounds. Organic pesticides belong to a variety of substance classes, including N- and P-containing substances. Based on their chemical family, the different molecules of organic pesticides may be grouped into classes, such as phenoxy- or thiocarbamate compounds. By contrast, inorganic pesticides are copper-containing products, or, to a lesser extent, zinc- and mercury-based compounds.

Most modern synthetic organic pesticides are manufactured entirely from intermediates derived from fossil fuels. Primary pesticide manufacturing conventionally entails several process steps involving a variety of unit operations such as heating, stirring, distilling, filtering, drying and similar processes to build up a biologically active chemical entity from raw materials and/or specific chemical intermediates (Bhat et al., 1994). Secondary processing involves the formulation of the pesticide in a marketable form, such as wettable powders, dusts, emulsifiable concentrates, granules, etc. This normally involves purely physical operations such as vessel charging, mixing, milling, warming, cooling, product transfer, granulation, drying, sieving and packaging. No chemical reactions take place during secondary processing.

Pesticides are intended to kill unwanted organisms. Most act by interfering with a variety of biochemical and physiological processes that are common to a wide range of organisms. Besides target pests, weeds and fungi, they also affect wildlife and human health. Some can be lethal, and many can cause illness at sub-lethal levels. But the risks differ greatly from pesticide to pesticide. Some are acutely toxic but produce no long-term effects, whilst others are of long-term health or environmental concern. Much of the information on these side-effects of pesticides remains contested, and so there is no agreement about how much harm they cause.

Pesticides are approved according to a precise use and in so far as no secondary damaging effects appear in humans, animals and the environment. Experts come to a conclusion about the approval according to data describing the spectrum of action of these substances and their behaviour in the environment. Maximum concentrations are established for food products. This authorization includes the conditions of use and application techniques (concentration), the time of application and the delay of harvest (time elapsed between treatment and harvest).

Residues are tolerated below a given level of risk for health and if technically unavoidable. Therefore a maximum concentration of residue is set for each substance and agricultural commodity according to good agricultural practice provided that the concentration lies under the toxicological limit. The maximum concentration is established by the degradation rate of the substance and the time lapse between treatment and harvest. The toxicological justifiable value corresponds to the acceptable daily intake of the substance for a human (ADI). This threshold is based on the dose of substance with no observed adverse effect (NOAEL) on animals and with a safety factor. In practice, supplemental security is given by the fact that the real residue level and the eventual exposure to human health is largely under the established acceptable daily intake. Consequently the user of plant treatment products applying good agricultural practices is assured to harvest products with a concentration of substance that does not exceed the commercially legal tolerable value. From the moment when a product is approved, official information available for the use of substances includes the domain of application (type of crop, targeted organism), some technical indications (concentration, technique of use, some indications for restricted annual use), the moment of application and the delay before harvest, the tolerable maximum concentration of substance in and on food products, the toxicological class of the substance, and general indications for the use and risks of toxic substances (Charles, 2004). According to the legislative framework, no residue of pesticide is found higher than the tolerable amount under conditions of good agricultural practices. However, neglecting unilateral prohibition of products, even lower concentrations of substance in harvested products may be required for specific environmental initiatives, for particular requests of consumers (e.g. labels) or for a wide-ranging effort to minimise the presence of even harmless residues in food. Admitting the hypothesis that residues are in principle undesirable, there is no admitted threshold below which the presence of a substance should not be considered. Consequently, the presence of residues in food becomes relevant under the legal maximum tolerable concentration. However, the presence of residue does not by itself explain the toxicity of a product. It is necessary to also take into account the exposure and the toxicological effect to effectively minimise the risk of toxicity.

Pesticides are not modern inventions, as they have long been used to control pests and diseases in agriculture (Carson, 1963; Conway and Pretty, 1991; Cremlyn, 1991; Dinham, 1993; van Emden and Peakall, 1996). In 2500 BC the Sumerians used sulphur compounds for insect control. Later, seeds were treated by Chinese farmers with various natural organic substances to protect against insects, mice and birds, whilst inorganic mercury and arsenic compounds were used to control body lice. The Greek and Roman writers Aristotle, Homer and Cato describe a variety of fumigants, oil sprays and sulphur ointments used by farmers, and Pliny recommends the use of arsenic as an insecticide. However, natural pesticides did not come into common use until the agricultural revolution of 17th–18th century Europe. Nicotine was used in the 1600s, and was followed by the discovery of the wood preservative properties of mercuric oxide in the early 1700s, and of the fungicidal properties of copper sulphate in the early 1800s. By the mid-19th century, rotenone from the roots of derris and pyrethrum from chrysanthemum flowers had been discovered, and these were accompanied by a rapid growth in the use of inorganic products, particularly of arsenic. Paris Green (copper arsenite) was first used in 1867, coming into such common use by the early 20th century in the US that it led to the world's first legislation to control pesticides. Bordeaux mixture (copper sulphate and lime) was discovered to be effective against powdery mildew in 1882. The local custom in France was to treat roadside vines with the mixture to prevent theft, and it was noticed that these vines also escaped infestation with the disease.

The early part of the 20th century saw the increased use of many dangerous products derived from arsenic, cyanide and mercury. Most were broad-acting in their effect on pests and diseases. Some, such as iron sulphate, were found to have selective herbicidal properties against weeds. Calcium arsenite came to replace Paris Green, and by the

1920s arsenic insecticides were in widespread use. This provoked considerable public anxiety about residues of these products on fruit and vegetables.

Against this disturbingly toxic background, the 1930s saw the beginning of the era of synthetic organic products. This decade saw the introduction of alkyl thiocyanate insecticides, the first organic fungicide, salicylanilide, dithiocarbamate fungicides, and later chloranil, before Paul Muller made the remarkable discovery in 1939 of the insecticidal properties of DDT (dichlorodiphenyltrichloroethane). It was first manufactured in 1943, and was initially valuable for delousing people to prevent the spread of typhus, and for the control of malarial mosquitoes. DDT was soon followed by the manufacture of several chlorinated hydrocarbon compounds, including aldrin, endrin, heptachlor, and the recognition of the herbicidal activity of phenoxyacetic acids, such as MCPA and 2,4-D. At that time, all of these synthesized products were valued for their persistence in the environment.

Organophosphates (OPs) emerged from wartime research on nerve gases. The first product that came into commercial use was parathion, an effective insecticide that was soon also found to be highly toxic to mammals. Malathion then came into wider use after 1950, as it had very low mammalian toxicity. OPs block cholinesterase, the chemical that transfers nerve impulses across synapses, and so their effect is primarily on the nervous system. The advantage of the OPs is that they are rapidly degraded in the environment to non-toxic secondary compounds – unlike the organochlorines (OCs). In a very short time, both OCs and OPs were being used in most countries of the world and on almost every crop. The immediate benefits were obvious, but it gradually became apparent that many of these new products also had severe drawbacks. They were affecting wildlife and people in ways that had not been anticipated. Later generations of pesticide products included the carbamates and synthetic pyrethroids. With some exceptions, these products were generally relatively less toxic to humans compared to the previous generation of OPs and OCs.

Over time, pesticide products have tended to become less broad-ranging in their effects and more targeted towards pests, weeds or diseases. However, such specificity does come at a cost. Broad-effect pesticides are both cheaper to manufacture and can be sold to more farmers. Specific products inevitably have smaller markets. However, a large number of new pest management technologies have become available in recent years, many using the term agrobiologicals. These products are mostly available only in OECD countries and a few developing countries, such as China and India.

1.2 Use of pesticides

Roughly 2.6 million tonnes of active pesticide ingredients with a market value of $US 38 billion were used worldwide in 1995. Europe, North America and Japan together account for three quarters of the world's pesticide consumption, with herbicides predominating (WRI 1998). The remaining one quarter is consumed in developing countries, where a large variety of pesticides no longer used in the developed nations is still being applied. Between 1950 and the end of the 1980s, pesticide use increased more than thirty-fold. In the 1990s, pesticide use showed a decreasing trend in developed countries (on the basis of the weight), partly as a result of the introduction of new, more-powerful chemicals that are used in much smaller quantities (Harrison & Pearce 2001). By way of comparison, annual sales of agricultural pesticides in the EU came to about 320,000 tonnes of active ingredients with a total value of around € 6 billion in 1999 (EC, 2002). Fungicides accounted for 41% of the total weight of active ingredients, followed by herbicides (39%) and insecticides (12%) (Lucas & Vall, 1999). Although the use of pesticides in absolute terms is dropping (the sales in the EU decreased about 8% between 1991 and 1996), this is not necessarily linked to a decrease in pesticide intensity, as the application rate of newer pesticides can be very low (Sattler et al., 2007). In the European Union alone, more than 700 different active ingredients are licensed (Stenzel 2001). About 6,000 different pesticides are used worldwide.

The global use of all pesticide products is highly concentrated on a few major crops, with some 85% by sales applied to fruit and vegetables (25%), rice (11%), maize (11%), wheat and barley (11%), cotton (10%) and soybean (8%) (UK Crop Protection Association, 2001). There is also considerable variation from country to country in the kinds of pesticide used. Herbicides dominate the North American and European domestic markets, but insecticides are more commonly used elsewhere in the world. In the US in the late 1990s, 14 of the top 25 pesticides used are herbicides (by kg a.i.). Glyphosate and 2,4-D were the most common products used in domestic and industrial settings (Environmental Protection Agency (EPA), 2001). In Asia, 40% of pesticides are used on rice, and in India and Pakistan, some 60% are used on cotton. India and China are the largest pesticide consumers in Asia. Pesticide consumption in Africa is low on a per hectare basis.

1.3 Life Cycle Assessment methodology

Life Cycle Assessment (LCA) is a tool to evaluate the environmental performance of products (SETAC, 1993; UNEP, 1996). LCA focuses on the entire life cycle of a product: from the extraction of resources and processing of raw material, through the manufacture, distribution, and use of the product, to the final processing of the disposed product. Environmental problems are associated with impact categories where the magnitude of the potential impact is determined. Through all these stages, extractions and consumptions or resources (including energy) and releases to air, water and soil are identified and quantified. Subsequently, the potential contribution of these resource extractions and consumptions, and environmental releases to several important types of environmental impact are assessed and evaluated (Curran, 1996).

The technical framework for the Life Cycle Assessment methodology has been standardised by the International Standards Organization (ISO). According to ISO 14040 (1997, 2006) LCA consists of four phases, as presented in Figure 1:

1. Goal and Scope Definition
2. Inventory Analysis
3. Impact Assessment
4. Interpretation

These phases are not simply followed in a single sequence. It is an iterative process, in which subsequent iterations (rounds) can achieve increasing levels of detail (from screening LCA to full LCA), or lead to changes in the first phase prompted by the results of the last phase. The Life Cycle Assessment has proven to be a valuable tool to document the environmental considerations of product systems that need to be part of decision-making towards sustainability. Products mean here goods and services.

ISO 14040 (1997, 2006) provides the general framework of LCA. ISO 14044 (2006) provides guidance for determining the goal and scope of an LCA study, and for conducting a life cycle inventory. It also provides information about the life cycle impact assessment phase, and furthermore provides guidance for the interpretation of results from an LCA study. Moreover, technical guidelines exist that illustrate how to apply the standards.

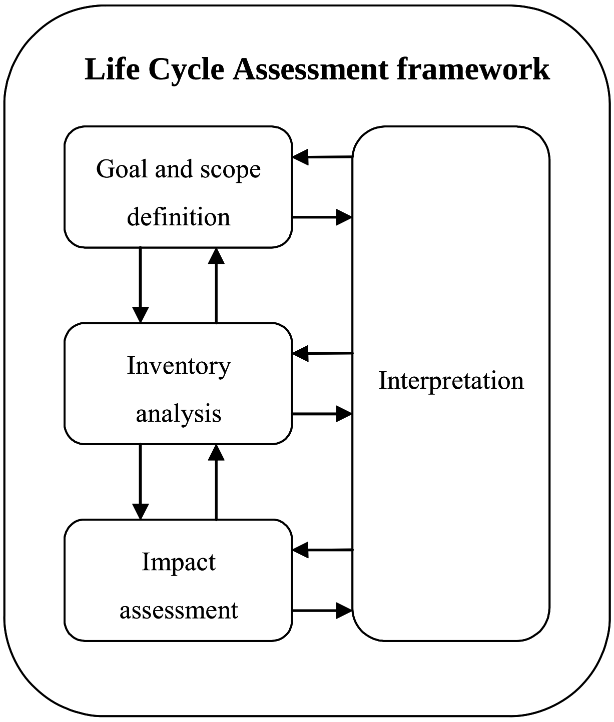

Figure 1. The phases of LCA according to ISO 14040

The first step in LCA is the Goal and Scope Definition phase which is designed to obtain the required specifications for the LCA study: What questions do we want to answer and who is the intended audience? The following steps must be taken:

1. *Defining the purpose of the LCA study*, ending with the definition of the functional unit, which is the quantitative reference for the study.
2. *Defining the scope of the study,* which includes the drawing up of a flowchart of the unit processes that constitute the product system under study, taking into account a first estimation of their inputs from and outputs to the environment (the elementary flows or burdens to the environment).
3. *Defining the data required*, which includes a specification of the data required both for the Inventory Analysis and for the subsequent Impact Assessment phase.

For LCA studies in the agricultural sector this could be for instance to investigate the environmental impacts of different intensities in crop production or to analyze the advantages and disadvantages of intensive or extensive arable farming systems.

The Inventory Analysis collects all data of the unit processes of the product system and relates them to the functional unit of the study. The following steps must be taken:

1. *Data collection*, which includes the specification of all input and output flows of the processes of the product system, both product flows (i.e. flows to other unit processes) and elementary flows (from and to the environment).
2. *Normalisation* to the functional unit, which means that all data collected are quantitatively related to one quantitative output of the product system under study, most typically 1 kg of material is chosen, but often other units like a car or 1 km of mobility are preferable.
3. *Allocation*, which means the distribution of the emissions and resource extractions of a given process over the different functions which such a process, e.g. petroleum refining, may provide.
4. *Data evaluation*, which involves a quality assessment of the data, e.g. by performing sensitivity analysis.

The result of the Inventory Analysis, consisting of the elementary flows related to the functional unit, is often called the "Life Cycle Inventory table".

The inventory analysis provides a matrix of emission related to the considered product. For that purpose, all the emissions occurring in different places at different times are added up per substance. It is then determined which emission contributes to each impact category. The impact categories (also called Midpoint categories) are presented in Figure 2.

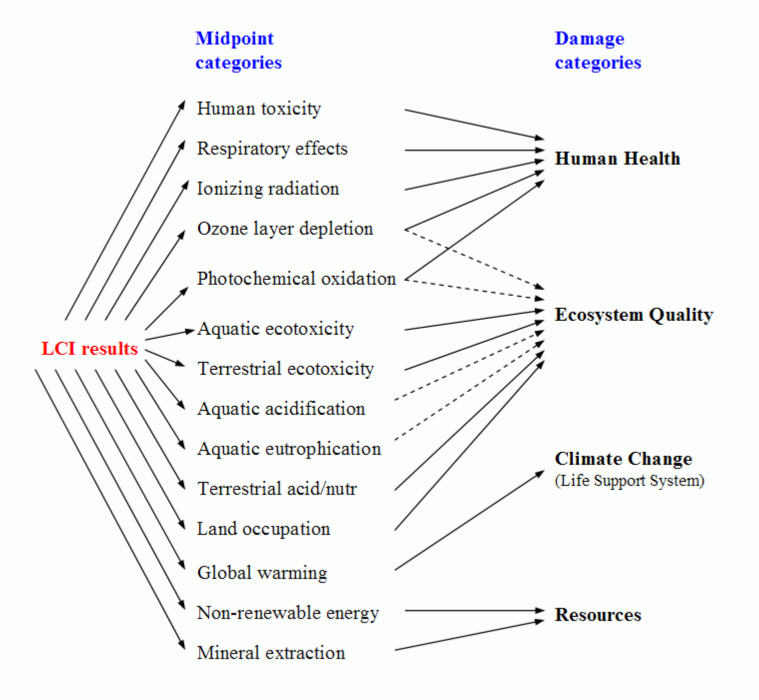

Figure 2. Overall scheme of the LCIA framework, linking Life Cycle Impact (LCI) results via the midpoint categories to damage categories (Jolliet et al., 2003)

After each substance has been linked to one or more categories, the emissions inventory data are multiplied by characterisation factors to provide indicators in the context of various impact categories (like the Midpoint categories presented in Figure 2). Characterisation factors therefore express the relative importance of emissions in the context of a specific environmental impact category (Margni 2003).

Nevertheless, as mentioned by Pennington et al. (2004), LCA is a comparative assessment methodology. Inconsistencies in the assessment can introduce unintentional bias. Direct adoption of regulatory methodology and data is not always appropriate. Regulatory methods and data, again particularly in toxicological risk assessment, are not always developed for use in a comparative context. A conservative estimate of the toxic effect of a substance is unwanted in this relative comparison context. Best-estimates are desirable in LCA, with the need to account for uncertainties when making distinction amongst results.

The Impact Assessment phase aims to make the results from the Inventory Analysis more understandable and more manageable in relation to human health, the availability of resources, and the natural environment. To accomplish this, the inventory table will be converted into a smaller number of indicators. The mandatory steps to be taken are:

1. *Selection and definition of impact categories*, which are classes of a selected number of environmental impacts such as global warming or acidification.
2. *Classification*, comprising the assignment of the results from the Inventory Analysis to the relevant impact categories.
3. *Characterisation*, which means the aggregation of the inventory results in terms of adequate factors, so-called characterisation factors, of different types of substances in the impact categories, therefore a common unit is to be defined for each category, the results of the characterisation step are entitled the environmental profile of the product system.

The Interpretation phase aims to evaluate the results from either Inventory Analysis or Impact Assessment and to compare them with the goal of the study defined in the first phase. The following steps can be distinguished:

1. *Identification* of the most important results of the Inventory Analysis and of the Impact Assessment.
2. *Evaluation* of the study's outcomes, consisting of a number of the following routines: completeness check, sensitivity analysis, uncertainty analysis and consistency check.

3. *Conclusions, recommendations and reporting*, including a definition of the final outcome; a comparison with the original goal of the study; the drawing up of recommendations; procedures for a critical review, and the final reporting of the results.

The results of the Interpretation may lead to a new iteration round of the study, including a possible adjustment of the original goal.

1.4 LCA of agricultural systems

The life cycle assessment method was first developed to assess the environmental impacts of industrial processes. In terms of their impact on the environment, agriculture and industrial processes differ in some important respects:

- Agricultural production is dependent on soil, water availability, the weather, and the presence or absence of weeds, insect pests and pathogens. For these reasons, yields can vary greatly from year to year.
- Agricultural production relies heavily on natural resources as solar energy.
- There is a strong seasonality of agricultural production in most regions, which depends on temperature and the availability of water.

Various adaptations were necessary in order to apply the LCA method to agricultural systems. These questions which concern the aspects of system boundaries, allocation, and environmental impacts were addressed by Sleeswijk et al. (1996), Audsley et al. (1997), Hauschild (2000), FAL (2002) and others.

In order to analyze agricultural products, the environmental impact of the product itself and the entire production system to produce it should be investigated. For crop production not only on-field activities but also all impacts related to the production of farm inputs, such as emissions and resource consumption due to the production of fertilizers, are included. All impacts are related to one common unit (e.g. 1 kg of tomato fruits) and summarized into environmental effects (such as climate change or acidification) or even aggregated into a summarizing environmental index. Such an index allows the ranking of different product or production alternatives according to their overall environmental performance. International Organization for Standardization (ISO) and Society for Environmental Toxicology and Chemistry (SETAC) provide a general description of the LCA methodology. However, the impact assessment procedure, the aggregation methods for the different impact categories and the final calculation of a summarizing environmental index are still in debate. Furthermore, if currently available LCA applications are used to investigate agricultural products or processes, the methods reveal some shortcomings, such as the missing integration of impacts relevant to agriculture (e.g. land use, resource consumption; Brentrup et al., 2001).

High yielding production systems maximising yield with large fertiliser supplies and crop protection interventions are economically advantageous in many European agricultural areas. On the other hand these high intensive systems are usually recognised for exposing the environment to damaging nitrogen, phosphorous and pesticides emissions. However, the "apriori" thinking that a low intensity crop is environmentally favourable is questioned regarding the reduction in productivity, which could simply lead to pollution shifting to other regions. As cultivation practices generally refer to a complex cropping system, these different factors interact and a combined assessment is therefore necessary. Best combination between agricultural inputs and land utilisation should therefore be explored together to design best production strategies on an environmental point of view. High intensity level is potentially favourable per ton of product (with constant quality), when demonstrating sufficient yield increase. On the other hand environmental impact per ton of product increases with intensification if agricultural inputs are not satisfactorily combined or more generally if the intensity level exceeds the production potential. In addition, impact per hectare increases with intensification for all environmental categories except land utilisation, showing that less intensive crops have to be considered for predominantly a land upkeep function. Thus pesticide or fertiliser use cannot be assessed alone, but as a whole with the rest of the system. Further studies about different utilisation strategies of lower production area due to higher productivity should measure the real impact of different intensity levels.

As introduction to this present study on pesticides, an LCA was completed to identify the key parameters of agricultural systems from an environmental point of view and for the role of pesticides (Antón, 2004; Antón et al., 2004). An environmental assessment of tomatoes was performed to optimise agricultural intensity of arable production systems, quality of agricultural products and environmental damages. To assess and compare different intensities of production, adequate functional units were developed to measure main functions of agricultural activity: production and upkeep of farmland. These methodological developments were applied to fertilisation as a factor determining the intensity of production and the quality of the products. Environmental assessment in agriculture has the particularity that the activity has a multifunctional role and evolves in a complex system close to the environment. Consequently the risk is high that the assessment is biased by reduction of system boundaries, the scenario definition, the choice of the functional unit and the considered impact indicators. The interactions between production inputs and yield are important, with influence on quantity and quality. The following elements of this study provide a better understanding of the methodology of LCA in agriculture and introduce the development of different methodologies to assess the fate and exposure of pesticides.

1.5 Pesticide assessment in LCA

There are several reasons why pesticides as a substance group need special attention in the Life Cycle Assessment of agricultural products. Firstly, they are distinguished by the fact that most other chemicals reach the environment as an unintentional consequence of their application, pesticides are spread on purpose in parts of the biosphere to control certain life forms. Secondly, pesticides have been designed to have strong and rather specific effects on selected groups of organisms in the environment while chemicals at large often have weaker and more unspecific effects. Thirdly, the use of pesticides is one of the main differences between conventional and organic agriculture.

Most agricultural production relies on the use of plant protection products to maintain high crop yields. Consequently the need for consistent environmental assessment methodologies is particularly required for pesticides on behalf of good reliability and admittance of these methods. Analytical processes usually perform the evaluation of pesticide residue in agricultural commodities. These analyses are often limited to the capacity of sampling and to high concentrations. Complementary or alternative approaches to the analytical ways are necessary to enlarge the possibilities for the evaluation of pesticide occurrence. According to this, the modelling of pesticide fate in agricultural production constitutes a challenge to be addressed. Modelling of pesticide residues is in continuous development in the frame of ecotoxicity assessment. These methods focus on the fate of substances in environmental media. Different methods effectively propose to evaluate the fate of pesticides and the risk of occurrence in the environment and in food. Most models including fate processes involved in the transfer of pesticides in the environment are specialised in a specific medium. Detailed processes included in these models complicate the distinction of main variables and their integration in multi-media models. In the frame of LCA methodological developments, we first need to identify the main processes and quantify the determining factors and variations. Consequently, normalised conditions for media and pollutants characteristics are generally adopted.

Different methods already offer an approach for the evaluation of residue in agricultural commodities. These approaches are often shortcuts from the environment to the food chain. Part of actual methods to assess pesticides in LCA can be qualified as partial, because they are based only on applied quantity (Goedkoop, 1995) or on toxicological data (Heijungs, 1992). Other methods (Jolliet and Crettaz, 1997, Jolliet, 1998, Huijbregts et al., 2000) propose to take into account fate and effect, and so are more adapted to LCA requirements and to overall comparison of different products. Margni et al. (2002) developed an approach for a full-fate analysis of pollutants through different media and pathways with impact on human health and ecosystems. They calculated that pesticide residues in food caused the highest toxic exposure, higher than consumption of drinking water or inhalation. Due to lack of available information, it was assumed that the pesticide concentrations in food correspond to the 5% of their respective tolerance value. They considered it was a priority to get better estimates of pesticide residues in food. Further study is needed to better quantify the concentration in agricultural products directly exposed to pesticides. For LCA, cumulative risk and potential impact per kg of emission (so called characterization factors) are traditionally calculated by combining cumulative chemical intake with risk-based effect factors.

Different environmental models refer to xenobiotics behaviour in vegetation. These models are first intended to assess fate of contaminants in the environment and are generally running in steady state models. They include some vegetation parameters for agricultural soils and can be used to determine pollutants concentration in vegetation as a function of concentrations in the environment. A one-compartment vegetation model, by Trapp and Matthies (1995), combines principal processes between the environment and plant. Hung and Mackay (1997) describe processes of vegetation uptake from soil and air involved in a three compartments system. Severinsen and Jager (1998) developed a vegetation sub-model to complete multimedia models. They show the influence of this added compartment on the environmental fate of xenobiotics on a regional scale. Cousins and Mackay (2001) presented parameters needed to include vegetation compartments in multi-media models and to identify chemical property ranges to measure the opportunity to take vegetation into account in multi-media models. These multi-media models do not accurately assess chemicals in agricultural systems. Specific dynamic processes occur during the use of plant treatment products from crop sowing to harvest time. However, part of the process relating a chemical’s fate between environment and plant is similar in environmental multi-media models and in agricultural systems.

Methodological hypothesis need specific improvements for fate and exposure assessment of pesticides in agricultural systems. However, most of these methods assume steady state conditions in the environment. The problem of the steady state assumption is that impact assessment based on non-linear dose-response curves is difficult to apply since neither the actual concentration increase nor the changes in the background concentration can be predicted (Hellweg, 2000). With the steady state assumption, all temporal aspects are omitted from the analysis. The implicit underlying assumption is that it does not matter when impacts occur. Dynamic models are much more complicated to apply and have not been used extensively in LCA so far. However, with temporally differentiated inventory data for foreground processes, dynamic models would have the big advantage of allowing an assessment of concentrations and emissions as a function of time (Hellweg, 2000; Margni, 2003). Although such models would enhance the complexity of LCA, the effort might be justified in applications such as agricultural production where temporal factors are crucial for the environmental assessment.

Once applied, pesticides are distributed between air, soil and plant, depending on crop development at the moment of pesticide application and on active ingredient behaviour. The uptake of pesticide sprayed directly on the plant represents a specific agricultural process, different from particle deposition on plant surfaces and uptake by plant tissue described by previously mentioned multi-media models. Other pathways for pesticide uptake, from the air and from the soil are generally included in environmental models. They represent the other fraction of pollutant sources in agricultural plants. The respective contribution to these different sources can vary greatly, as a function of crop stage at application time, vegetation development and available quantity.

Next to uptake processes, pesticides are translocated, diluted and degraded in different physiological organs of the growing plant. All these processes must be included in a dynamic solution so that stage of growth at spray application and time gap between application and harvest are taken into account. Main differences in chemical accumulation must be explored between plant organs according to harvested parts. The choice of determinant transport processes according to LCA and a multi-media development framework are necessary to use key parameters for pesticide characterisation, to avoid unnecessary complexity. These points have been addressed by Charles (2004) by identifying the main processes responsible for the transfer of substances applied directly on plants and in the near environment and for the dynamic behaviour of substances in plant systems.

Figure 3 presents the impact assessment of pesticides in LCA. It can be divided into four parts. Fate modelling relates the emission in the Life Cycle Inventory with the increase in concentration in a given medium. The impact model includes three parts, the exposure model which quantifies the amount of substances absorbed by the organism depending on the concentration in the different media, the impact model that relates the amount absorbed to the effect on the organism, and the damage model translating the effect on the organisms in a change integrated over time and space for a group of organisms (humans or biodiversity).

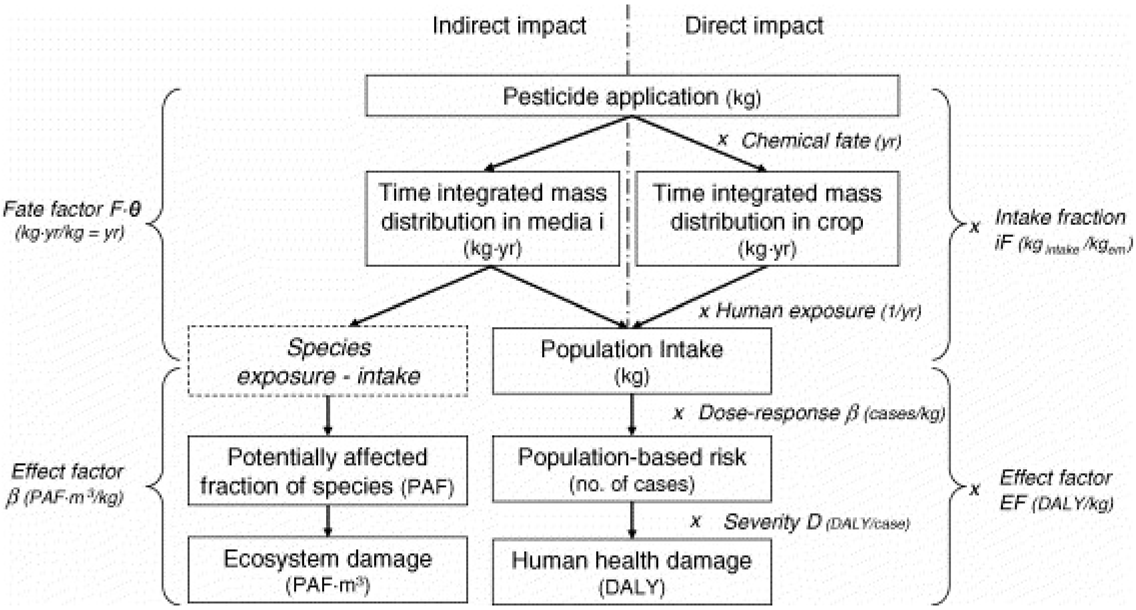

Figure 3. General framework for assessing the human health and ecosystem damage of a pesticide application (Humbert et al., 2007)

Impacts on human health from pesticide application can be divided into indirect and direct impacts as shown in Fig. 3. Both consider the same effect factor, but adopt two distinct intake fractions. The first one considers the indirect fate of pesticides in the multimedia environment that will eventually be inhaled or absorbed by humans. The second accounts for the direct transfer of pesticide residues into the treated plant. Intake fractions for indirect impacts are evaluated with multimedia and multi-pathways, fate, exposure and effect models which enable estimation of chemical mass (or concentration) in environmental media at a regional and a global scale, including multiple exposure pathways that link a chemical concentration in the atmosphere, soil, surface water and vegetation to human intake through inhalation and ingestion.

1.6 Objectives of the thesis

This dissertation focuses on the fate and the exposure of pesticides emitted to the environment from their source to human intake for assessing the impacts of toxics on human health and ecosystems for Life Cycle Impact Assessment (LCIA). Furthermore, the goal of this work is to evaluate the environmental impacts of pesticides using a comprehensive life-cycle impact approach that considers the impacts of residues of plant protection products in arable crops. The dissertation will address the following questions:

- How can the fate of pesticides in plants cultivated in greenhouses be measured and modelled?
- How does dynamic behaviour affect the final residues in edible parts of plants?
- How can the degradation of pesticides on plant surfaces and within plants be measured and modelled?
- How can a relative risk indicator for pesticides be developed using fate, exposure and toxicity characteristics?

After a short introduction to environmental assessment approaches and the specific problems related to the application of pesticides and their characteristics in *Chapter 1*, *Chapter 2* proposes an approach for modelling pesticide residues in greenhouse tomato plants. This fate and exposure model considers the time between pesticide application and harvest, the time between harvest and consumption, the absorption of spray deposit on plant surfaces, transfer properties through the cuticle, degradation inside the plant and loss due to food processing. The model is validated with experimental data which was obtained from field trials conducted in the Catalan Institute for Food and Agricultural Research and Technology (Institut de Recerca i Tecnologia Agroalimentàries; IRTA) in Cabrils (Barcelona). The goal is to model human intake fractions of pesticides due to ingestion of tomatoes representing a realistic scenario of human exposure to pesticide residues in foods.

In *Chapter 3*, two generic estimation routines for substance specific half-lives of pesticides (i) on plant surfaces and (ii) within plants to be used in fate and exposure models are presented. First, an extrapolation routine for the estimation of pesticide half-lives on plant surfaces based on a conversion factor from half-lives of pesticides in soil is proposed. Furthermore, a tentative estimation method for the calculation of metabolism half-lives of pesticides in inner parts of plants based on experimental data is presented.

Chapter 4 presents a follow-up of *Chapter 2* and *Chapter 3*. Previous results are combined with new experimental assessment to measure the uptake, translocation and persistence behaviour of pesticides in tomato fruits treated by (i) standard foliar spray application and (ii) soil application using direct localised drip irrigation into root zone. A dynamic root uptake model for pesticides aiming at the estimation of time dependent contaminant concentrations in fruits is proposed. Finally, experimental results are compared with model estimates in terms of human population intake fractions of pesticides. These investigations aim to evaluate the environmental performance of pesticides when the same active ingredient is applied to crops by different application techniques.

Chapter 5 illustrates the development of a new method entitled PestScreen, to calculate the relative risk level of pesticides with the aim of ranking them from lowest to highest degree of concern. The approach is an estimation method of relative risk levels and allows comparing environmental and human health risks of specific pesticide types through their ranking. The method is developed to serve as an analytical tool in screening and identification of pesticides of environmental concern used in agriculture.

PestScreen incorporates both the toxic effects of pesticides and their fate and exposure characteristics in different compartments of the environment. This is done by combining measures of chemical toxicity pertaining to both human health and the environment with chemical release amounts and information on overall environmental persistence, long-range transport potential and human population intake fractions. In *Chapter 6* the most important results are summarized and recommendations for further research are discussed.

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Chapter 2

Human intake fractions of pesticides via greenhouse tomato consumption: comparing model estimates with measurements for captan

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Abstract

Human intake due to pesticide residues in food commodities can be much higher than those related to water consumption and air inhalation, stressing the importance to correctly estimate pesticide uptake into plants and predict subsequent intake by humans. We calculated the human intake fraction of Captan via tomato consumption taking into account the time between pesticide application and harvest, the time between harvest and consumption, the absorption of spray deposit on plant surfaces, transfer properties through the cuticle, degradation inside the plant and loss due to food processing. Human population intake fractions due to ingestion were calculated for complete, washed and peeled tomatoes. The calculated intake fractions were compared with measurements derived from an experimental setup in a Mediterranean greenhouse. The human population intake fraction for Captan is on average 10^{-2}-10^{-5} kg of pesticide ingested by humans per kg applied in the greenhouse as plant treatment, depending on the time between pesticide application and ingestion of tomatoes and the processing step considered. Model and experimentally derived intake fractions deviated in less than a factor of 2 for complete and washed tomatoes and a factor of 3 for peeled tomatoes.

Keywords: Captan; Human intake fraction; Life Cycle Impact Assessment (LCIA); Pesticide fate and exposure model

1. Introduction

A variety of pesticides is used in greenhouses to maintain high crop yields. An important side effect of the use of pesticides is the potential harm it can cause to humans and the environment. In recent years there has been an increasing concern that pesticides constitute a risk to the general human population through residues in the food supply (Bolognesi, 2003; Gold et al., 2001). Since plants form the basis of food webs, potentially harmful organic contaminants could find their way into human populations via this route. At present, the level of uncertainty associated with predicted organic contaminant doses via this exposure pathway exceeds the level of uncertainty associated with other potential pathways like inhalation and contamination due to drinking water (Collins & Fryer, 2003). Pesticide residue evaluation in agricultural products can be carried out by analytical methods. These experimental approaches are often limited by high costs, the time involved and analytical detection limits. An alternative approach to the classical laboratory analysis is pesticide fate and exposure modelling. A greenhouse tomato model developed by Antón et al., (2004), describes human exposure pathways for pesticides applied in greenhouses in Spain.

For all pesticides, exposure via tomato intake marked the most important exposure pathway for humans. However, the uncertainty in the estimates of this pesticide pathway was large. Therefore, further development and increasing understanding of how plants accumulate and eliminate pesticides will have substantial benefits for risk assessment purposes. This study updates the tomato exposure part of the greenhouse model of Antón et al. (2004) and now includes model estimations of human exposure via complete, washed, and peeled tomatoes, respectively. It also validates the model estimations with experimental data for Captan, a fungicide that is commonly used in greenhouses.

2. Materials and Methods

2.1 Fate and Exposure Model

2.1.1 Fruit deposition after spraying

Since (i) pesticide deposition on soil, (ii) deposition on plants and (iii) wind drift from the greenhouse must sum up to one, the plant deposition fraction (f_{plant}) of a pesticide after application is given by:

$$f_{plant} = 1- (f_{drift} + f_{soil}) \tag{1}$$

The drift fraction (f_{drift}) used in the model is fixed to a value of 0.05 derived from the work of Egea González (1999) and Leistra et al. (2001). They presented drift fractions between 0.01 and 0.09 for the application in greenhouses depending on the vapour pressure of the active ingredient. With a simple exponential model, based on plant growth stage and capture efficacy, the soil deposition is described by the following equation:

$$f_{soil} = e^{-k_p \times LAI} \tag{2}$$

where k_p is the pesticide capture coefficient (-) and LAI is the leaf area index ($m^2_{leaves}\ m^{-2}_{soil}$). According to Gyldenkaerne (1999), pesticide capture coefficients (k_p) of 0.35 and 0.55 are suggested for the pesticide spray solutions prepared with and without surfactants or adjuvants, respectively.

The fraction that reaches the fruit (f_{fruit}) is derived from the plant deposition fraction (f_{plant}) by correction for the difference between the leaf area index (LAI) and the fruit area index (FAI):

$$f_{fruit} = \frac{FAI}{LAI} \times f_{plant} \tag{3}$$

The fruit area index is calculated by:

$$FAI = N \times A \times \delta \tag{4}$$

where N is the number of fruits per plant (-), A is the surface area of a tomato calculated as a sphere surface (m^2) and δ is the plant density per unit of soil (m^{-2}).

2.1.2 Fruit concentrations

The decline of pesticide concentration with time is often described according to first-order kinetics (Beulke and Brown, 2001) and can be written as:

$$C_{tomato}(t) = C_0 \times e^{-k_r \times t} \tag{5}$$

where $C_{tomato}(t)$ is the concentration at time t (mg kg^{-1}), C_0 is the concentration at time zero (mg kg^{-1}) and k_r is the removal rate ($days^{-1}$). The concentration at time zero (C_0) can be written as:

$$C_0 = \frac{f_{fruit} \times M_{applied}}{M_{fruit}} \tag{6}$$

where f_{fruit} is the fruit fraction (-), $M_{applied}$ is the mass of active ingredient applied in the greenhouse (kg m^{-2}) and M_{fruit} is the mass of fruits at the time of application (kg m^{-2}). The removal rate k_r is the sum of the degradation rate (k_d), the growth rate (k_g) and the loss by volatilization (k_v) and is given by:

$$k_r = k_d + k_g + k_v \tag{7}$$

Pesticide concentration in the peeled tomato can be described as a cascade of two compartments with transport from the spray deposition on the cuticle to the inner part of the plant. The reverse transfer (translocation of pesticide out of the plant) can be neglected due to the rapidity of the transfer. The concentration of a pesticide as a function of time in a peeled tomato can be described as:

$$C_{peeled\ tomato}(t) = \frac{C_0 \times k_{d-c}}{k_{r,in} \times k_{r,out}} \times (e^{-k_{r,out} \times t} - e^{-k_{r,in} \times t}) \tag{8}$$

In the case that the removal rates inside ($k_{r,in}$) and outside ($k_{r,out}$) of the plant are equal, the concentration in peeled fruits as a function of time can be approximated by:

$$C_{peeled\ tomato}(t) \approx C_0 \times k_{d-c} \times t \times e^{-k_r \times t} \tag{9}$$

In order to calculate the pesticide concentration in a peeled tomato the transfer and permeability properties of agrochemicals through plant cuticles are required. The plant cuticle is an extracellular lipophilic biopolymer covering leaf and fruit surfaces. Its main function is the protection from uncontrolled water loss (Schreiber, 2005). In agriculture, plant cuticles often represent the major barrier for pesticides sprayed on the leaf surface. The permeation through the cuticle depends on the solute mobility in the limiting skin, the path length of the limiting skin and the partition coefficient between the cuticle and the deposited surface residue (Baur et al., 1997; Baur et al., 1999; Schönherr et al., 1999). The transfer rate between pesticide spray deposit and the cuticle (k_{d-c}) can be described as:

$$k_{d-c} = k^* \times K_{cw} \tag{10}$$

where k^* is the solute mobility in plant cuticles (day^{-1}) and K_{cw} the cuticle-water partition coefficient. Schreiber (2005) describes a linear relationship between the molecular weight (MW) of a solute and its solute mobility in plant cuticles (k^*) which can be written as:

$$\log k^{*} = -0.011 \times MW - 2.46 \tag{11}$$

The partition coefficient between cuticle and surface residue (K_{cw}) can be calculated from the octanol-water partition coefficient (K_{ow}) (Schönherr and Riederer, 1989; Trapp, 2004).

$$\log K_{cw} = 0.057 + 0.979 \times \log K_{ow} \tag{12}$$

2.1.3 Intake fraction

The intake fraction (iF) is described as the fraction of mass of chemical released into the environment that is ultimately taken in by the human population (Bennett et al., 2002a, 2002b; Huijbregts et al., 2005). The intake fraction is expressed in kg intake by tomato consumption per kg applied in the greenhouse ($\text{kg}_{\text{ingested}}\ \text{kg}_{\text{applied}}^{-1}$) and is defined here as:

$$iF(t)_x = f_{fp} \times \frac{C(t)_x \times Y}{M_{applied,x}} \tag{13}$$

where (f_{fp}) is the food processing factor (-), $C(t)_x$ is the concentration of a given substance at the time t, Y is the yield (kg m^{-2}) and ($M_{applied,x}$) the mass of active ingredient applied in the greenhouse (kg m^{-2}). After the tomato is harvested it usually undergoes processing steps until it becomes the final food commodity. In this case study, one product is a fresh washed tomato where the processing step is given by washing the harvested fruit with tap water. The second product is a washed and peeled tomato. The removal of several pesticides from a variety of fruits and vegetables was studied by Teixeira et al. (2004) and Ramesh & Balasubramanian (1999). Processing factors reported ranged between 0.02 and 0.7. A default value of 0.3 is used in the model as food processing factor due to washing with tap water.

2.2 Experimental Procedures

2.2.1 Field trial design

In order to compare measured and estimated pesticide residue levels, a field trial was carried out in a 230 m^2 greenhouse located in the Institut de Recerca i Tecnologia Agroalimentària, Cabrils (Barcelona). Tomato plants, cultivar *Bond*, were cultivated in a spring-summer cycle with a density of 2.2 plants m^{-2} and a total yield of 18.7 kg m^{-2} of tomato fruits. The surface ratio of developed plants versus fruits (*FAI/LAI*) at the day of application was 0.09. The leaf area index was measured as 3.11. The weight of fruits at the day of application was 2.1 kg m^{-2}.

The treatment was carried out using a portable motor sprayer equipped with a gun nozzle using the following commercial formulation: Karnak-85® (85% of Captan). Spraying was carried out at the recommended dose of 2 g L^{-1} and a total consumption of 35 L. Sampling were made before and after the treatment and repeated after 1, 3, 5, 7, 10, 14 and 21 days. According to Garau et al. (2002) the amount of water evaporating from the tomato fruits and the amount of liquid provided to the fruits by the plant are equal for mature tomato fruits (growth rate of tomatoes is equal to zero). Therefore the effect of dilution by growth can be neglected in this case study because only mature fruits were used for analysis.

2.2.2 Analytical method

The analysis of pesticide residues was carried out by adapting a method described by Garau et al., (2002) and used in the determination of pesticides on tomato plants. Whole tomatoes were homogenized in a waring blender. 10 g of homogenized tomatoes were weighed in a 50 mL screw-capped test tube; 1 g of NaCl and 20 mL of acetone/petroleum ether (1/1; v/v) mixture were added. The tube was agitated for 20 minutes using a magnetic stirrer, the phases were allowed to separate. 10 mL of the organic extract layer was evaporated to dryness using a gentle nitrogen stream and then transferred quantitatively in 1 mL of acetone into a 2 mL gas chromatography test vial with 1 g Na_2SO_4 ready for injection. The same procedures described above were used for the sample preparation of tap water washed and peeled tomato fruits. In order to avoid contamination from the deposition residue on the outer side of the cuticle, all tomato samples were washed before peeling.

In order to evaluate the efficiency of the analytical procedures a recovery assay was conducted. Samples of untreated tomato fruits were spiked with 1 and 0.1 ppm of Captan standard solution and processed according to the extraction procedure four times. The recovery assay yielded good recoveries in the extracting process (from 95 to 112%) with a maximum standard deviation of 6%. These levels can be considered as satisfactory for residue determinations and are comparable to results reported by Sadło (2002). The coefficient of determination (R^2) in the range of 0.1-10 ppm was 0.998 (n = 6). In order to determine the amount of pesticide removed from the fruit due to home processing, tomato fruits were washed with cold (21°C) and warm (47°C) tap water. The water used for washing in all processing steps was tap water without detergents.

2.2.3 Apparatus and Chemicals

A gas chromatograph, Agilent Technologies HP6890N, equipped with an electronic capture detector (ECD) and a DB-1701P fused silica capillary column (J&W Scientific, Folsom, USA) were used to detect Captan. The injector and the detector were operated at 200 and 325 °C, respectively. The samples (1μL) were injected in splitless mode and the oven temperature was programmed as follows: 40 °C for 1 min, raised to 140 °C (20 °C min^{-1}), raised to 280 °C (11 °C min^{-1}), and held for 7 min. Helium was used as carrier gas (29.2 cm sec^{-1}), nitrogen at 30 mL min^{-1} as makeup gas. Acetone and petroleum ether were pesticide grade solvents (Merck, Darmstadt, Germany and Riedel de Haën, Seelze, Germany). Captan standard solution (100 ppm) was purchased from LGC Promochem, Barcelona, Spain.

3. Results

Pesticide residue data in tomato fruits obtained in the disappearance study of Captan and a first order decay fit are presented in Figure 1. As expected, residues at time zero were in proportion to the dosage applied. Average residue concentrations on tomato fruits ranged from 12.7 mg kg^{-1} at day zero to 0.4 mg kg^{-1} two weeks after the spray application with a coefficient of variation of 10%. Three weeks after the fungicide was applied, Captan levels for all samples dropped under the analytical detection limit. The degradation kinetics of Captan deposits were well described by a first-order decay equation ($C(t) = 13 \times e^{-0.27 \times t}$; R^2=0.99). According to our experimental results the half-life of Captan is 2.5 days if applied on tomato fruits. Captan on tomatoes dropped by 69% using cold tap water (21°C) and by 78% using warm tap water (47°C). From these results an experimental tap water washing processing factor of 0.27 can be estimated for Captan.

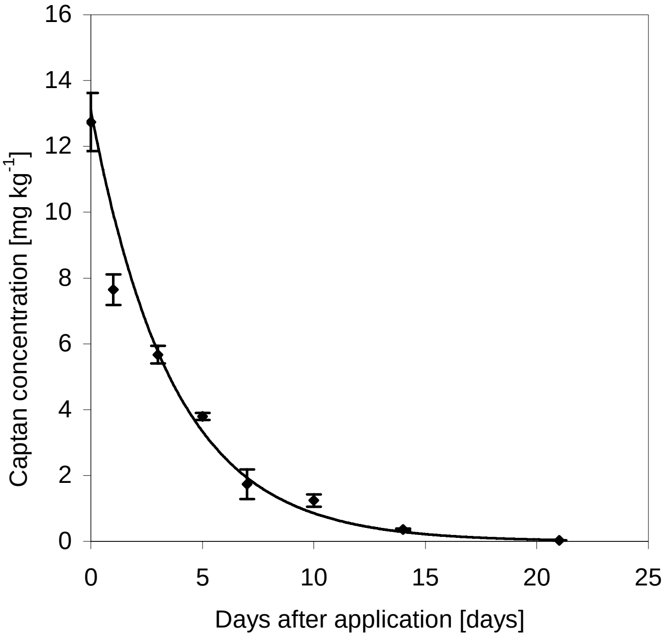

Fig. 1. Disappearance of Captan on tomato fruits ($C(t) = 13 \times e^{-0.27 \times t}$; R^2=0.99)

Figure 2 shows the comparison between measured and modelled Captan concentrations on tomato fruits. The concentrations of Captan on tomato fruits for the first two days estimated by the model were somewhat overestimated (5-33%) compared to the result derived from the field experiment. From day two after spraying until the end of the experiment the values calculated by the model where somewhat lower (19-36%) than the experimental values.

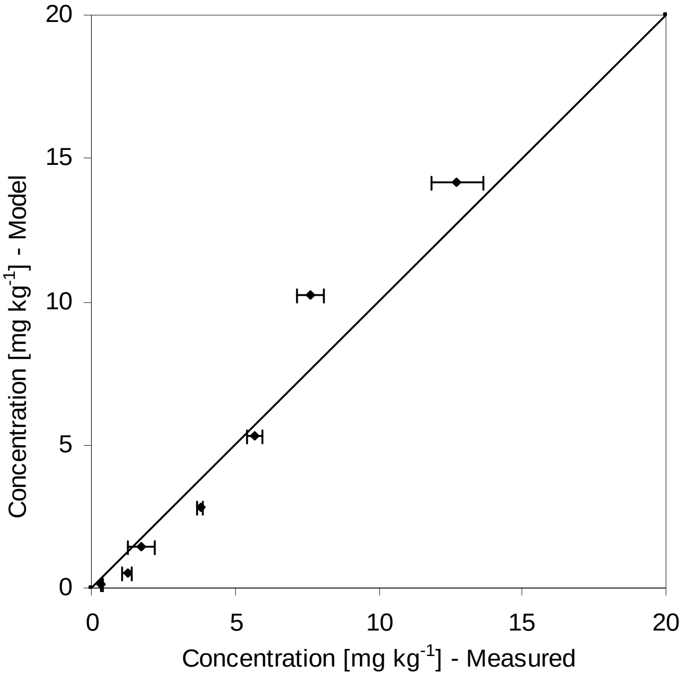

Fig. 2. Comparison of measured and estimated Captan residues on tomato fruits; (R^2=0.97)

Captan was not detectable in peeled tomatoes collected directly after the spray application (Figure 3). The maximum residue (0.54 mg kg^{-1}) in peeled tomatoes was detected at day seven after the treatment, declining to a non-detectable residue level three weeks after the pesticide application. The model shows the same trend, although actual concentration estimates differ from the measured values up to a factor of 3, particularly between day one and five.

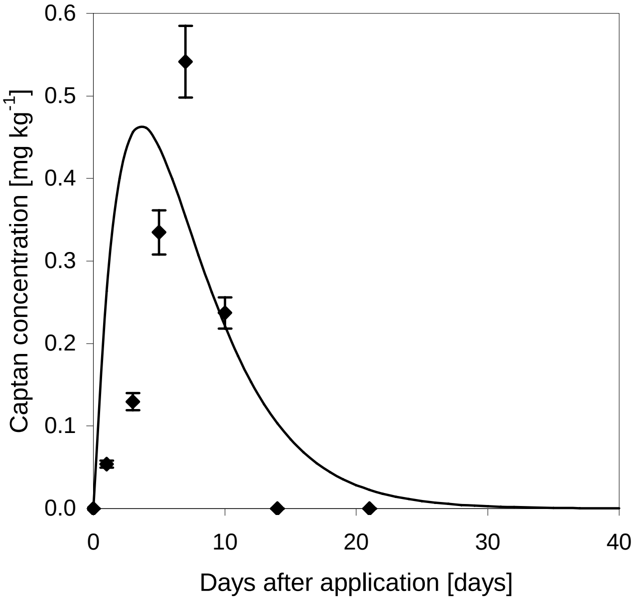

Fig. 3. Measured and modelled Captan concentrations in peeled tomato fruits

Table 1. Time dependent human population intake fractions ($kg_{ingested}\ kg_{applied}^{-1}$)

						pre- harvest ←	→ post- harvest		
Days after application		0	1	3	5	7	10	14	21
iF (unwashed)	measured	5×10^{-2}	3×10^{-2}	2×10^{-2}	1×10^{-2}	6×10^{-3}	5×10^{-3}	1×10^{-3}	nd
	modelled	5×10^{-2}	4×10^{-2}	2×10^{-2}	1×10^{-2}	5×10^{-3}	2×10^{-3}	6×10^{-4}	2×10^{-4}
iF (washed)	measured	1×10^{-2}	9×10^{-3}	6×10^{-3}	4×10^{-3}	2×10^{-3}	1×10^{-3}	4×10^{-4}	nd
	modelled	2×10^{-2}	1×10^{-2}	6×10^{-3}	3×10^{-3}	2×10^{-3}	6×10^{-4}	2×10^{-4}	6×10^{-5}
iF (peeled)	measured	nd	2×10^{-4}	5×10^{-4}	1×10^{-3}	2×10^{-3}	9×10^{-4}	nd	nd
	modelled	0	1×10^{-3}	2×10^{-3}	2×10^{-3}	1×10^{-3}	8×10^{-4}	3×10^{-4}	7×10^{-5}

nd: not detectable

Measured and modelled time dependent intake fractions for (i) unwashed, (ii) washed and (iii) washed and peeled tomatoes are presented in Table 1. The intake fraction for unwashed tomatoes varies between 10^{-2}-10^{-4} ($kg_{ingested}\ kg_{applied}^{-1}$), depending on the time of consumption. The intake fraction for washed tomatoes ranges between 10^{-2}-10^{-5}

($kg_{ingested}$ $kg_{applied}^{-1}$), while the intake fraction for washed and peeled tomatoes varies between 10^{-3}-10^{-5} ($kg_{ingested}$ $kg_{applied}^{-1}$).

4. Discussion

Although model estimates and measurements of the intake fraction via tomato consumption correspond well within a factor of 3, the pesticide model is not without uncertainties.

Firstly, variation between measured and estimated values obtained one day after the spray application is high. This may be explained by the bi-phasic degradation of pesticides. Bi-exponential non-linear kinetics may also be used and may give a better fit to the data (Beulke and Brown, 2001). However, the derived parameters can often not be used as input data for simulation modelling as most models are restricted to the assumption of first-order kinetics. Typical pre-harvest intervals for pesticides used for the treatment of tomato crops are between seven and twenty-one days (Gambacorta et al., 2005). Residues after more then ten days following the pesticide application are therefore more relevant for the estimation of intake fractions. This makes the use of a first-order kinetic fit satisfactory for our model purpose.

Secondly, intake fractions are largely influenced by degradation half-life estimates of pesticides in plants. Different methods describing metabolism in plants often lead to large uncertainties (Komoßa et al., 1995). According to Satchivi et al. (2000), the collected values for the metabolism of substances in plant show high variations, from a short half-life of some days up to high values of about one month depending on the active ingredient.

Thirdly, the extent to which pesticide residues are removed by food processing depends on a variety of factors such as the chemical properties of the pesticide, the nature of the food commodity and the processing step (Chavarri et al., 2005; Boulaid et al., 2005). Washing tomato fruits with tap water reduced Captan concentrations by up to 80%.

Values for Captan reported in the literature (El-Zemaity, 1988) even reach 98%. This experiment and our results show that washing tomato fruits with tap water before consumption substantially reduces the human ingestion intake fraction and describes the importance of including food processing factors in intake fraction calculations.

Forthly, the measured amount of Captan lost due to peeling at the pre-harvest interval is 80%. The loss estimated by the model is 90%. These results are consistent with those reported in a previous study (Fernández-Cruz et al., 2004) and underline the role of fruit cuticles as the main barrier for pesticides from the spray deposit. The advantage of the model is that residue concentrations under the analytical detection limit can be estimated and herewith, human population intake fractions can be calculated.

Lastly, Captan residues in washed and peeled tomatoes show variation between measured and modelled concentrations, especially in the first five days after application. The model uses one single transfer rate from the cuticle into the tomato fruit as of the time of application. An initial phase with a slower transfer rate could be the explanation for the apparent time lag between modelled and measured residue values (Figure 3). Future research on transfer of pesticides through cuticles including (i) a slower transfer rate, in which the active ingredient has to pass the cuticular waxes, and (ii) a faster rate constant inside the fruit will be necessary.

5. Conclusion

Dynamic model calculations and measurements for human intake fractions via tomato consumption correspond well for Captan. The human population intake fraction calculated is typically 10^{-2}-10^{-4} ($kg_{ingested}$ $kg_{applied}^{-1}$) for unwashed tomatoes and decreases by 73% when washed before consumption. Human population intake fractions for tomatoes that were peeled after washing are 10^{-3}-10^{-5} ($kg_{ingested}$ $kg_{applied}^{-1}$). Intake fractions between complete and peeled tomatoes deviate in the first week after Captan application but hardly differ three weeks following the pesticide treatment.

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Chapter 3

Estimating half-lives of pesticides in/on vegetation for use in multimedia fate and exposure models

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Abstract

Degradation half-lives in/on vegetation are needed in environmental risk assessment of pesticides, but these data are often not available for most active ingredients. To address this, we first correlated experimental soil degradation half-life data of forty one pesticides obtained from the reviewed literature with the corresponding experimental half-lives on plant surface. Degradation half-lives in soil were found to be four times slower compared with half-lives on plant surfaces. In a second step, we explored measured plant surface half-lives directly with those in vegetation. The results were validated by comparing computed values with results obtained from an experimental set-up. The uptake and dissipation of alpha-cypermethrin (insecticide) and bromopropylate (acaricide) was studied by detecting pesticide residues in whole and peeled tomato fruits using gas chromatography. Half-lives within vegetation were found to be four times faster compared with plant surface half-lives. Using this experimental based approach, it is concluded that the estimation of degradation half-lives of pesticides in/on vegetation to be used as input data in environmental mass balance models can be directly correlated from the more abundant ready experimental degradation half-life data for soil.

Keywords: Pesticides; Life-cycle impact assessment (LCIA); Mass balance model; half-life

1. Introduction

Multimedia fate and multipathway human exposure mass balance models such as CalTOX 4.0 (McKone and Enoch, 2002), EUSES 2.0.3 (RIVM, 2005), IMPACT 2002 (Jolliet et al., 2003; Pennington et al., 2005) and USES-LCA 2.0 (Huijbregts et al., 2005) are widely used in pesticide risk assessment at the regional scale. In order to estimate the fraction of a pesticide that will be taken in by the entire human population due to the ingestion of residual pesticide concentrations in agricultural crops (mainly vegetables and fruits), these models incorporate a vegetation compartment including a plant uptake model in their methodology.

A number of vegetation uptake models have already been developed for fate assessment of pesticides in plants (Trapp and Pussemier, 1991; Trapp and Matthies, 1995; Hung and Mackay, 1997; Severinsen and Jager, 1998; Cousins and Mackay, 2001). Although these models have successfully exhibited the most probable partitioning and distribution pathways of pesticides in plants, metabolism and dissipation in/on plants was not fully taken into account. Although each of the listed models contained a parameter regarding the pesticide loss by metabolism/degradation, there were no or few studies explaining the actual method for obtaining the degradation rate constant.

Metabolism and degradation half-lives or rate constants of pesticides in/on plants are key data required for the assessment of plant protection products when fate and exposure models are used (Humbert et al., 2007). The problem is that the development and popularity of these models have greatly outpaced the availability of measured half-lives needed to run them. However, the fact is that half-lives in/on plants generally still have not been measured for most chemicals and the data are often scarce or highly uncertain and mostly derived from laboratory screening tests and not from realistic environmental conditions (Bennett et al., 1998; Gouin et al., 2004). In these cases, one way to obtain the missing data for a wide range of chemicals is to extrapolate from one medium to another in order to derive some sort of estimate of the biotransformation rate in the medium of interest (Boethling et al., 1995; Jaworska et al., 2003). Severinsen and Jager (1998) introduced a metabolism rate constant in vegetation estimated from the soil half-life based on data for one single pesticide. Huijbregts et al. (2005) presented an estimation routine for the calculation of half-lives in vegetation based on standardized plant cell culture tests (Komoßa et al., 1995). Charles (2004) and Juraske et al. (2007) developed vegetation models aiming to address the challenge of measuring the dynamic behaviour of pesticides in/on plants by taking into account the time between pesticide application and harvest and to better estimate the pesticide half-life in/on plants. Charles (2004) introduced a default half-life of five days for pesticides on plant surfaces based on experimental data provided by Willis et al. (1987). Furthermore, an estimation routine for half-lives of pesticides in vegetation based on the assumption that pesticide degradation in plants is more efficient than in soil but slower than in air was established. All the approaches mentioned correlate half-lives in plants with degradation in soil but their results show variation ranging up to eight-fold in predicting the conversion factor between the compartments. However, no extrapolation routine was established by any of the methods for (i) the calculation of individual pesticide half-lives on plant surfaces based on a wide range of experimental data and (ii) for the estimation of half-lives in vegetation due to metabolism, based on realistic field experiments. Given that half-lives of pesticides in/on plants are the most important factors in terms of uncertainty propagation and that their availability and quality is limited, there is a need to develop new extrapolation methods for the calculation of pesticide specific half-lives in/on vegetation.

This study updates the biotransformation and removal part of the pesticide fate and exposure model of Juraske et al. (2007) by (i) developing an extrapolation routine for the estimation of pesticide half-lives on plant surfaces based on a conversion factor from half-lives of pesticides in soil and (ii) introducing a tentative estimation method for the calculation of metabolism half-lives of pesticides in inner parts of plants based on experimental data for bromopropylate (CAS# 18181-80-1) and alpha-cypermethrin (CAS# 67375-30-8), both applied on greenhouse tomato plants.

2. Materials and Methods

2.1 Gathering of experimental biodegradation data

Environmentally relevant biodegradation data was collected for 41 pesticides in order to calculate the ratio of mean half-lives for degradation in soil to the corresponding value for plant surfaces of agricultural crops. The goal of this approach is to develop scaling factors that represent a sort of average multiplier for all substances, for a given set of conditions. Only studies in which at least two experimental biodegradation rates or half-lives were reported or could be calculated from the data were included in the analysis. Degradation rate constants were converted to half-lives assuming pseudo first-order kinetics with no lag period. This model was taken as the default because it requires fewer assumptions about the degradation process and variables that affect it than do more complex kinetic models (Aronson et al., 2006). The geometric mean was used as a measure of central tendency because it tends to reduce the influence of extreme values (Boethling et al., 1995).

2.1.1 Degradation of pesticides in soil

Microbial degradation is the result of microbial metabolism of pesticides, and is often the main source of pesticide biodegradation in soils (Gavrilescu, 2005). It occurs when fungi, bacteria and other microorganisms in the soil use pesticides as a source of carbon and energy, or consume the pesticides along with other sources of food.

Soil degradation rates were selected as a surrogate for removal rates in/on plants because of different reasons: (i) soil half-lives are well documented in several databases and the reviewed literature, (ii) multiple half-lives measured under different conditions are easily available for one active ingredient, (iii) soil as a compartment in environmental multimedia models is especially important, because soil forms the principal sink for many organic substances including pesticides, and (iv) microbial cultures (microorganisms) in soil metabolize xenobiotics in a similar manner as enzymes in plant material (Van Eerd et al., 2003). Experimental degradation rate constants and half-lives of pesticides in soil were collected from (1) Physical-Chemical Properties and Environmental Fate Handbook (Mackay et al., 2000); (2) Handbook of Environmental Degradation Rates (Howard et al., 1991); (3) The e-Pesticide Manual (Tomlin, 2002) and (4) Linders et al. (1994).

2.1.2 Dissipation of pesticides on plant surface

The dissipation of foliar pesticide deposit is considered to be a complex process of environmental factors (temperature, relative humidity and UV irradiation), metabolism and translocation (foliar penetration and plant growth), application technique and pesticide formulation (Brouwer et al., 1997). Photodegradation, volatility of active ingredients from the foliage back to the air, and penetration of pesticides through cuticular waxes are the main sources for breakdown of pesticides on foliage and other plant surfaces (McCrady and Maggard, 1993; Katagi, 2004).

Through pesticide field dissipation studies and bioremediation research, field data of pesticide half-lives on plant surfaces are now available for a substantial number of active ingredients. In most cases these half-lives are reported as plant surface half-lives although field experiments usually account for concentrations measured in the whole plant/fruit. However, model calculations presented by Mercer (2007) showed that pesticides decrease in concentration vertically through the cuticle and that the concentration in the subcuticle cells often is effectively zero. Furthermore, pesticide residues in fruits were found to be reduced between 80-90% after peeling (Fernández-Cruz et al., 2004; Juraske et al., 2007). From these findings we assume that most of the pesticide residues in plants treated by foliar spray application can be found in/on the cuticle and that the half-lives selected for this study can be used as a starting point for modelling the processes occurring on plant surfaces. Experimentally derived removal half-lives of the active ingredients included in the study were obtained through a literature review. Substance specific information can be found in the supporting information. Most of these half-lives were derived from experiments conducted with fruits and vegetables as edible parts of agricultural products represent the main source of direct contaminant exposure through residues in food. However, as reported by Antonious et al. (1998) and Sadło (2002), differences between half-lives of pesticides on fruits and leaves were relatively small (average ratio 'Half-life$_{\mathrm{fruit}}$/Half-life$_{\mathrm{leaves}}$' ranged between 0.6 and 1.4) leading to the assumption that the half-lives on plant surfaces included in this analysis can represent vegetation as a whole.

2.1.3 Metabolism of pesticides in plants

Pesticide biotranformation may occur via multi-step processes known as metabolism. Enzymatic transformation, which is mainly the result of biotic processes mediated by plants and microorganisms, is by far the major route of detoxification and metabolism of pesticides in vegetation (Van Eerd et al., 2003). Once in inner parts of plants, a pesticide can metabolise via internal enzyme systems. Such biological transformations, which involve enzymes as catalysts, frequently bring about extensive modification in the structure and toxicological properties of pollutants. Plants generally metabolise pesticides to water-soluble conjugate compounds and bound residues which are less or non-toxic and can stay in the plant (Hatzios, 1991). Field half-lives of pesticides within vegetation do not belong to the available values in databases and the literature and were therefore derived from the experiments conducted in this work.

2.2 Modelling of pesticide residues

Pesticide concentrations in/on plants treated by spray application were estimated using the pesticide fate and exposure model presented by Juraske et al. (2007), which allows one to calculate the concentration of a pesticide as a function of time between application and harvest. The model takes the time between harvest and consumption, absorption of pesticide spray deposit on plant surfaces, transfer properties through the cuticle, degradation of active ingredient on and inside the plant and loss of pesticide due to food processing into account.

2.3 Experimental Procedures

2.3.1 Design of the field trials

In order to compare measured and estimated pesticide residue levels, two field trials were carried out in a 230 m^2 greenhouse located in the Institut de Recerca i Tecnologia Agroalimentària, Cabrils (Barcelona). Tomato plants, cultivar *Caramba*, were cultivated in a spring-summer cycle with a density of 2.2 plants m^{-2} and a total yield of 16 kg m^{-2} of tomato fruits. The treatments were carried out using a portable motor sprayer equipped with a gun nozzle using the following commercial formulations: Neoron®50 (50% of bromopropylate) on June 2nd 2006 and Fastac®10 (10% of alpha-cypermethrin) on July 4th 2006. Spraying was carried out at the recommended concentrations of 0.75 g a.i. L^{-1} and 0.04 g a.i. L^{-1}, respectively. A total consumption of 0.3 L m^{-2} was applied in both cases. The leaf area index was measured as 2.43 and 2.76. The weight of fruits at the day of application was 2.4 kg m^{-2}. Fruits were sampled before and one hour after the treatment and again after 1, 4, 5, 7, 11, 21, 28 and 32 days in the case of bromopropylate and 1, 2, 3, 7, 10, 14 and 21 days in the case of alpha-cypermethrin.

2.3.2 Analytical method

The analysis of pesticide residues was carried out by adapting methods described by Garau et al., (2002) and Juraske et al. (2007), both used in the determination of pesticides on tomato plants. Whole tomatoes were homogenized in a waring blender. Twenty g of homogenized tomatoes were weighed in a 100-mL screw-capped test tube; 2 g of NaCl and 40 mL of acetone/petroleum ether (1/1; v/v) mixture were added. The tube was agitated for 20 minutes using a magnetic stirrer, the phases were allowed to separate. Ten mL of the organic extract layer was evaporated to dryness using a gentle nitrogen stream and then transferred quantitatively in 1 mL of acetone into a 2-mL gas chromatography test vial with 1 g Na_2SO_4 ready for injection. The same procedures described above were used for the sample preparation of tap water washed and peeled tomato fruits. In order to avoid contamination from the deposition residue on the outer side of the cuticle, all tomato samples were washed before peeling.

In order to evaluate the efficiency of the analytical procedures a recovery assay was conducted. Samples of untreated tomato fruits were spiked with 1, 0.1 and 0.01 mg L^{-1} of standard solution and processed according to the extraction procedure four times. The recovery assay yielded good recoveries in the extraction process, from 91 to 106% with a maximum standard deviation of 9% in the case of bromopropylate and recoveries from 89 to 102% with a maximum standard deviation of 12% in the case of alpha-cypermethrin. These levels can be considered as satisfactory for residue determinations and are comparable to results reported by Sadło (2002) and Juraske et al. (2007). Coefficient of determination (r^2) in the range of 0.01-10 mg L^{-1} were 0.999 and 0.997 (n = 5), respectively for Bromopropylate and alpha-cypermethrin. In order to determine the amount of pesticide removed from the fruit due to home processing, tomato fruits were washed with cold (19°C) tap water. The water used for washing in all processing steps was tap water without detergents.

2.3.3 Apparatus and Chemicals

A gas chromatograph, Agilent Technologies HP6890N, equipped with an electronic capture detector (ECD) and a DB-1701P fused silica capillary column (J&W Scientific, Folsom, USA) were used to detect bromopropylate and alpha-cypermethrin. The injector and the detector were operated at 200 and 325 °C, respectively. The samples (1 µL) were injected in splitless mode and the oven temperature was programmed as follows: 40 °C for 1 min, raised to 140 °C (20 °C min^{-1}), raised to 280 °C (11 °C min^{-1}), and held for 7 min. Helium was used as carrier gas (29.2 cm sec^{-1}), nitrogen at 30 mL min^{-1} as makeup gas. Acetone and petroleum ether were pesticide grade solvents (Merck, Darmstadt, Germany and Riedel de Haën, Seelze, Germany). Bromopropylate and alpha-cypermethrin standard solutions (100 mg L^{-1}) were purchased from LGC Promochem, Barcelona, Spain.

3. Results & discussion

3.1 Estimation of plant surface half-life

Figure 1 shows the correlation between estimated and measured half-lives on plant surfaces for the pesticides included in the study. Substance specific information can be found in the supporting information.

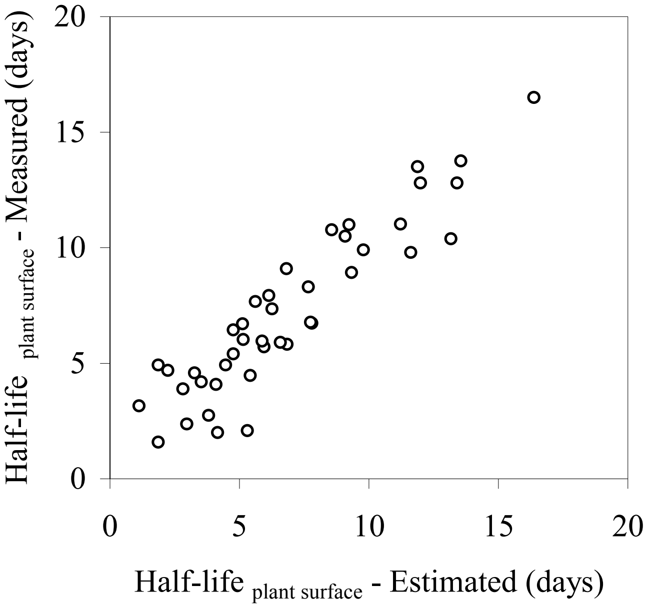


Fig. 1. Comparison of measured and estimated (using Eq.1) pesticide half-lives on plant surfaces ($r^2 = 0.85$).

Based on empirical information of 41 active ingredients on degradation half-lives in soil and degradation half-lives on plant surfaces derived from field experiments (including bromopropylate and alpha-cypermethrin analyzed in this work), the following estimation routine for degradation half-lives on vegetation is suggested:

$$Half-life_{plant\ surface} = \frac{Half-life_{soil}}{4} \qquad (1)$$

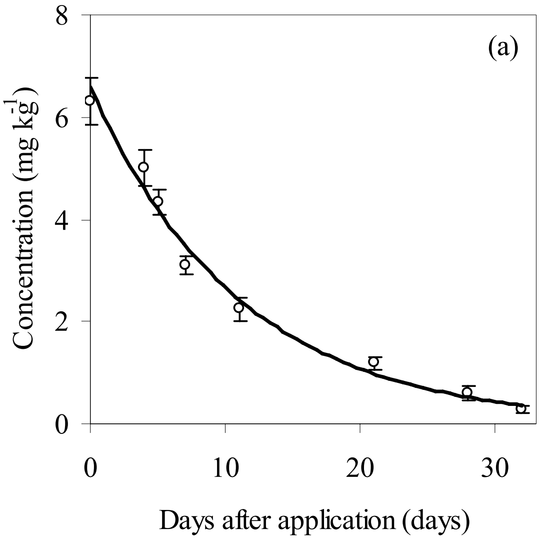
The factor proposed in Eq. 1 to convert degradation half-lives in soil to half-lives on vegetation is set equal to the geometric average ratio 'Half-life$_{soil}$/Half-life$_{plant\ surface}$' of all the pesticides included. The geometric mean of half-lives in soil was 28 days, while the geometric mean of pesticide half-life on plant surfaces was 7 days. The 97.5th percentiles of the half-lives in soil and plant surfaces are 54 and 14 days, respectively. The 2.5th percentiles are 8 days for half-lives in soil and 2 days in the case of half-lives on plant surfaces. The typical uncertainty, represented by the range factor which is defined as the square root of the ratio of the 97.5th to the 2.5th percentile, is a factor of 3 for both, half-life in soil and half-life on plant surfaces. However, much higher factors (10-15) have been reported by Fenner (2002) for a site-dependent degradation of the herbicide atrazine in soil. 'Half-life$_{\text{soil}}$/Half-life$_{\text{plant surface}}$' ratios vary between 1 and 6, stressing the importance of uncertainty when Eq. 1 is used. Although degradation processes in soil and on plant surfaces are of different nature, the correlation coefficient (r^2) between measured and estimated half-lives of pesticides on plant surfaces using Eq. 1 exceeded 0.85, which shows good correlation.

Charles (2004) assumed degradation of pesticides on plant surfaces as non-specific to the substance and introduced a default half-life of 5 days for all active ingredients. From this point of view, we have improved the estimation of the foliar half-life of pesticides by presenting a generic estimation routine for substance specific half-lives based on experimental data. In the absence of data on pesticide degradation in soil, a default half-life of 7 days (geometric mean of experimental pesticide half-lives on plant surfaces) can be used as a rough estimation.

Finally it has to be noted that the dataset used to establish Eq.1 is dominated by insecticides and fungicides as degradation data on herbicides is still scarce and difficult to find in the literature.

3.2 Measured and modelled pesticide concentrations on whole fruits

Pesticide residue concentrations on tomato fruits obtained in the dissipation study of bromopropylate and alpha-cypermethrin and the corresponding first order decay fits are presented in Figure 2.



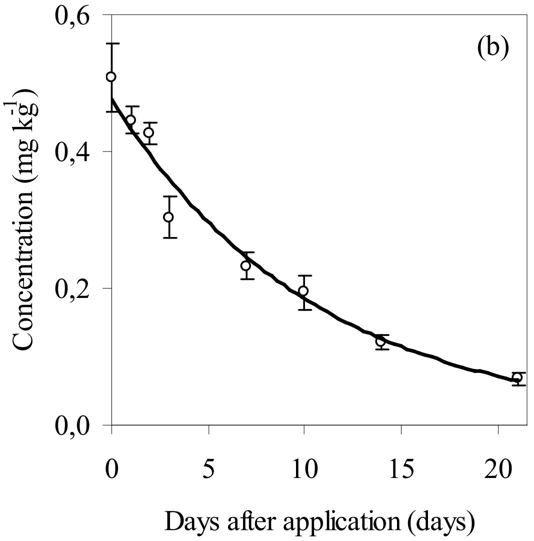


Fig. 2. (a) Dissipation of bromopropylate from tomato fruits (±SE); (b) dissipation of alpha-cypermethrin from tomato fruits (±SE).

As expected, residues at time zero were in proportion to the rate applied. Average residue concentrations of bromopropylate on tomato fruits ranged from 6.32 mg kg^{-1} at day zero to 0.29 mg kg^{-1} thirty two days after the spray application with a coefficient of variation of 6%. Alpha-cypermethrin concentrations ranged from 0.51 mg kg^{-1} at day zero to 0.07 mg kg^{-1} twenty one days after the spray application with a coefficient of variation of 7%. The degradation kinetics of both pesticide deposits were well described by first-order decay equations, ($C(t) = 7 \times e^{-0.091 \times t}$; r^2=0.98) for bromopropylate and $C(t) = 0.5 \times e^{-0.095 \times t}$; r^2=0.99) in the case of alpha-cypermethrin. According to our experimental results, the half-lives of bromopropylate and alpha-cypermethrin are 7.7 and 7.3 days if applied on tomato fruits. Bromopropylate half-lives on plant surfaces found in the literature ranged from 4.5 days (Barba et al., 1991) up to 8.8 days reported by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR, 1993). In the case of alpha-cypermethrin a half-life of 6.2 days on vegetation was reported by Westcott et al. (1987). The values reported in the literature are in accordance with our experimental results. However, the experimental half-life values of pesticides on plants show variation for the same substance. This could be explained by the fact that half-lives were measured on different kinds of crops with different plant surface properties and that the experiments were conducted under different environmental conditions like temperature, relative humidity and UV irradiation. The concentrations of bromopropylate on tomato fruits calculated by the model for the first eleven days after spray application were somewhat overestimated (13-21%) compared to the results derived from the field experiment (Table 1). From day twenty one after spraying until the end of the experiment, the values calculated by the model where somewhat lower (16-17%) than the experimental values. In the case of alpha-cypermethrin the experimental results were always underestimated (1-23%) by the model.

Table 1. Measured and modelled pesticide concentrations on whole tomato fruits

alpha-cypermethrin								
Days after application	0	1	2	3	7	10	14	21
Concentration (mg kg-1)								
measured	0.51	0.45	0.43	0.30	0.23	0.19	0.12	0.06
modelled	0.41	0.37	0.34	0.30	0.20	0.15	0.10	0.05

bromopropylate								
Days after application	0	4	5	7	11	21	28	32
Concentration (mg kg-1)								
measured	6.32	5.00	4.34	3.09	2.24	1.19	0.61	0.29
modelled	7.16	4.91	4.47	3.70	2.54	0.99	0.51	0.35

The variation between measured and estimated values can be mainly explained by the fact that the pesticide fate and exposure model uses simplified first-order kinetics to describe pesticide degradation processes on vegetation. Bi-exponential non-linear kinetics may result in a better fit to the data, but parameters estimated using non-linear equations are thus usually inappropriate as most models are restricted to the assumption of first-order kinetics (Beulke and Brown, 2001). Food processing studies provide basic information on the reduced levels of residues in passing from the raw agricultural commodity to a processed commodity. The processing factor is the residue level in the processed product divided by the residue level in the raw agricultural commodity. Bromopropylate and alpha-cypermethrin concentrations on tomatoes were reduced by 41% and 54% when washed in cold tap water (19°C), respectively. From these results an experimental tap water washing processing factor of 0.59 and 0.46 can be estimated for bromopropylate and alpha-cypermethrin. Our results for bromopropylate differ from those reported by Sadło (1996) stating that bromopropylate residues on apples before and after washing stayed at similar levels. No data on the washing effect for alpha-cypermethrin was found in the literature. Generally it can be concluded that washing tomato fruits with tap water can substantially reduce pesticide residues and that including food processing factors is of importance for human intake estimates of pesticides.

3.3 Estimation of metabolism half-life within vegetation

Pesticide concentrations in peeled tomato fruits represent the amount of active ingredient transferred from the spray deposit on the plant surface to the inner part of the plant.

Bromopropylate and alpha-cypermethrin residues were not detectable in peeled tomatoes collected one hour after the spray application (Figures 3 and 4). The maximum residue of bromopropylate (3.31 mg kg^{-1}) in peeled tomatoes was detected at day five after the treatment (Figure 3), while the maximum concentration of alpha-cypermethrin (0.2 mg kg^{-1}) was detected at day three after the spray application (Figure 4). The coefficient of variation of bromopropylate and alpha-cypermethrin dissipation in peeled tomato fruits was 13% and 10%, respectively. Maximum residues of bromopropylate and alpha-cypermethrin in peeled tomato fruits were 48% and 61% lower than the highest concentration found on whole tomato fruits, respectively.

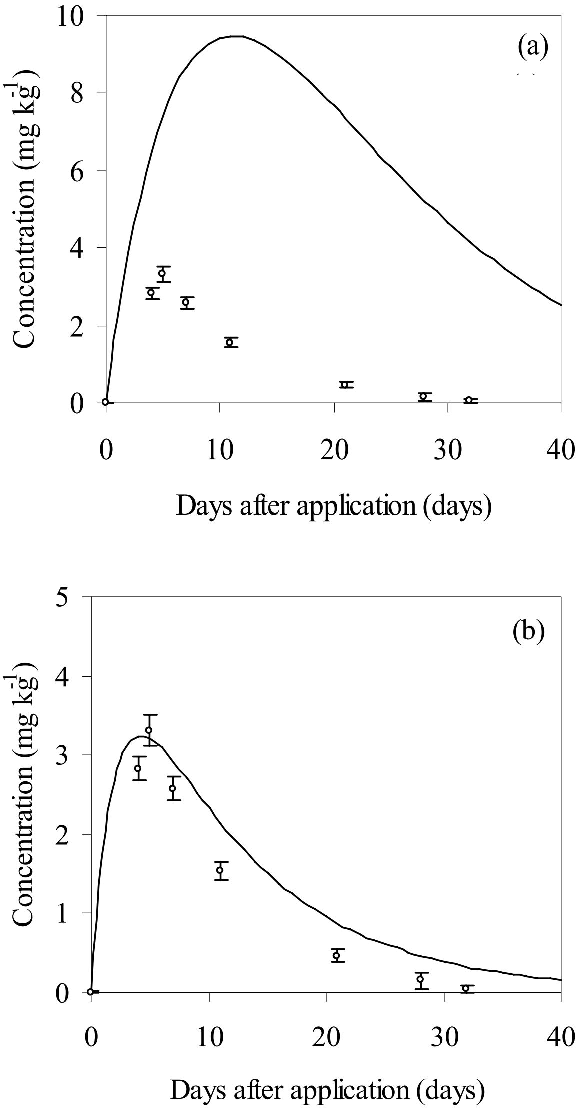


Fig. 3. Measured and modelled bromopropylate concentrations in peeled tomato fruits. (a) Half-life on plant is equal to half-life in plant; (b) Half-life in plant set 4.5 times faster than on plant.

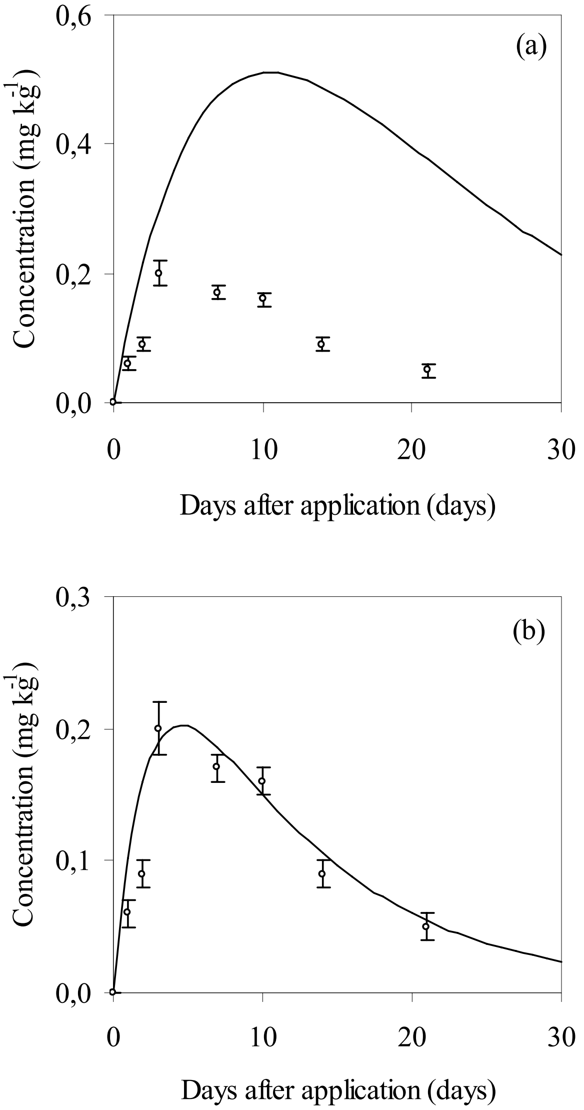


Fig. 4. Measured and modelled alpha-cypermethrin concentrations in peeled tomato fruits, (a) half-life on plant equal to half-life in plant; (b) half-life in plant set 4 times faster than on plant.

Measured amounts of bromopropylate and alpha-cypermethrin lost due to peeling at the typical time-span of consumption (7-14 days after harvest) are 31-61% and 25-30%, respectively. The amount of pesticide lost due to peeling varies between active ingredients. This can be clarified by the fact that each agrochemical has specific transfer and permeability properties to cross through plant cuticles. The permeation through plant cuticles depends on the solute mobility in the limiting skin, the path length of the limiting skin and the partition coefficient between cuticle and deposited surface residue (Schreiber, 2005). The comparison between measured and modelled bromopropylate and alpha-cypermethrin concentrations in peeled tomato fruits is presented in Figures 3 and 4.

In both cases, measured and modelled pesticide concentrations show the same trend, although actual maximum concentration estimates differ from the maximum measured values up to a factor of three when the degradation rate constant in plant and on plant surface are set equal to each other. Fourteen to twenty one days after the pesticide spray application, measured and estimated concentrations deviated up to a factor of ten (Fig. 3a and Fig. 4a). The best correlation (r^2 = 0.94) between measured and modelled concentrations was observed when the metabolism half-life of bromopropylate in vegetation was set 4.5 times faster to the plant surface half-life (Fig. 3b). In the case of alpha-cypermethrin, the best correlation (r^2 = 0.82) between measured and modelled concentrations in peeled fruits was observed when the half-life in vegetation was set 4 times faster to the half-life on the plant surface (Fig. 4b).

These results indicate that the metabolism half-life of bromopropylate and alpha-cypermethrin within plant tissue (mainly caused by enzymatic transformation) is faster than the half-life on plant surface (mainly induced by photodegradation), when applied on tomato fruits. Similar results have been reported by Fujisawa et al. (2003), observing more metabolic degradation in grape fruits as compared with leaves. High enzymatic activity in plant cell tissue of peeled tomato fruits and favourable conditions for factors mediating pesticide metabolic fate in plants like abiotic environmental conditions (temperature, moisture, pH, etc.), plant species, pesticide characteristics, and biological and chemical reactions (Van Eerd et al., 2003) are the main factors explaining this relationship.

The relatively high octanol/water- partition coefficient (K_{ow}) of bromopropylate and alpha-cypermethrin (log K_{ow} = 5.2 and 5.4) is the main physical-chemical property explaining the tendency of these active ingredients to be retained by fatty plant surface tissue (Fujisawa et al., 2002), favouring the partitioning into the inner plant cells where enzymatic transformation is the main route of degradation/detoxification.

Based on the field experiment results and the comparison of measured and modelled pesticide concentrations of bromopropylate and alpha-cypermethrin, the following tentative relationship between metabolism half-lives of pesticides in vegetation and half-lives on plant surface is suggested:

$$Half-life_{in\ vegetation} = \frac{Half-life_{plant\ surface}}{4} \tag{2}$$

Applying our experimental results for plant surface half-lives to Eq. 2, the estimated half-lives of bromopropylate and alpha-cypermethrin in vegetation are 1.9 and 1.8 days if applied to tomato fruits.

In the case that no experimental plant surface half-life data is available, the pesticide half-life within vegetation can tentatively be approximated by the following equation:

$$Half-life_{in\ vegetation} = \frac{Half-life_{soil}}{16} \tag{3}$$

Relationships between soil half-lives and half-lives within plants were presented in the reviewed literature but no common consensus between the methods was observed. Huijbregts et al. (2005) presented a conversion factor of 15 based on degradation half-lives derived from standardized plant cell culture tests (Komoßa et al., 1995). Plant cell suspension cultures are extremely useful for determining metabolic patterns of pesticides (Schmidt, 2001) but laboratory screening test and in vitro methods are not intended to replace whole-organism studies and can not reflect realistic environmental conditions. However, the mean half-life in plant cells calculated was 2.7 days, which is reasonably close to the values calculated for both pesticides studied in this work. Severinsen and Jager (1998) introduced a conversion factor of 10 based on the metabolism rate of bromacil in vegetation and correlated this value with the corresponding rate in soil. Charles (2004) introduced a conversion factor of 2 for the calculation of half-lives in plants assuming that degradation of pesticides in plants is more efficient than in soil but slower than in air.

From this point of view, the estimation of pesticide half-life within plants has been improved by presenting a generic estimation routine for substance specific half-lives based on experimental field data. However, the relationship suggested is not without uncertainties and is based only on the two pesticides analyzed in this study. Finally it has to be pointed out that our findings are intended for use where intermedia extrapolation is necessary for screening and relative risk assessment of pesticides, they are not to be taken as a substitute for scientific understanding of pesticide degradation/metabolism.

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Supporting information

Table A1

Geometric mean half-lives and ratios of 41 pesticides in soil and plant surfaces

Pesticide	Soil Half-life (days)	Plant surface Half-life (days)	Ratio soil/plant surface Half-life	References
Alpha-Cypermethrin	31	7	5	Juraske et al. (this work); Westcott et al., 1987
Azoxystrobin	45	11	4	Angioni et al., 2004; Schirra et al., 2002
Benalaxyl	31	7	5	Cabras et al., 1985; Gambacorta et al., 2005
Bromopropylate	38	7	5	Barba et al. 1991; JMPR, 1993; Juraske et al., (this work)
Buprofezin	27	6	5	Cabras et al., 1998
Captan	8	4	2	Alcoser et al., 1995; Juraske et al., 2007
Chinomethionat	14	4	3	Stensvand and Christiansen, 2000
Chlorothalonil	19	5	4	Gambacorta et al., 2005; Stensvand and Christiansen, 2000
Chlorpyrifos-methyl	16	4	4	Navarro et al., 2001; Putman et al., 2003
Cypermethrin	31	7	5	El-Sebae, 1989; Zhang et al., 2006
Cyprodinil	22	5	5	Garau et al., 2002
Deltamethrin	24	6	4	Paras et al., 2005; Zhang et al., 2006
Dicofol	27	5	5	Brouwer et al., 1997
Dimethoate	18	5	4	Cabras et al., 1997; Goedicke et al., 1988
Endosulfan	21	6	3	Antonious et al., 1998; Mousa et al., 2004
Fenitrothion	20	8	3	Cabras et al., 1997; Fernandez-Cruz et al., 2004
Fludioxonil	48	14	4	Cabras et al., 2000; Garau et al., 2002
Furalaxyl	13	5	3	Cabras et al., 1985;
Imazalil	20	7	3	Stensvand and Christiansen, 2000
Iprodione	34	11	3	Cabras et al., 1985; Stensvand and Christiansen, 2000
Kresoxim-metil	54	13	4	Cabras et al., 1985
Mancozeb	7	5	2	Banerjee et al., 2005; Wauchope et al., 1992
Mepanipyrim	48	13	4	Cabras et al., 1998
Metalaxyl	54	14	4	Goedicke et al., 19888; Marucchini et al., 2002
Methidathion	9	4	2	Kyriakidis et al., 2000; Willis and McDowell, 1987
Myclobutanil	36	11	3	Panagiotis et al., 2003
Penconazole	25	7	3	Navarro et al., 2001; Stensvand and Christiansen, 2000
Permethrin	25	8	3	IPCS, 1990
Procymidone	37	11	3	Cabras et al., 1985; Castillo-Sanchez et al., 2000
Profenofos	7	2	5	Paras et al., 2005; Radwan et al., 2005
Propargite	48	11	4	Pree et al., 1992; Smith, 1991
Pyrethrins	11	4	3	Angioni et al., 2005
Pyrimethanil	22	4	5	Garau et al., 2002; Sadlo, 2002
Pyridaben	37	9	4	Cabras et al., 1998
Rotenone	4	3	1	Cabizza et al., 2004; Cabras et al., 2002
Tebuconazole	46	8	6	Cabras et al., 1997
Tolylfluanid	23	6	4	Stensvand and Christiansen, 2000
Triadimefon	65	17	4	Athanasopoulos et al., 2003
Triadimenol	26	6	4	Stensvand and Christiansen, 2000
Vinclozolin	19	6	3	Navarro et al., 2001; Stensvand and Christiansen, 2000
Ziram	39	10	4	Cabras et al., 1997
	geom. mean 28	geom. mean 7	mean ratio 4	

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Chapter 4

Comparing uptake and persistence of imidacloprid in tomatoes treated by soil chemigation and foliar spray application: Measurements and model estimates

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Abstract

The uptake and persistence behaviour of the insecticide imidacloprid in greenhouse tomato plants treated by (i) foliar spray application and (ii) soil chemigation (localised drip irrigation) was studied and compared using two specific plant uptake models. A pesticide deposition model and a new developed dynamic root uptake and translocation model, both predicting residual concentrations of pesticides in/on fruits. The results were validated by comparing computed values with results obtained from an experimental set-up. The uptake and dissipation of imidacloprid was studied by detecting residual concentrations in complete, washed and peeled tomato fruits using high performance liquid chromatography (HPLC). The fraction of imidacloprid applied in the greenhouse as plant treatment that eventually is ingested by the human population is on average 10^{-2}-10^{-6}, depending on the time between pesticide application and ingestion of tomatoes, the processing step considered and the application method. Model and experimentally derived intake fractions deviated in less than a factor of 2 for both application techniques in the typical time frame of tomato consumption. Total imidacloprid residues were up to five times higher in plants treated by foliar spray application, indicating lower chemical loading using drip irrigation in a closed hydroponic system making this application technique a viable alternative to the standard spray application method by minimizing worker and consumer exposure to pesticides and preventing runoff of pesticide by spray drift into the environment.

Keywords: Pesticides; Plant uptake; Persistence; Human exposure; Hydroponics

1. Introduction

Uptake, translocation and persistence of pesticides in plants may lead to high toxic substance levels that are a hazard to human health and ecosystems, explaining the large interest in the prediction of the amount of these residues (Trapp, 2004). The transfer of organic chemicals into plants occurs via two major pathways: (i) desorption from soil followed by root uptake from soil solution and (ii) through transfer from air through dry and wet deposition of particles on plant surfaces followed by desorption into the inner parts of the plant (Collins et al., 2006). Studies describing the transfer of pesticides into plants are of importance for the development and validation of plant uptake models allowing the prediction of contaminant accumulation, translocation and transformation in edible parts of plants as these represent the main entry of pesticides into the food chain.

Experiments designed to measure plant uptake and translocation under controlled environmental conditions provided insight and information enabling the development of mathematical plant uptake models. The prediction of pesticide uptake was first reported by Shone and wood (1974) who described a relationship between the concentration of pesticides in roots and external solution (soil water), the RCF (Root Concentration Factor). They furthermore established a relationship between the translocation (concentration in xylem sap) and the external solution of pesticides, the TSCF (Transpiration Stream Concentration Factor). Briggs et al. (1982) followed by correlating the RCF and TSCF to the lipophilicity of pesticides.

Based on these studies, several uptake models have already been developed for fate and exposure assessment of pesticides and other organic chemicals in plants (Trapp and Pussemier, 1991; Trapp and Matthies, 1995; Hung and Mackay, 1997; Severinsen and Jager, 1998; Trapp, 2000; Fujisawa et al., 2002; Trapp et al., 2003; Antón et al., 2004; Charles, 2004; Juraske et al., 2007). Although these models have successfully demonstrated the most probable distribution pathways of pesticides in plants, none of the listed models was directly applicable for the simulation of dynamic root uptake and translocation of imidacloprid into tomato fruits treated by soil application (local drip-irrigation). Imidacloprid (CAS# 138261-41-3) is a broad-spectrum neonicotinoid systemic insecticide recommended for treatment in different crops for the control of various sucking pests (Byrne and Toscano, 2006). It can be applied by both foliar spray application and in soil application (Nauen et al., 1999) and was used in this case study for the comparison of both application techniques and for the validation of the developed root uptake model for tomato fruits.

For the development and improvement of modern pest management and fate and exposure assessment of pesticides in edible crops, a new approach is needed in order to have a better understanding of the overall impact of pesticides on human health when the same active ingredient is applied to crops by different application techniques. The present paper addresses these needs, aiming at the following specific goals:

- To measure the uptake, translocation and persistence behaviour of imidacloprid in tomato fruits treated by (i) standard foliar spray application and (ii) soil application using direct localised drip irrigation into root zone.
- To develop a dynamic root uptake model for pesticides aiming at the estimation of time dependent contaminant concentrations in fruits (edible part of tomato crops).
- To compare the experimental results with model estimates in terms of human population intake fractions of imidacloprid due to the consumption of tomatoes and to compare those with indirect exposure pathways like air inhalation and consumption of drinking water.

2. Materials and Methods

2.1 Root uptake and translocation model

2.1.1 Concentration in soil solution

The time dependent concentration of pesticide in the soil solution is given by the initial concentration of active ingredient in the watering solution which is prepared before irrigation and the removal rate of the pesticide in soil media (Sarkar et al., 2001) and can be described as a first order equation:

$$C_{soil\ solution}(t) = C_0 \times e^{-k_{r,\,soil} \times t} \tag{1}$$

where $C_{\text{soil solution}}(t)$ is the pesticide concentration at time t (mg kg^{-1}), C_0 is the initial concentration at time zero (mg kg^{-1}) and $k_{\text{r, soil}}$ is the removal rate of the pesticide in the soil media (days^{-1}).

2.1.2 Concentration in roots

The uptake of pesticides from soil solution into roots depends on the properties of the chemicals and of the plant (Trapp, 2000). The main processes considered are advective uptake with transpiration and diffusion. The concentration in plant roots can be described as a cascade of two compartments with transport from the soil solution to the inner part of the plant. The time dependent concentration of pesticide in roots can be described as:

$$C_{roots}(t) = \frac{C_{0,soil} \times k_{soil-root}}{k_{r,root} - k_{r,soil}} \times (e^{-k_{r,soil} \times t} - e^{-k_{r,root} \times t}) \tag{2}$$

where $C_{\text{roots}}(t)$ is the pesticide concentration in roots at time t (mg kg^{-1}), $C_{0,\text{ soil}}$ is the initial concentration at time zero (mg kg^{-1}) in the soil solution, , $k_{\text{r, soil}}$ is the removal rate of the pesticide in the soil media (days^{-1}), $k_{\text{r, root}}$ is the removal rate of the pesticide in the roots (days^{-1}) and $k_{soil\text{-}root}$ is the transfer rate between soil solution and roots (days^{-1}). Methodological developments for the transport of pesticides from soil to roots were described by Trapp et al. (1995) and Charles (2004). The concentration ratio between xylem sap and soil solution, the transpiration stream concentration factor (TSCF), corresponds to the fraction of substance that enters the xylem. Consequently, the fraction of pesticide that enters the plant with the transpiration stream but is reflected back by the endodermis is considered to remain in the roots. According to this assumption, the transfer rate from soil solution to the roots ($k_{soil\text{-}root}$) can be written as:

$$k_{soil-root} = \frac{Q_w \times (1 - TSCF)}{V_s \times K_{sw}} \tag{3}$$

where Q_w is the plant transpiration stream (m^3 day^{-1}), V_s is the volume of soil (m^{-3}), TSCF is the transpiration stream concentration factor (-) and K_{sw} is the partition coefficient between bulk soil and soil water (-). The TSCF accounts for the reduction in concentration of active ingredient in the pore water as it crosses the root membrane and moves through the xylem to the stem. Burken and Schnoor (1998) proposed the following TSCF correlation based on the octanol/water partition coefficient (K_{ow}):

$$TSCF = 0.756 \times \exp\left[-\frac{(\log K_{ow} - 2.50)^2}{2.58}\right] \tag{4}$$

The availability of a pesticide in soil water solution is given by the partition coefficient between bulk soil and soil water (K_{sw}) equal to the ratio of pesticide concentration in water solution and in bulk soil (Charles, 2004). It considers the different fractions composing the bulk soil, the matrix, the solution and the gas fractions and the equilibrium between the different phases (Trapp and Matthies, 1995) and can be written as:

$$K_{sw} = P_W + K_{aw} \times (P_A - P_W) + (OC \times K_{oc}) \times \frac{\rho_{bs}}{\rho_w} \tag{5}$$

where P_W and P_A are the volume fractions of water and air in soil ($l\ l^{-1}$), K_{aw} is the partition coefficient between air and water (dimentionless Henry's Law constant), OC is the fraction of organic carbon ($kg\ kg^{-1}$), ρ_{bs} and ρ_w are the densities of dry soil and water (kg m^{-3}) and K_{oc} is the partition coefficient between organic carbon and water which was described by Sabljic et al. (1995) and can be written as:

$$\log K_{oc} = 0.81 \times \log K_{ow} + 0.1 \qquad (6)$$

2.1.3 Concentration in stem

Water and solutes are transported upward from the roots into other plant parts through the xylem (Collins et al., 2006). This flux is driven by the water potential gradient, created throughout the plant during transpiration. It is a combination of the solubility of the pesticide in water and within the cell membrane that determines the translocation of the contaminant to the upper parts of the plant (Trapp, 2000). The concentration of pesticide residue in the stem as a function of time can be described as:

$$C_{stem}(t) = \frac{C_{0,soil} \times k_{root-stem}}{k_{r,stem} - k_{r,root}} \times (e^{-k_{r,root} \times t} - e^{-k_{r,stem} \times t}) \qquad (7)$$

where $C_{\mathrm{stem}}(t)$ is the pesticide concentration in the stem at time t (mg kg^{-1}), $C_{0,\ \mathrm{soil}}$ is the initial concentration at time zero (mg kg^{-1}) in the soil, $k_{\mathrm{r,\ root}}$ is the removal rate of the pesticide in the roots (days^{-1}), $k_{\mathrm{r,\ stem}}$ is the removal rate of the pesticide in the stem (days^{-1}) and $k_{root\text{-}stem}$ is the transfer rate between the roots and the stem (days^{-1}) which can be written as:

$$k_{root-stem} = \frac{Q_w}{V_r \times K_{rw}} \qquad (8)$$

where Q_w is the plant transpiration stream (m^3 day^{-1}), V_r is the root volume (m^{-3}) and K_{rw} is the partition coefficient between roots and water (-). Partitioning of water with roots is characterized by the lipophilic behaviour of the substance and by the composition of the plant tissue (Trapp, 2000; Charles, 2004) and can be described as:

$$K_{rw} = (P_{r,w} + P_{r,l} \times K_{ow}{}^{b}) \times \frac{\rho_r}{\rho_w} \tag{9}$$

where $P_{r,w}$ and $P_{r,l}$ are the water and lipid weight fraction of the root (kg kg^{-1}), K_{ow} is the octanol/water partition coefficient, b is an empirical constant to correct differences between plant lipids and octanol and ρ_r and ρ_w are the densities of roots and water (kg m^{-3}).

2.1.4 Concentration in fruits

The main routes for water and nutrition transport into sink organs such as fruits are xylem and phloem. Phloem translocation from leaves to sink organs is driven by the pressure flow of sap which is regulated by the long distance transport in the plant and postphloem transport in sink organs (Malone and Andrews, 2001). Respiration of fruits closely relates to the phloem sap flux which is responsible for the growth of the fruit (Kawabata et al., 2005). The concentration of pesticide in fruits can be written as:

$$C_{fruit}(t) = \frac{C_{0,soil} \times k_{stem-fruit}}{k_{r,fruit} - k_{r,stem}} \times (e^{-k_{r,stem} \times t} - e^{-k_{r,fruit} \times t}) \tag{10}$$

where $C_{\mathrm{fruit}}(t)$ is the pesticide concentration in the fruits at time t (mg kg^{-1}), $C_{0,\mathrm{soil}}$ is the initial concentration at time zero (mg kg^{-1}) in the soil, , $k_{\mathrm{r,\ fruit}}$ is the removal rate of the pesticide in the fruits (days^{-1}), $k_{\mathrm{r,\ stem}}$ is the removal rate of the pesticide in the stem (days^{-1}) and $k_{stem\text{-}fruit}$ is the transfer rate between the stem and the fruits (days^{-1}) which can be written as:

$$k_{stem-fruit} = \frac{Q_w}{V_{st} \times K_{stw}} \tag{11}$$

where Q_w is the plant transpiration stream (m^3 day^{-1}), V_{st} is the volume of the stem (m^{-3}) and K_{stw} is the partition coefficient between the stem and water (-). Similar to the partitioning of water with root tissue, the partitioning between stem and fruit is characterized by the lipophilic behaviour of the substance and by the composition of the plant specific tissue and can be described as:

$$K_{stw} = (P_{st,w} + P_{st,l} \times K_{ow}{}^{b}) \times \frac{\rho_{st}}{\rho_{w}} \qquad (12)$$

where $P_{st,w}$ and $P_{st,l}$ are the water and lipid weight fraction of the stem (kg kg^{-1}), (K_{ow}) is the octanol/water partition coefficient, *b* is an empirical constant to correct differences between plant lipids and octanol and ρ_{st} and ρ_w are the densities of stem tissue and water (kg m^{-3}).

2.2 Spray deposition model

Pesticide concentrations on and within plants treated by foliar spray application were estimated using the pesticide fate and exposure model described by Juraske et al. (2007), which allows one to calculate the concentration of a pesticide as a function of time between application and harvest. The model takes the time between harvest and consumption, absorption of pesticide spray deposit on plant surfaces, transfer properties through the cuticle, degradation of active ingredient on and inside the plant and loss of pesticide due to food processing like washing and peeling into account.

2.3 Human intake fraction

The intake fraction (*iF*) is described as the fraction of mass of chemical released into the environment that is ultimately taken in by the human population (Bennett et al., 2002; Huijbregts et al., 2005). In this case study, the intake fraction is expressed in kg intake by tomato consumption per kg of pesticide applied in the greenhouse ($kg_{ingested}$ $kg_{applied}^{-1}$). The estimation of dynamic human intake fractions of imidacloprid which were compared with calculated human intake fractions based on experimental data was conducted using the pesticide fate and exposure model described by Juraske et al. (2007).

2.4 Experimental Procedures

2.4.1 Design of the field trials

In order to compare measured and estimated pesticide residue levels and, to compare the uptake and persistence of imidacloprid in tomato fruits treated by (i) foliar spray application of tomato plants cultivated in soil and (ii) soil chemigation using drip irrigation of hydroponically grown tomatoes, two field trials were carried out in two similar greenhouses located in the Institut de Recerca i Tecnologia Agroalimentària, Cabrils (Barcelona).

2.4.2 Spray application on tomato plants cultivated in soil

Tomato plants, cultivar *Caramba*, were cultivated in a spring-summer cycle with a density of 2.2 plants m^{-2} and a total yield of 16 kg m^{-2} of tomato fruits. The treatment was carried out using a portable motor sprayer equipped with a gun nozzle using the following commercial formulation: (Confidor®20 LS; 20% of imidacloprid p/v (200 g/l); soluble concentrate; Bayer CropScience) on June 6th, 2006. Spraying was carried out at the recommended concentration of 0.15 g a.i. l^{-1} and a total consumption of 0.3 l m^{-2}. The leaf area index was measured as 2.46. The weight of fruits at the day of application was 2.4 kg m^{-2}. Fruits were sampled before and one hour after the treatment and again after 1, 3, 7, 14, 21 and 28 days.

2.4.3 Soil chemigation of hydroponically grown tomato plants

The cultivation of hydroponic tomato plants, cultivar *Caramba*, was carried out in bags of perlite with localised watering and a total yield of 26 kg m^{-2} of tomato fruits. Water was delivered to each plant by a drip irrigation stake that delivered water at a rate of 4 l h^{-1} directly into the root zone. Imidacloprid (Confidor®20 LS; 20% of imidacloprid p/v (200 g/l); soluble concentrate; Bayer CropScience) was applied by chemigation, utilizing a drip irrigation system on June 6th, 2006. Chemigation was carried out at the recommended dose of 600 g a.i. ha^{-1} by adding the active ingredient directly into the watering system. A total consumption of 0.8 l of irrigation solution was applied to each plant. Fruits were sampled before and directly after the treatment and again after 1, 3, 7, 14, 21 and 28 days.

2.4.4 Analytical method

The analysis of imidacloprid residues was carried out by adapting analytical methods described by Fernandez-Alba et al. (1996) and Obana et al. (2002), both used in the determination of imidacloprid in tomato plants. Whole tomatoes were homogenized in a waring blender. Twenty g of homogenized tomatoes were extracted with acetonitrile (100 mL) for 2 min with an Ultra-Turrax® T18-basic disperser (IKA®, Staufen, Germany).

The extract, with a paper filtration, was transferred to a 200-mL separatory funnel. Sodium chloride (5 g) was added, and the solution was shaken for 1 min to salt out the water layer. An aliquot of the extract (50 mL) was collected. Ten mL of the organic extract layer was evaporated to dryness using a gentle nitrogen stream, and the residue was dissolved in acetonitrile (5 mL). This final solution was filtered through a polytetrafluorethylene (PTFE) membrane filter disc (0.45 µm) attached to the end of a syringe (10 mL) ready for HPLC analysis. The same procedures described above were used for the sample preparation of tap water washed and peeled tomato fruits. In order to avoid contamination from the deposition residue on the outer side of the cuticle, all tomato samples were washed before peeling.

In order to evaluate the efficiency of the analytical procedures a recovery assay was conducted. Samples of untreated tomato fruits were spiked with 2, 1, 0.5 and 0.1 mg L^{-1} of imidacloprid standard solution and processed according to the extraction procedure four times. The recovery assay yielded good recoveries in the extraction process, from 84 to 96% with a maximum standard deviation of 9%. These levels can be considered as satisfactory for residue determinations of imidacloprid and are comparable to results reported by Obana et al. (2002) and Blasco et al. (2002). Coefficient of determination (r^2) in the range of 0.1-2 mg L^{-1} was 0.997 ($n = 5$). In order to determine the amount of pesticide removed from the fruit due to home processing, tomato fruits were washed with cold (21°C) tap water. The water used for washing in all processing steps was tap water without detergents.

2.4.5 Apparatus and Chemicals

High-performance liquid chromatography (HPLC) analysis was carried out using an Agilent Technologies 1100 Series (Santa Clara, CA, USA) analytical system, equipped with a photodiode-array detector. HPLC separation was conducted using a Hypersil ODS-C18 (5 µm particle size) column (4.6 × 250 mm ID) (Agilent Technologies, Santa Clara, CA, USA) and the temperature was maintained at ambient (23 ºC). The mobile phase was acetonitrile/water (30:70 v/v) at a flow rate of 1 ml min^{-1}. The sample size was 20 µl and the detector was set at 270 nm. Acetonitrile was a HPLC grade solvent (Riedel de Haën, Seelze, Germany). Imidacloprid standard solution (100 mg L^{-1}) was purchased from LGC Promochem, Barcelona, Spain.

3. Results & discussion

3.1 Foliar spray application

Pesticide residue concentrations in whole tomato fruits obtained in the dissipation study of imidacloprid after spray application and the corresponding first order decay fit are presented in Fig. 1.

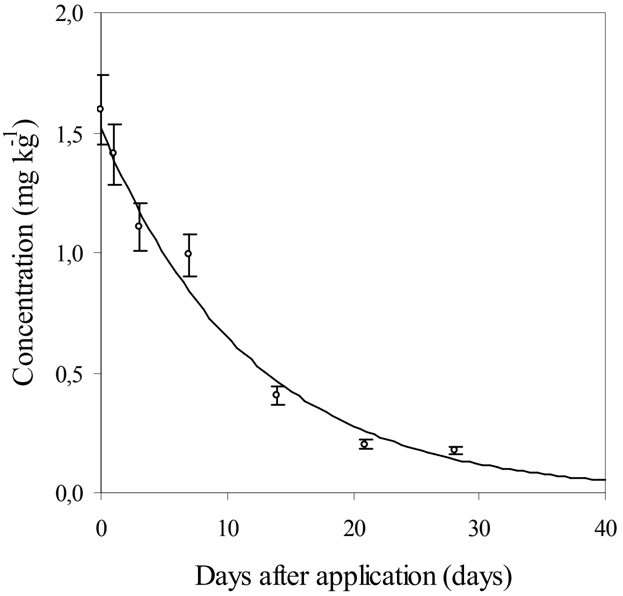

Fig. 1. Dissipation of imidacloprid from tomato fruits treated by foliar spray application (±SE).

Average residue concentrations of imidacloprid on tomato fruits ranged from 1.60 mg kg^{-1} at day zero to 0.18 mg kg^{-1} twenty eight days after the spray application with a coefficient of variation of 6%. The degradation kinetics of imidacloprid deposits were well described by a first-order decay equation, ($C(t) = 1.5 \times e^{-0.085 \times t}$; r^2=0.97). According to our experimental results, the half-life of imidacloprid is 8.2 days if applied on tomato fruits. Imidacloprid half-lives on plant surfaces found in the literature ranged from 3 days (Mukherjee and Gopal, 2000) up to 32 days reported by Vogeler et al. (1992). The value reported in this study lies within the range of experimental values found in the literature. However, experimental half-life values of imidacloprid on plants show large variation. This could be explained by the fact that half-lives were measured on different kinds of crops with different plant surface properties and that the experiments were conducted under different environmental conditions (temperature, relative humidity and UV irradiation).

The concentrations of imidacloprid on tomato fruits calculated by the spray deposition model deviated between 2-27% from the field experiment results. A mean error of 12% was observed between experimental results and model estimates during the complete dissipation study (28 days).

Imidacloprid residues were not detectable in peeled tomatoes collected throughout the whole field experiment. The maximum concentration of imidacloprid in peeled tomato fruits estimated by the model was 0.001 mg kg^{-1} (day 6 after the spray application), a concentration which lies approximately 100 times under the detection limit of the experimental setup. However, measurements and model estimates indicate that imidacloprid from spray deposition on the plant surface does not tend to cross through the cuticle of tomato fruits and suggest a low potential for bioaccumulation.

This can be clarified by the fact that each agrochemical has specific transfer and permeability properties to cross through plant cuticles. The permeation through plant cuticles depends on the solute mobility in the limiting skin, the path length of the limiting skin and the partition coefficient between cuticle and deposited surface residue

(Schreiber, 2005; Trapp, 2004). The latter is directly related to the octanol-water partition coefficient (K_{ow}), which is a key parameter in the studies of the environmental fate of chemical substances. It is a useful parameter in the prediction of adsorption behaviour of pesticides. Nemeth-Konda et al. (2002) reported log K_{ow} values between 0.56 and 0.92, relatively low values suggesting a low hydrophobicity of imidaloprid. The low octanol-water partition coefficient furthermore indicates low adsorption behaviour of the active ingredient into organic matter. Nauen et al. (1999) and Buchholz and Nauen (2001) reported that imidacloprid can be penetrated through plant cuticles via diffusion, but in contrary to our experiments, the active ingredient was applied using surfactants or emulsifiers (leaf wetting agents) favouring a penetration. However, the main portion of imidacloprid applied to the plants resided on the surface or in the epicuticular waxes of the cuticle. Food processing studies provide basic information on the reduced levels of residues in passing from the raw agricultural commodity to a processed commodity. The processing factor can be described as the residue level in the processed product divided by the residue level in the raw agricultural commodity. Imidacloprid concentrations on tomatoes were reduced by 22% when washed in cold tap water (21°C). From these results an experimental tap water washing processing factor of 0.78 can be estimated for imidacloprid. Processing factors for imidacloprid reported in the literature vary between 1 (0% of imidacloprid removed from cherries) reported by Spiegel and Neigl (2000) and 0.25 (75% of imidacloprid removed from grapes) reported by Spiegel (2001). The value reported in this study lies within the experimental values found in the literature. However, the experimental processing factors for imidacloprid show large variation when applied to different types of crops.

Generally it can be concluded that washing tomato fruits with tap water can substantially reduce pesticide residues and that including food processing factors is of importance for human intake fraction estimates of pesticides.

3.2 Root uptake and translocation after chemigation

Pesticide residue concentrations in whole tomato fruits obtained in the dissipation study of imidacloprid after direct soil chemigation and the corresponding estimates calculated using the root uptake and translocation model are presented in Fig. 2.

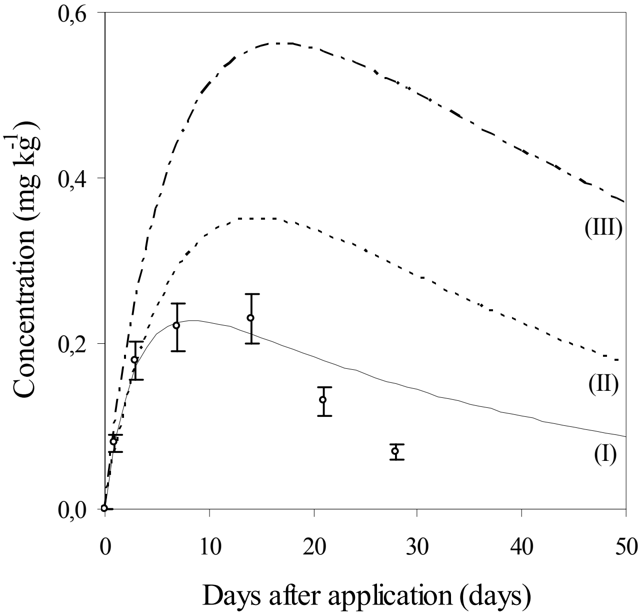

Fig. 2. Measured (○ ±SE) and modelled imidacloprid concentrations in tomato fruits (I), stem (II) and roots (III) treated by soil chemigation.

Imidacloprid was not detectable in tomato fruits collected directly after chemigation (Fig. 2). The same result was obtained using the root uptake model. According to model estimates, no imidacloprid residues are to be found in roots and stem directly after chemigation. For chemicals taken into roots to reach the xylem, they must penetrate a number of layers: the epidermis, cortex, endodermis, and pericycle (Trapp, 2004; Collins et al., 2006). At the endodermis all materials must pass through at least one cell membrane. An immediate uptake of active ingredient directly after irrigation is therefore not expected. The maximum residue in tomato fruits (0.23 mg kg^{-1}) was detected fourteen days after chemigation. The same maximum concentration (0.23 mg kg^{-1}) in tomato fruits was also predicted by the model but for day nine after the pesticide was applied. Measurements and model estimates for imidacloprid concentrations in tomato fruits correspond well from the day of application until day fourteen after chemigation. For the rest of the experiment, model calculations overestimated the measured values by a factor of two. A mean error of 20% was observed between experimental results and model estimates during the complete uptake and translocation study (28 days). An underestimation of the metabolism rate of imidacloprid in fruits used in the model compared to field conditions may be one explanation for this result. Estimated imidacloprid concentrations in roots were the highest throughout the whole experiment compared with concentrations in stem and fruits. Slower degradation of imidacloprid in soil compared to metabolism in plant tissue (Nauen et al., 1999; Sarkar et al., 2001) and the fact that a fraction of active ingredient is reflected back by the endodermis and remains in the roots (Trapp, 2000) are the main factors leading to higher concentrations in roots.

Imidacloprid concentrations in whole tomato fruits measured after foliar spray application were higher than those detected in whole fruits treated by soil application throughout the entire dissipation study. Assuming that the typical time of tomato consumption is between day seven and twenty one after the pesticide application, imidacloprid concentrations in fruits after spray application exceeded those in fruit after soil application by up to a factor of five indicating that the use of drip irrigation systems for the application of systemic pesticides would have advantages over spray applications. It would minimize worker and consumer exposure to the pesticide, result in a uniform application, and prevent runoff of pesticide by spray drift into the environment.

A comparative field study of the systemic efficacy of imidacloprid against whiteflies conducted by Buchholz and Nauen (2001) revealed that the active ingredient was more effective after soil application as compared with foliar application. Van Iersel et al. (2000) reported that the control of whiteflies was better after subirrigation than on hand-watered plants that received a drench application of imidacloprid. These results demonstrate that soil application of imidacloprid is a viable alternative to the standard spray application not only in terms of human and ecosystem health but also in terms of pest control quality.

3.3 Comparison of measured and estimated human intake fractions

Measured and modelled time dependent intake fractions of imidacloprid for (i) unwashed, (ii) washed and (iii) washed and peeled tomatoes, representing the fraction of pesticide applied in the greenhouse that eventually passes into the human population through direct ingestion of fruits, are presented in Table 1. The intake fraction for unwashed tomatoes varies between 10^{-2}-10^{-3} ($kg_{ingested}$ $kg_{applied}^{-1}$) for both application techniques, depending on the time of consumption. The intake fraction for washed tomatoes treated by spray application ranges between 10^{-2}-10^{-3} ($kg_{ingested}$ $kg_{applied}^{-1}$), while the intake fraction for washed and peeled tomatoes varies between 10^{-5}-10^{-6} ($kg_{ingested}$ $kg_{applied}^{-1}$).

Table 1. Time dependent human population intake fractions ($kg_{ingested}$ $kg_{applied}^{-1}$)

Foliar spray application								
Days after application		0	1	3	7	14	21	28
iF (unwashed)	measured	8×10^{-2}	7×10^{-2}	6×10^{-2}	5×10^{-2}	2×10^{-2}	1×10^{-2}	9×10^{-3}
	modelled	8×10^{-2}	7×10^{-2}	6×10^{-2}	4×10^{-2}	2×10^{-2}	1×10^{-2}	7×10^{-3}
iF (washed)	measured	6×10^{-2}	6×10^{-2}	4×10^{-2}	4×10^{-2}	2×10^{-2}	8×10^{-3}	7×10^{-3}
	modelled	6×10^{-2}	5×10^{-2}	5×10^{-2}	3×10^{-2}	2×10^{-2}	1×10^{-2}	6×10^{-3}
iF (peeled)	measured	nd	nd	nd	nd	nd	nd	nd
	modelled	0	3×10^{-5}	7×10^{-5}	7×10^{-5}	4×10^{-5}	2×10^{-5}	4×10^{-6}
Soil application								
Days after application		0	1	3	7	14	21	28
iF (unwashed)	measured	nd	4×10^{-3}	9×10^{-3}	1×10^{-2}	1×10^{-2}	7×10^{-3}	4×10^{-3}
	modelled	0	4×10^{-3}	9×10^{-3}	1×10^{-2}	1×10^{-2}	9×10^{-3}	8×10^{-3}

nd: not detectable

In order to compare intake fractions from direct ingestion of tomato fruits to those deriving from air inhalation and the consumption of drinking water, the commonly used multi-media fate, exposure and effect model USES-LCA 2.0 (Huijbregts et al., 2005) was applied. Intake fraction for imidacloprid due to air inhalation and drinking water consumption varies between 10^{-5}-10^{-9} ($kg_{ingested}$ $kg_{applied}^{-1}$). Intake fractions due to air inhalation and consumption of drinking water are expected to be significantly lower (up to 6 orders of magnitude) than those for the intake of tomatoes in this case study. These results are consistent with those presented by Margni et al. (2002) and Juraske et al.

(2007) and confirm the potential importance of intake of pesticides by ingestion of food as a direct route into the human population.

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Chapter 5

PestScreen: A screening approach for scoring and ranking pesticides by their environmental and toxicological concern

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Abstract

A chemical ranking and scoring method entitled PestScreen has been developed as a screening tool to provide a relative assessment of pesticide hazards to human health and the environment. The method was developed to serve as an analytical tool in screening and identification of pesticides of environmental concern used in agriculture. PestScreen incorporates both the toxic effects of pesticides and their fate and exposure characteristics in different compartments of the environment. This is done by combining measures of chemical toxicity pertaining to both human health and the environment with chemical release amounts and information on overall environmental persistence, long-range transport potential and human population intake fractions. Each hazard measure is scored and weighted and finally combined with the pesticide application dose to provide a single final indicator of relative concern (PestScore). Results for 217 pesticides are presented and the practical implementation is illustrated on behalf of three practical case studies.

Keywords: Pesticide; Ranking; Risk assessment; Risk indicator; Screening

1. Introduction

Pesticides are specifically used in agriculture for the control of pests, weeds or plant diseases. Their application is still the most effective and accepted means for the protection of plants from pests, and has contributed significantly to enhanced agricultural productivity and high crop yields (Bolognesi, 2003). However, the use of plant treatment products represents toxicological and ecotoxicological risks like exposure of non-target organisms, undesirable side-effects on some species, communities or on ecosystems as a whole.

The use of comparative assessment methodologies like impact rating systems are of great value and can be used as an aid in reducing these risks (Hansen et al. 1999). For this purpose pesticide risk indicators and pesticide ranking and scoring systems have been developed to predict the environmental impact of agrochemicals.

Several methods have been proposed and evaluated in the literature to estimate the relative impact of pesticides on the environment (Levitan et al., 1995; van der Werf, 1996; Pennington and Bare, 2001; Margni et al., 2002; Reus et al., 2002; Antón et al., 2004; Alister and Kogan, 2006). Early approaches (Levitan et al., 1995; van der Werf, 1996) have focused primarily on toxicity comparisons or the amount of pesticide applied to the field. However, pesticide risk cannot be adequately assessed either by simply quantifying application rates or by evaluating only toxicity potential because different chemicals have quite different fate and transport characteristics, and non-target effects (Levitan, 2000).

More recently, methodologies incorporated physical-chemical properties and environmental fate and exposure considerations into a pesticide ranking system and integrated them with toxicity (Pennington and Bare, 2001; Margni et al., 2002; Reus et al., 2002; Antón et al., 2004; Alister and Kogan, 2006). However, these methods do not consider a full evaluation of exposure pathways which are directly linked to the transfer of applied pesticides into the food chain. Methods presented by Margni et al. (2002) and Antón et al. (2004) only provide estimations of direct contaminant exposure which are based on the maximum residue limit (MRL) of one single pesticide. Furthermore, the combination of relevant hazard metrics for screening and assessment of chemicals like long-range transport potential (LRTP) and overall environmental persistence (Klasmeier et al., 2006) have readily been used in ranking and scoring systems of chemicals (Ranke and Jastorff, 2000; ChemSCORER, 2002), but have not been considered in any pesticide specific assessment method yet.

In order to evaluate the overall impact of pesticides on human and ecosystem health, there is a need for development of a new ranking approach which includes not only indicators of toxic effects and bioaccumulation but also incorporate indicators addressing the lifetime and mobility of pesticides.

To address these needs, this paper develops a ranking procedure to quantify the relative risk of pesticides by providing (a) the amount of pesticide released into the environment in terms of active ingredient; (b) fate and exposure indicators, based on multimedia model calculations and (c) human and ecotoxicological indicators. A single score for each pesticide is obtained by means of multicriteria analysis. The application of the screening methodology is shown in three case studies and the advantages and limitations of the ranking approach are discussed.

2. Methods

2.1 Selection of indicators

2.1.1 Overview

Table 1 summarizes the impact categories used for the environmental assessment of pesticide application and shows an inventory of possible indicators and measures found in the reviewed literature.

Table 1

Inventory of possible indicators for pesticide screening

Dose	Fate	Exposure	Toxicity
Application dose*	Degradation half-life	BCF fish	Ecotox. (aquatic):
			LC50 algae
Frequency	Drift	Intake fraction*	LC50 crutaceans
			LC50 fish*
World sales	Leaching:	Kow	
	Koc		Ecotox. (terrestrial):
World use	solubility		LD50 birds
			LD50 earthworms
	LRTP*		LD50 honey bees*
	Overall persistence*		Human toxicity:
			acute: LD50 rat*
	Volitalisation:		acute: LD50 mouse
	vapour pressure		acute: LD50 dog
	henry´s law constant		chronic: ADI*

* indicators used in PestScreen

The selected indicators and the explanations for their selection for the use in PestScreen are presented in the following section.

2.1.2 Dose

The application dose (*D*) is the amount of active ingredient applied to the field given in kilograms per hectare of cultivated area. The greater amount applied increases the environment chemical-loading and potential for contamination. Pesticides for use in sprays are generally available as wettable or soluble powders and as liquid concentrates. These must be diluted, usually with water, before use. Application rates can be used on the basis of recommendations from manufacturers (label recommendations) and other agencies (e.g. Food and Agriculture Organization of the United Nations (FAO)).

The application dose (alternatively referred to as application rate) was selected as an indicator because it gives the exact amount of active ingredient entering the environment per area of cultivation. World sales and total amount of pesticides used annually world-wide can only be approximated and do not provide information about the exact cultivation area. The application frequency does not give any information about the concentration and the area the pesticide was applied to.

2.1.3 Overall environmental persistence

Overall persistence is the residence time of a contaminant in a defined environment. Its value accounts for the different volumes of, and concentrations and removal rate constants in, the various environmental media (MacLeod and McKone, 2004). The calculated overall residence time of a substance in a multimedia environment is taken as a measure of persistence (van de Meent et al., 2000):

$$P_{ov} = \tau_{overall} = \frac{\sum M_i}{\sum (M_i \times k_i)} = \frac{1}{\sum (\varphi_i \times k_i)} = \frac{1}{\ln 2 \times \sum (\varphi_i / t_{½,i})} \qquad (1)$$

where M_i is the steady state mass inventory (kg day^{-1}), φ_i the mass fraction (kg kg^{-1}), k_i the first-order transformation rate constant (day^{-1}), and $t_{1/2,i}$ the half-life of the substance in medium i (days). Defined this way, overall persistence is the mass-distribution weighted average environmental residence in time units (days).

Because there are currently no monitoring strategies that allow these properties to be measured directly, multimedia models are used. Level III multimedia fugacity models calculate persistence in the entire environment from estimated half-lives in individual media. A comparison among several models and modelling approaches carried out by Fenner et al. (2005) shows that ranking of chemicals according to overall persistence (P_{ov}) are highly correlated among all models used and are largely determined by the chemical properties. In this work, overall persistence was calculated using the multimedia fate model SimpleBox 3.0 (Den Hollander et al., 2004).

2.1.4 Long-Range Transport Potential

Long range transport potential (LRTP) can be described as a distance-related measure that either estimates the fraction of the total emission (between 0 and 1) carried out of the source region and thus transported over a fixed distance at steady state (Klasmeier et al., 2006). LRTP is relevant to the screening and assessment of chemicals because it indicates whether a chemical has a potential for leading to an exposure burden that will continue into future time or be displaced to remote regions (Scheringer et al., 2001). Of particular concern is transport from populous industrial temperate regions where the low temperatures tend to favour partitioning from the atmosphere to solid and liquid media and to reduce rate constants for degrading reactions, resulting in increased persistence and exposure (UNEP, 2001; Mackay et al., 2006). The "acid rain" and polar ecosystem contamination issues are of this type.

In this work, long-range transport potential *F* (dimensionless fraction) of pesticides was calculated using the multimedia fate model SimpleBox 3.0 (Den Hollander et al., 2004). The model takes weather conditions (wind, precipitation and temperature), soil properties (organic matter content and soil depth) and site characteristics into account. The LRTP metric is the ratio of the steady state mass flux leaving the inner (continental) box and the emission mass flux ("outflow ratio") and can be described as:

$$F = \frac{k_{o,s} \times m_s + k_{o,w} \times m_w + k_{o,a} \times m_a}{\sum_i q_i} \qquad (2)$$

where $k_{o,i}$ (day^{-1}) is the output rate constant of compartment *i* (soil, water and air). The m_i (kg) are masses in compartments *i* at steady state and the q_i (kg day^{-1}) are the release mass fluxes to compartments *i*. In SimpleBox 3.0, the regional scale is represented as a densely populated Western European region. The continental scale is a copy of the regional scale, with adjusted parameters to represent the whole European region.

Applying physical-chemical properties of pesticides like vapour pressure, water solubility or the Henry´s law constant as measures for their tendency to distribute in the environment only provides a first step evaluation to assess the partitioning of pesticides into different compartments (Gramatica and Di Guardo, 2002). Degradation half-lives provide information about the persistence of a pesticide in one compartment but can not be used as an indicator representing the environment as a whole.

2.1.5 Intake Fraction

A common tool to express human fate and exposure is the intake fraction (iF), representing the fraction of the quantity of chemical emitted that enters the human population (Bennett et al., 2002). The intake fraction is described as the ratio of the rate of pollutant intake by the population (mg day^{-1}) to the rate of release into the environment (mg day^{-1}) (MacLeod et al., 2004). In this case, the human intake fraction is defined as the rate of pesticide intake by the human population divided by the emission rate under the assumption of steady-state conditions. It is a relative measure of exposure, neglecting the dynamic nature of the application of pesticides. The intake fraction is calculated using the multi-media fate, exposure and effect model USES-LCA 2.0 (Huijbregts et al., 2005) which incorporates the SimpleBox 3.0 model (Den Hollander et al., 2004) as a fate module, and can be described as:

$$iF_{r,i,s,a} = \frac{\partial I_{r,s,a}}{\partial M_{i,s}} = \frac{\partial I_{r,s,a}}{\partial C_{j,s}} \times \frac{\partial C_{j,s}}{\partial M_{i,s}} \tag{3}$$

in which $iF_{r,i,s,a}$ represents the human population intake fraction at geographical scale a (continental, moderate, arctic, tropic) that accounts for transport of substance s via intake route r (ingestion, inhalation) from emission compartment i (dimensionless), $\partial I_{r,s}$ is the marginal change in the intake of substance s by the human population via intake route r (kg day^{-1}), $\partial C_{j,s}$ is the marginal change in the dissolved steady state concentration of substance s in compartment j (kg m^{-3}) and $\partial M_{i,s}$ is the marginal change in the emission of substance s to compartment i (kg day^{-1}).

The human population intake fraction was selected as an indicator in the exposure category which describes the accumulation of pesticides in the human food chain. This indicator already includes the bioconcentration factor in fish (BCF_{fish}) because it considers ingestion via fresh fish intake as an exposure route in its calculations (Huijbregts et al., 2005).

The octanol/water partition coefficient (K_{ow}) is often used to predict BCFs and would basically provide the same information as the BCF_{fish}. However, including the median lethal concentration (LC_{50}) of pesticides as a toxicity indicator implicitly includes BCF in the method, since LC_{50} is highly correlated with Log K_{ow} and BCF (Mackay et al., 2001). Both, BCF_{fish} and K_{ow} can therefore be neglected as independent indicators in order to prevent double counting of one indicator in the same hazard category.

The human population intake fraction is calculated using integrated model predictions which consider ingestion of food and drinking water (surface water and ground water) and air inhalation as exposure pathways, which makes the necessity of an independent leaching potential indicator negligible.

2.1.6 Acceptable Daily Intake

Acceptable Daily Intake (ADI) refers to the estimate of the amount of a pesticide that can be ingested daily over a lifetime without appreciable health risk to the consumer (MacNeil, 2005). It is normally expressed in milligrams of the substance per kilogram of body weight per day. For calculation of the daily intake per person, a standard body mass of 60 kg is used. The determination of the ADI is based on the following method: First, a no-observed-adverse effect level (NOAEL) is obtained, based on results of long-term animal safety studies. The NOAEL refers to a level that does not have any adverse effect on the health of the experimental animals. Then, the ADI is calculated by dividing the NOAEL by a safety factor (usually 100) obtained from inter-species variability between humans and test animals and intra-species variability between human individuals (Walker, 1998). The ADI value is used as an indicator for potential risk deriving from a chronic exposure of pesticides to the human population. Data availability and a wide consensus between existing methods were the main criteria for the selection of this indicator.

2.1.7 Median Lethal Dose for rats

The median lethal dose (LD_{50}) is a statistically derived dose of a chemical or physical agent (radiation) expected to kill 50% of test organisms in a given population under defined conditions (Stephenson et al., 2006). A high LD_{50} implies a lower toxicity because more of the pesticide is required to result in death. The LD_{50} measures acute effects, and therefore provides no information about a chemical's connection to chronic (long-term) health effects. The oral LD_{50} to rats (*Rattus norvegicus*) is given in milligram of active ingredient per kilogram body weight and is used as an indicator of the acute mammalian pesticide toxicity since these determinations are standard procedures in toxicology (WHO, 2005).

2.1.8 Median Lethal Dose for bees

Pollinators such as honey bees are considered of being crucial to the functioning of almost all terrestrial ecosystems including those dominated by agriculture and are therefore excellent samplers of environmental pollution (Thompson, 2003). The oral LD_{50} to honey bees (*Apis mellifera*) is given in microgram of substance per bee and is used as an indicator of acute ecotoxicological effects to insects in terrestrial habitats. Earthworm toxicity could be considered as an alternative and/or additional indicator in this section but data on toxicity to earthworms are scarce and could not be found for the complete dataset.

2.1.9 Median Lethal Concentration for fish

The median lethal concentration (LC_{50}) is a statistically derived concentration of a substance in an environmental medium expected to kill 50% of test organisms in a given population under defined conditions (Stephenson et al., 2006). LC_{50} values are obtained from studies of dose-response and represent only adverse effects of finite duration occurring within a short time (up to 14 days). The acute toxicity of pesticides to aquatic organisms is evaluated with the LC_{50} to rainbow trout (*Oncorhynchus mykiss*) which is given in milligram of contaminant per litre of water. Aquatic toxicity of pesticides can also be assessed by determining toxicity to algae or crustaceans. To simplify the risk evaluation, fish toxicity was selected as a single indicator. Again, data availability and a wide consensus between existing methods were the main criteria for the selection of this indicator.

2.2 PestScore

A number of different types of risks are associated with pesticides. According to Reus et al. (2002) and Antón et al. (2004), the impact of pesticides on the environment will depend on (1) the amount of the active ingredient applied and its site of application; (2) its partitioning to the various environmental compartments; (3) its rate of degradation in each compartment; and (4) its toxicity to the species present in these compartments. Taking all the above mentioned impacts into account, the following general equation is presented for the calculation of a final single impact score (PestScore) to compare pesticides in terms of environmental and human health concern:

$$PestScore = D \times \left(\frac{\sum F_{i=2}}{2} + \frac{E_{i=1}}{1} + \frac{\sum T_{i=4}}{4} \right) \tag{4}$$

This score provides a simple categorical distinction between pesticides in terms of application dose (*D*) and the following three hazard categories: fate (*F*), exposure (*E*), and toxicity (*T*). Each hazard category is given the same weight, where *i* represents the number of indicators used in each category. The final score represents a risk-based indicator in which the value of zero can be reported when no pesticide is applied. The application dose is used as an indicator of chemical loading and is therefore separated from the hazard indicators. Each *F* ,*E* & *T* hazard-indicator is scored on a 1 to 4 scale (low to very high concern), the scores are then added to form the hazard-index which is finally multiplied by the application dose to obtain the overall impact score (PestScore) (Table 2).

Table 2

The level of concern and assigned intervals proposed for final impact score

Level of concern	Class	PestScore
low	I	≤ 2.5
medium	II	2.5 ≤ 5.9
high	III	5.9 < 12.0
very high	IV	≥ 12.0

Each of the *F*, *E* & *T* sub-scores is calculated using key physical-chemical properties and cut-off criteria. Table 3 summarizes the categorization of risk levels, sub-scores and the assigned ranking intervals of selected indicators used in PestScreen.

Table 3

The level of concern and assigned intervals proposed for each hazard-indicator

Level of concern	Sub-score	Indicators and ranking intervals			
		Pov (days)	LRTP (-)	iF (kg day^{-1}/kg day^{-1})	$LC50_{fish}$ (mg/L)
low	1	≤ 44	$\leq 10^{-04}$	$\leq 2\times10^{-06}$	≥ 25
medium	2	44 ≤ 61	$10^{-04} \leq 10^{-03}$	$2\times10^{-06} \leq 4\times10^{-06}$	25 ≥ 2.5
high	3	61 < 106	$10^{-03} < 6\times10^{-03}$	$4\times10^{-06} < 10^{-05}$	2.5 > 0.2
very high	4	≥ 106	$\geq 6\times10^{-03}$	$\geq 10^{-05}$	≤ 0.2

Level of concern	Sub-score	Indicators and ranking intervals		
		ADI (mg/kg bw day)	$LD50_{rat}$ (mg/kg bw)	$LD50_{bee}$ (µg/bee)
low	1	≥ 0.05	≥ 5000	≥ 100
medium	2	0.05 ≥ 0.01	5000 ≥ 1800	100 ≥ 20
high	3	0.01 > 0.005	1800 > 250	20 > 1.5
very high	4	≤ 0.005	≤ 250	≤ 1.5

Four levels of concern (low, medium, high and very high) were identified by dividing the dataset into four groups using the three quartiles (25th, 50th and 75th percentiles) of the dataset. This procedure was carried out for all hazard indicators and for the final

PestScore. The ranking intervals of each sub-category were set by assigning the interval between the 0th percentile up to the lower quartile (25th percentile) as the low level of concern. Medium level of concern was defined as the interval between the lower quartile and the median (50th percentile). The interval between the median and the upper quartile (75th percentile) was identified as the high level of concern and the very high level of concern was assigned to the interval between the upper quartile and the 100th percentile.

2.3 Input data

In order to compile a database needed for the scoring and ranking of the 217 pesticides studied in PestScreen, in which the main selection criterion was the availability of data (see supporting information), experimental and estimated data were gathered from several sources.

Physical-chemical properties for the calculation of the overall persistence, long-range transport potential and the human intake fraction were obtained from the USES-LCA 2.0 database (Huijbregts et al., 2005). Sources for experimental data used in the database were: (1) Physical-Chemical Properties and Environmental Fate Handbook (Mackay et al., 2000); (2) Handbook of Environmental Degradation Rates (Howard et al., 1991); (3) The e-Pesticide Manual (Tomlin, 2002) and (4) Linders et al., (1994). Application rates of all agrochemicals used in the study were taken from Linders et al. (1994) and the Food and Agriculture Organization of the United Nations (FAO, 2001). Data on the acceptable daily intake of pesticides were taken from the German Federal Institute for Risk Assessment (BfR, 2003). Toxicological data on the lethal dose to rats were obtained from the World Health Organization (WHO, 2005). Eco-toxicological parameters regarding the lethal dose to honey bees and lethal concentrations to fish were taken from Linders et al. (1994) and Villa et al. (2000). In the case that no experimental data were found, the estimation method for biodegradation half-lives described by Aronson et al. (2006) and the physical/chemical property and environmental fate estimation model EPI Suite™ (USEPA, 2005) were used.

2.4 Case studies

To illustrate the applicability of PestScreen, three case studies were carried out on the example of tomato production in Catalonia (Spain). Three different active ingredients were applied in each of the three main pesticide classes (fungicides, herbicides and insecticides) illustrating a practical pesticide application example. The specific examples presented in this work were chosen because of their general interest in tomato production, reflecting common pest management problematic in agricultural production.

3. Results & Discussion

3.1 Pesticide scores

Table 4 summarizes the results of PestScreen. Substance-specific properties and PestScores can be found in the Supporting Information.

About 95% of the pesticides included in the database can be divided into three main groups consisting of 71 insecticides (33%), 69 herbicides (32%) and 65 fungicides (30%). The remaining 12 pesticides (5%) include: acaricides, antifeedants, molluscicides, plant growth regulators and rodenticides.

Table 4

General summary of PestScreen results

Level of concern	Class	Pesticide class			
		Herbicides	Insecticides	Fungicides	Rest
low	I	15 (22%)	20 (28%)	17 (26%)	3 (25%)
medium	II	8 (11%)	23 (33%)	19 (29%)	4 (33%)
high	III	22 (32%)	13 (18%)	17 (26%)	3 (25%)
very high	IV	24 (35%)	15 (21%)	12 (19%)	2 (17%)

Two-third of the halogenated insecticides included in the method show a high or very high level of concern in terms of human and ecosystem health. This can be explained by the fact that already banned organochlorine insecticides like Aldrin, DDT and Lindane are included in PestScreen. Although industrialized nations have restricted or banned many of these pesticides, they continue to be manufactured for export to other countries. In Spain, the use of some organochlorine pesticides was restricted in the mid-1980s but recent reports show relative high concentrations of pesticide residues of organochlorines in food, human blood and surface water of lakes and rivers (Carraño et al., 2007; Gómez-Gutiérrez et al., 2006). Organochlorine compounds are of special interest because of their ubiquitous overall persistence and their strong ability to bioaccumulate and biomagnify and were therefore included in the dataset.

3.2 Correlation between individual indicators

A Spearman rank correlation test was applied to the full dataset in order to identify the correlation between the individual sub-indicators.

Table 5

Rank correlation coefficients between individual sub-indicators

	Dose	Pov	LRTP	iF	ADI	LD50 rat	LD50 bee	LC50 fish
Dose	1.00							
Pov	0.02	1.00						
LRTP	0.21	0.25	1.00					
iF	0.00	0.63	0.34	1.00				
ADI	0.00	0.00	0.10	0.10	1.00			
LD50 rat	0.00	0.00	0.00	0.20	0.62	1.00		
LD50 bee	0.00	0.00	0.00	0.10	0.52	0.67	1.00	
LC50 fish	0.00	0.10	0.00	0.10	0.28	0.33	0.38	1.00

Table 5 shows that the ranking coefficient between the indicators included in PestScreen is generally low ($r < 0.50$). Intermediate correlations ($r = 0.5$-0.7) were found for (i) the human population intake fraction and the overall environmental persistence ($r = 0.63$), and (ii) the acceptable daily intake, the lethal dose to rats and the lethal dose to bees ($r = 0.52$-0.67). Fish toxicity did not correlate well with any of the other toxicological indicators. The correlation between the acceptable daily intake and the rat toxicity can be clarified by the fact that the ADI has to be estimated from the no-observed effect level (NOAEL) in rats using an interspecies conversion factor to chronic human conditions. The relationship between the human population intake fraction and the overall environmental persistence can be explained by the fact that chemicals can have a relatively high potential for population exposure in the case they are highly persistent in the environment (MacLeod et al., 2004).

3.3 Comparing PestScreen with existing ranking methodologies

In order to compare PestSceen with existing pesticide ranking methodologies, it was compared with seven indicators which have been developed throughout the European Union. These indicators were already evaluated and compared with each other elsewhere (Reus et al., 2002) on behalf of fifteen pesticides.

For the comparison of PestScreen with these methods, the following eleven active ingredients (maximum amount of pesticides available in all methods) were identified: Chlorothalonil, Dimethoate, Glyphosate, Imidacloprid, Isoproturon, Kresoxim-methyl, Mancozeb, MCPA, Pirimicarb, Rimsulfuron and Tolylfluanid. The pesticides belong to various chemical groups and include some older pesticides and some new products. The results of PestScreen (PestScores) were compared to the relative rankings of the other methods by testing the level of correlation using the Spearman rank correlation test. Table 6 shows the correlation between rankings of the eleven pesticides for total environmental risk by eight ranking methodologies including PestScreen.

Table 6

Correlation between rankings of pesticides by PestScreen and other seven methods

	EYP	SYNOPS	p-EMA	Ipest	EPRIP	SyPEP	PERI	PestScreen
EYP	1.00							
SYNOPS	0.55	1.00						
p-EMA	0.41	0.30	1.00					
Ipest	0.78	0.66	0.68	1.00				
EPRIP	0.38	0.19	0.85	0.55	1.00			
SyPEP	0.60	0.70	0.39	0.49	0.26	1.00		
PERI	0.38	0.01	0.25	0.10	0.33	0.17	1.00	
PestScreen	0.39	0.04	0.91	0.73	0.78	0.34	0.06	1.00

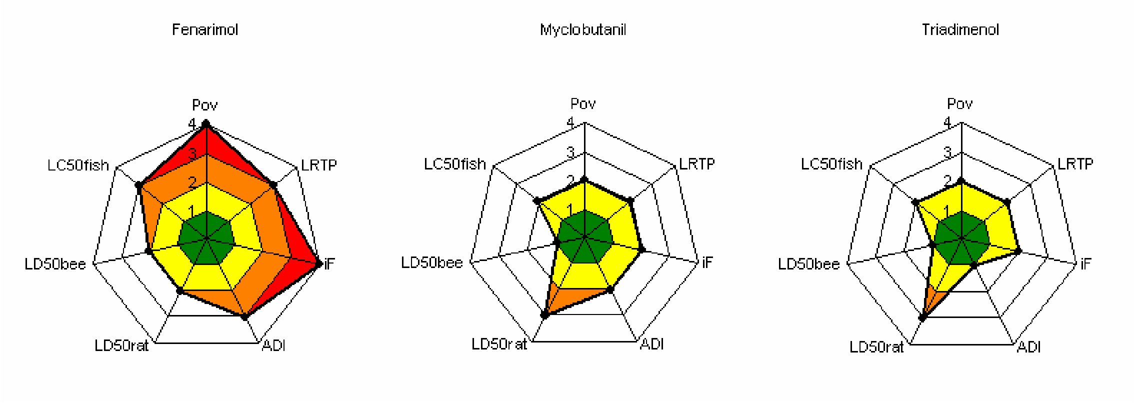
Abbreviation	Method	Country
EYP	Environmental Yardstick	The Netherlands
SYNOPS	SYNOPS	Germany
p-EMA	Environmental performance indicator of pesticides	United Kingdom
Ipest	Pesticide environmental impact indicator	France
EPRIP	Environmental potential risk indicator for pesticides	Italy
SyPEP	System for predicting the environmental impact of pesticides	Belgium
PERI	Pesticide environmental risk indicator	Sweden

The rankings differ when the score for the environment as a whole is concerned. The differences between PestScreen and other methods can be explained by the fact that large differences exist in the type of environmental indicators taken into account. Only three methods include the risk to human health. Bioaccumulation and effects on bees are included in only two existing indicators. Long-range transport potential and human population intake fraction are not included in any of the methodologies compared with PestScreen. PestScreen correlates best with p-EMA ($r = 0.91$) which also uses a scoring table to produce a total score for environmental risk. Pesticides are classified according to certain chemical properties and scores for each property are combined in a scoring table or algorithm to assess the relative overall environmental impact of pesticides. PestScreen correlates well with EPRIP ($r = 0.78$) and Ipest ($r = 0.73$). EPRIP uses a risk ratio approach, i.e. the ratio between exposure (concentration in a certain environmental compartment) and toxicity for relevant organisms. In Ipest the score of a pesticide is based on chemical properties, application factors and a set of decision rules using a fuzzy expert system. The comparison with PERI resulted in the lowest correlation of rankings ($r = 0.06$). The ranking by PERI deviated from the rankings by all other indicators due to the importance of the leaching potential of pesticides in this method (Reus et al., 2002).

3.4 Example 1: Application of fungicides for the control of powdery mildew

Powdery mildew is one of the most serious disease groups in agricultural production which is caused by fungal growth, leading to economic loss and reduction in fruit quality. However, three systemic fungicides typically used in the production of tomatoes are Fenarimol, Myclobutanil and Triadimenol with a PestScore of 2.0 (low), 1.2 (low) and 0.6 (low), respectively.

Using the hazard distribution plots for the evaluation of each pesticide included in this example (Figure 1), it can be demonstrated that Fenarimol suffers the highest PestScore value due to its very high scores of overall persistence and human population intake fraction. High levels of concern are presented in the case of LRTP, fish toxicity and human chronic toxicity.



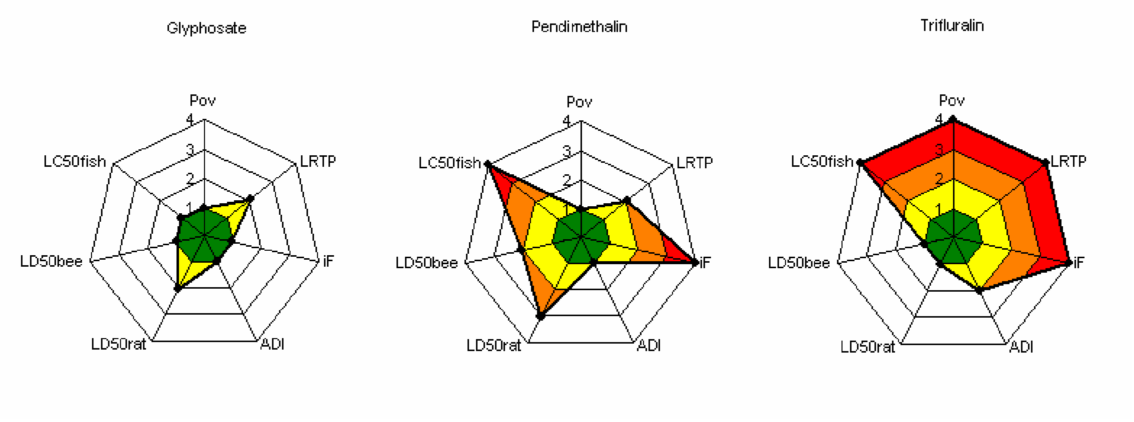
PestScore: 2.0 PestScore: 1.2 PestScore: 0.6

Figure 1. Hazard distribution plots and PestScores of fungicide example

Myclobutanil and Triadimenol show the same hazard distribution except for the somewhat higher chronic human toxicity in the case of Myclobutanil. The main difference between Myclobutanil and Triadimenol lies in the use pattern, Myclobutanil being mainly applied in spray application and Triadimenol mainly as a seed treatment. Both pesticides can be considered preferable to Fenarimol with Triadimenol having the lowest PestScore due to its lower application dose.

3.5 Example 2: Application of herbicides for the control of grasses and weeds

Three herbicides commonly applied for the control of grasses and weeds in the production of tomatoes are Glyphosate, Pendimethalin and Trifluralin with a PestScore of 4.5 (moderate), 10.4 (high) and 12.5 (very high), respectively. Pendimethalin and Trifluralin are selective herbicides used to control most annual grasses and certain broadleaf weeds. Glyphosate is a broad-spectrum, non-selective systemic herbicide used for control of annual and perennial plants including grasses, sedges, broad-leaved weeds, and woody plants. It can be used on non-cropland as well as on a great variety of crops. Since the use of one single herbicide is sufficient for the control of weeds and grasses, in this case Glyphosate would be preferable due to its lowest PestScore which generally indicates less environmental risk compared to Pendimethalin and Trifluralin. The hazard distribution plots of the herbicides used in this example (Figure 2) allow a more detailed analysis of the advantages and drawbacks of each active ingredient.



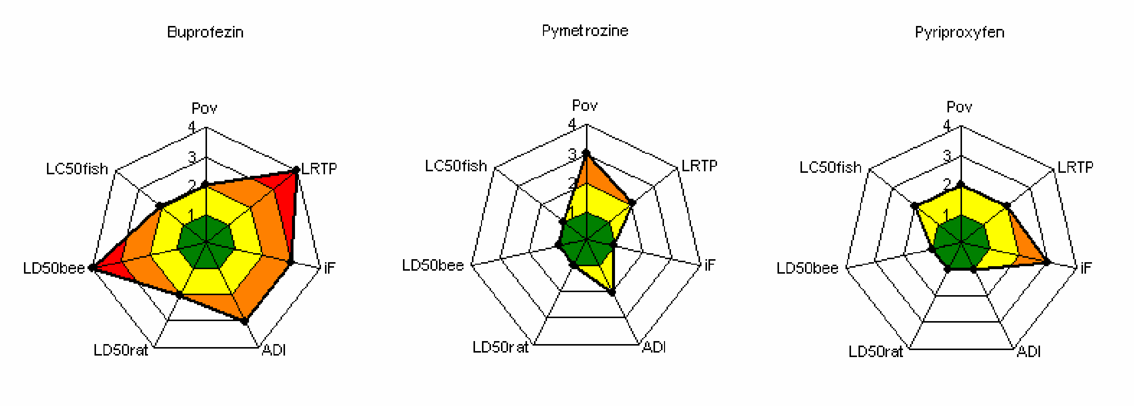
PestScore: 4.5 PestScore: 10.4 PestScore: 12.5

Figure 2. Hazard distribution plots and PestScores of herbicide example

Pendimethalin and Trifluralin show similar plots regarding the very high risk potential deriving from the human population intake fraction and toxicity to fish. The very high toxicity of Trifluralin and Pendimethalin to aquatic organisms makes it an unfavourable active ingredient when the application site is located close to fish habitats like rivers or lakes. Trifluralin shows very high risk levels in Long-range transport potential and overall persistence. The advantages of Glyphosate are its low environmental persistence and its generally low toxicity profiles.

3.6 Example 3: Application of insecticides for the control of white flies

Trialeurodes vaporariorum, commonly known as the greenhouse whitefly inhabits the world's temperate regions. It is a primary insect pest of many fruit, vegetable and ornamental crops, frequently being found in greenhouses and other protected horticultural environments. Buprofezin, Pymetrozine and Pyriproxyfen are three of the suggested insecticides for the control of greenhouse whiteflies in greenhouse tomato cultivation with a PestScore value of 5.3 (moderate), 1.4 (low) and 1.9 (low), respectively. Buprofezin and Pyriproxyfen are both used as insecticide growth regulators being more selective active ingredients compared to the conventional pesticides due to their interference with specific insect targets, namely the insect endocrinology. Therefore, these compounds are used worldwide in integrated pest management (IPM) programs. Interpreting the insecticide hazard distribution plots (Figure 3), the main drawbacks of Buprofezin are its very high toxicity to honey bees and a very high long-range transport potential.



PestScore: 5.3 PestScore: 1.4 PestScore: 1.9

Figure 3. Hazard distribution plots and PestScores of insecticide example

Pymetrozine is used as a feeding inhibitor (systemic antifeedant), belonging to the class of chemicals known as pyridine-azomethines. Its PestScore is lower than those calculated for Buprofezin and Pyriproyfen due to its low human population intake fraction and a generally low toxicity to honey bees, fish and rats. Recently introduced into the market, Pymetrozine can be considered as a replacement for many organophosphate (OP) pesticides used for the same use pattern. Pymetrozine and Pyriproxyfen show similar PestScores but the low human population intake fraction of Pymetrozine makes it a more favourable active ingredient.

4. Conclusion

A new method was developed and presented in this study to calculate the relative risk level of pesticides with the aim of ranking them from lowest to highest degree of concern. The approach is an estimation method of relative risk levels and allows comparing environmental and human health risks of specific pesticide types through their ranking.

PestScreen is similar to other environmental ranking methods in relation to the selected physical-chemical properties, but uses a wide range of indicators to rank agrochemicals in a simple way. Additionally, the method uses multi-media models for the calculation of non-detectable measures.

The method described may easily be used for determining the most environmentally friendly active ingredient prior to application, thus leading to better management and decision-making about pesticide use. PestScreen is therefore recommended as a practical tool to screen, rank and score the relative risk of alternative pesticides with the same agricultural effect.

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Supporting Information

Table A1

Median and range factors (RF) of 217 pesticides used in PestScreen

Indicators	median	unit	RF
Dose	0.75	kg/ha	10
Fate			
Pov	61	days	23
LRTP	9×10^{-04}	(-)	21
Exposure			
iF	4×10^{-06}	kg/kg	67
Human Toxicity			
ADI	0.01	mg/kg bw day	34
LD50 rat	1800	mg/kg bw	5
Terrestrial Ecotoxicity			
LD50 bee	20	µg/bee	15
Fresh water Ecotoxicity			
LC50 fish	3	mg/L	23

RF = range factor, defined as the square root of ratio 97.5th to 2.5th percentile.

Table A2

Full list of 217 pesticides studied and their physical-chemical properties, sub-indicator scores, hazard-index and final PestScore

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		LD50$_{rat}$ mg/kg.bw		LD50$_{bee}$ µg/bee		LC50$_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
1	94-75-7	S	H	2,4-D	1,4E+00	7,5E+01	3	1,1E-05	1	1,6E-06	1	5,0E-02	1	3,8E+02	3	1,6E+01	3	1,1E+00	3	5,5	7,7	high	III
2	71751-41-2	S	I	Abamectine	7,0E-01	1,0E+02	3	7,5E-05	1	7,4E-06	3	2,0E-04	4	9,8E+02	3	1,0E-01	4	1,0E+02	1	8,0	5,6	moderate	II
3	30560-19-1	S	I	Acephate	4,5E-01	4,9E+01	2	1,1E-02	4	1,7E-06	1	3,0E-03	4	9,5E+02	3	1,2E+00	4	1,0E+03	1	7,0	3,2	moderate	II
4	74070-46-5	S	H	Aclonifen	2,0E+00	1,1E+02	4	4,4E-04	2	6,6E-06	3	1,0E-02	3	5,0E+03	1	1,9E+02	1	6,7E-01	3	8,0	16,0	very high	IV
5	116-06-3	S	I	Aldicarb	2,2E+00	2,5E+02	4	1,8E-02	4	5,1E-04	4	3,0E-03	4	9,3E-01	4	2,5E-01	4	6,0E-02	4	12,0	26,4	very high	IV
6	309-00-2	S	I	Aldrin	3,3E+00	2,3E+02	4	1,8E-02	4	4,6E-06	3	1,0E-04	4	3,9E+01	4	2,0E-01	4	6,0E-02	4	11,0	36,3	very high	IV
7	55634-91-8	S	H	Alloxydim sodium	1,1E+00	6,0E+01	2	3,2E-04	2	2,1E-06	2	5,0E-02	1	2,3E+03	2	1,6E+01	3	2,0E+03	1	5,8	6,0	high	III
8	101-05-3	S	F	Anilazine	1,9E+00	3,4E+00	1	9,1E-07	1	2,2E-07	1	1,0E-01	1	2,7E+03	2	2,3E+01	2	1,5E-01	4	4,3	8,2	high	III
9	3337-71-1	S	H	Asulam	1,9E+00	3,9E-01	1	3,9E-06	1	5,3E-08	1	2,0E-02	2	4,0E+03	2	2,4E+01	2	2,0E+03	1	3,8	7,1	high	III
10	1912-24-9	S	H	Atrazine	3,0E+00	2,0E+02	4	2,6E-02	4	4,7E-06	3	5,0E-03	4	2,0E+03	2	9,7E+01	2	1,2E+01	2	9,5	28,5	very high	IV
11	86-50-0	S	I	Azinphos-methyl	3,5E-01	7,9E+01	3	9,2E-05	1	4,4E-07	1	5,0E-03	4	1,6E+01	4	6,3E-02	4	4,7E-02	4	7,0	2,5	low	I
12	131860-33-8	S	F	Azoxystrobin	2,5E-01	2,4E+02	4	1,4E-02	4	7,7E-06	3	1,0E-01	1	5,0E+03	1	2,1E+02	1	4,7E-01	3	8,5	2,1	low	I
13	71626-11-4	S	F	Benalaxyl	2,0E-01	5,9E+01	2	2,8E-03	3	6,7E-06	3	5,0E-02	1	4,2E+03	2	1,9E+02	1	3,8E+00	2	7,0	1,4	low	I
14	22781-23-3	S	I	Bendiocarb	3,0E+00	2,3E+01	1	4,8E-03	3	4,2E-06	2	4,0E-03	4	5,5E+01	4	2,5E-01	4	1,2E+00	3	7,8	23,3	very high	IV
15	17804-35-2	S	F	Benomyl	7,5E-01	2,2E+01	1	5,9E-05	1	5,2E-08	1	3,0E-02	2	1,0E+04	1	5,0E+01	2	2,9E-01	3	4,0	3,0	moderate	II
16	25057-89-0	S	H	Bentazone	8,4E-01	1,6E+02	4	8,0E-04	2	4,4E-05	4	1,0E-01	1	1,1E+03	3	1,0E+02	1	6,4E+02	1	8,5	7,1	high	III
17	82657-04-3	S	I	Bifenthrin	1,0E-01	7,7E+02	4	4,2E-04	2	2,8E-05	4	1,0E-02	3	5,5E+01	4	1,5E-02	4	2,5E-04	4	10,8	1,1	low	I
18	92-52-4	S	F	Biphenyl	2,5E+00	7,7E+00	1	1,1E-01	4	2,3E-06	2	1,3E-01	1	3,3E+03	2	5,0E+01	2	1,5E+00	3	6,5	16,3	very high	IV
19	13181-17-4	S	H	Bromofenoxim	1,5E+00	2,7E+02	4	2,8E-03	3	1,1E-05	4	1,5E-03	4	1,2E+03	3	1,6E+01	3	1,3E-01	4	11,0	16,5	very high	IV
20	4824-78-6	L	I	Bromophos-ethyl	5,0E-01	6,1E+01	2	1,3E-04	1	7,2E-06	3	4,0E-03	4	9,0E+01	4	4,4E-01	4	1,8E-01	4	8,5	4,3	moderate	II
21	18181-80-1	S	AC	Bromopropylate	7,5E-01	2,1E+02	4	9,3E-04	3	1,9E-05	4	3,0E-02	2	5,0E+03	1	1,8E+02	1	1,9E+01	2	9,0	6,8	high	III
22	41483-43-6	S	F	Bupirimate	8,1E-01	5,9E+01	2	6,5E-04	2	2,3E-06	2	5,0E-02	1	4,0E+03	2	5,0E+01	2	1,3E+00	3	6,0	4,9	moderate	II
23	69327-76-0	S	I	Buprofezin	6,0E-01	5,3E+01	2	6,7E-03	4	9,9E-06	3	1,0E-02	3	2,2E+03	2	2,3E-01	4	2,7E+00	2	8,8	5,3	moderate	II
24	95465-99-9	L	I	Cadusafos	5,1E+00	1,5E+01	1	1,5E-03	3	1,5E-06	1	1,0E-06	4	3,9E+02	3	2,1E+00	3	1,7E-01	4	6,5	33,2	very high	IV
25	115-32-2	S	F	Captafol	1,2E+00	2,2E+02	4	2,0E-05	1	4,3E-06	3	1,0E-02	3	5,0E+03	1	2,2E+01	2	1,5E-01	4	8,0	9,6	high	III
26	133-06-2	S	F	Captan	1,0E+00	7,0E-01	1	1,1E-05	1	4,3E-08	1	3,0E-01	1	9,0E+03	1	1,2E+02	1	5,0E-02	4	3,8	3,8	moderate	II
27	63-25-2	S	I	Carbaryl	1,6E+00	1,7E+01	1	1,6E-05	1	3,4E-07	1	1,0E-02	3	3,0E+02	3	1,8E+00	3	1,3E+00	3	5,0	8,0	high	III
28	16118-49-3	S	H	Carbetamide	1,8E+00	1,6E+01	1	5,5E-05	1	7,0E-07	1	3,0E-02	2	1,0E+04	1	1,1E+02	1	3,5E+02	1	3,3	5,9	moderate	II
29	1563-66-2	S	I	Carbofuran	1,5E+00	4,4E+01	1	7,1E-04	2	1,7E-06	1	2,0E-03	4	8,0E+00	4	2,0E-01	4	7,0E-03	4	6,5	9,8	high	III
30	5234-68-4	S	F	Carboxin	4,0E-01	5,9E+01	2	6,1E-04	2	2,1E-06	2	8,0E-02	1	3,8E+03	2	1,8E+02	1	1,2E+00	3	5,8	2,3	low	I
31	2439-01-2	S	F	Chinomethionat	8,8E-01	6,1E+01	2	1,8E-03	3	6,8E-06	3	6,0E-03	3	2,5E+03	2	8,5E+00	3	3,3E-02	4	8,5	7,5	high	III

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		$LD50_{rat}$ mg/kg.bw		$LD50_{bee}$ µg/bee		$LC50_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
32	13360-45-7	S	H	Chlorbromuron	1,0E+00	1,1E+02	3	1,1E-03	3	5,1E-06	3	2,0E-02	2	5,0E+03	1	2,7E+01	2	7,0E+00	2	7,8	7,8	high	III
33	470-90-6	L	I	Chlorfenvinphos	2,5E+00	1,3E+02	4	3,0E-04	2	2,0E-05	4	5,0E-04	4	3,1E+01	4	4,1E+00	3	4,0E-02	4	10,8	27,2	very high	IV
34	1698-60-8	S	H	Chloridazon	2,2E+00	7,2E+01	3	3,8E-02	4	8,1E-07	1	6,0E-02	1	2,4E+03	2	8,7E+01	2	2,0E+01	2	6,3	13,4	very high	IV
35	7003-89-6	S	PGR	Chlormequat	1,0E+00	5,8E+01	2	8,6E-04	2	2,7E-05	4	5,0E-02	1	6,7E+02	3	2,4E+01	2	7,7E+02	1	7,8	7,9	high	III
36	1897-45-6	S	F	Chlorothalonil	1,0E+00	5,6E+01	2	2,5E-01	4	2,7E-06	2	3,0E-02	2	1,0E+04	1	1,8E+02	1	4,5E-02	4	7,0	7,0	high	III
37	15545-48-9	S	H	Chlorotoluron	1,5E+00	2,6E+02	4	1,6E-02	4	2,1E-06	2	2,0E-02	2	1,0E+04	1	2,1E+01	2	1,5E+02	1	7,5	11,3	high	III
38	1982-47-4	S	H	Chloroxuron	2,0E+00	6,1E+01	3	7,2E-05	1	2,9E-06	2	1,0E-02	3	3,7E+03	2	2,1E+01	2	5,9E+01	1	6,0	12,0	high	III
39	101-21-3	S	PGR	Chlorpropham	1,4E+00	1,4E+02	4	8,9E-04	3	1,7E-05	4	5,0E-02	1	5,0E+03	1	3,5E+01	2	1,4E+01	2	9,0	12,6	very high	IV
40	5598-13-0	S	I	Chlorpyrifos-methyl	7,2E-01	5,4E+01	2	5,7E-03	3	9,4E-06	3	1,0E-02	3	3,0E+03	2	3,8E-01	4	3,0E-01	4	8,8	6,3	high	III
41	2921-88-2	S	I	Chlorpyriphos	2,0E+00	5,4E+01	2	4,0E-03	3	1,5E-05	4	3,0E-03	4	1,8E+02	4	1,5E-01	4	3,0E-03	4	10,5	21,0	very high	IV
42	105512-06-9	S	H	Clodinafop-propargyl	1,0E-01	3,1E+01	1	6,7E-05	1	1,6E-06	1	4,0E-03	4	1,8E+03	2	1,0E+02	1	4,0E-01	3	4,5	0,5	low	I
43	74115-24-5	S	AC	Clofentezine	4,0E-01	1,1E+02	3	7,5E-04	2	4,2E-06	2	2,0E-02	2	5,2E+03	1	2,5E+01	2	1,0E-01	4	6,8	2,7	moderate	II
44	21725-46-2	S	H	Cyanazine	2,8E+00	5,2E+01	2	1,2E-03	3	1,0E-06	1	2,0E-03	4	2,9E+02	3	1,6E+01	3	6,6E+00	2	6,5	17,9	very high	IV
45	1134-23-2	L	H	Cycloate	2,5E+00	4,5E+01	2	2,0E-02	4	8,3E-06	3	5,0E-03	4	2,0E+03	2	2,7E+01	2	4,5E+00	2	8,5	21,4	very high	IV
46	101205-02-1	S	H	Cycloxydim	4,0E-01	6,2E+01	3	4,5E-05	1	3,1E-06	2	6,0E-02	1	3,9E+03	2	1,0E+02	1	1,8E+02	1	5,3	2,1	low	I
47	68359-37-5	S	I	Cyfluthrin	1,0E-01	1,1E+02	3	5,4E-07	1	9,5E-06	3	2,0E-02	2	2,5E+02	4	9,8E-03	4	1,5E-03	4	8,5	0,9	low	I
48	298-04-4	S	F	Cymoxanil	6,0E-01	2,4E+01	1	2,1E-03	3	4,0E-06	2	2,5E-02	2	1,2E+03	3	8,5E+01	2	8,1E+01	1	6,0	3,6	moderate	II
49	52315-07-8	L	I	Cypermethrin	5,5E-01	1,8E+02	4	3,8E-05	1	1,0E-02	4	5,0E-02	1	2,5E+02	4	3,0E-02	4	7,0E-04	4	9,8	5,4	moderate	II
50	113096-99-4	S	F	Cyproconazole	2,8E-01	1,0E+02	3	9,5E-04	3	4,0E-06	2	1,0E-02	3	1,0E+03	3	1,0E+02	1	1,9E+01	2	7,3	2,0	low	I
51	121552-61-2	S	F	Cyprodinil	3,6E-01	6,1E+01	2	1,4E-04	1	3,4E-06	2	3,0E-02	2	5,0E+03	1	6,2E+01	2	2,4E+00	3	5,5	2,0	low	I
52	66215-27-8	S	I	Cyromazine	4,5E-01	5,2E+02	4	7,7E-02	4	7,6E-04	4	2,0E-02	2	3,3E+03	2	5,2E+00	3	9,0E+01	1	10,0	4,5	moderate	II
53	75-99-0	S	H	Dalapon	5,7E+00	6,6E+01	3	8,1E-02	4	1,7E-05	4	5,0E-02	1	9,3E+03	1	1,3E+01	3	2,9E+02	1	9,0	51,3	very high	IV
54	1596-84-5	S	H	Daminozide	2,1E+00	1,6E+01	1	1,6E-04	1	2,1E-06	2	7,0E-01	1	8,4E+03	1	1,4E+02	1	1,5E+02	1	4,0	8,4	high	III
55	50-29-3	S	I	DDT	3,4E+00	6,5E+03	4	2,2E-02	4	1,4E-04	4	2,0E-03	4	1,1E+02	4	6,2E+00	3	9,0E-03	4	11,8	40,0	very high	IV
56	52918-63-5	S	I	Deltamethrin	1,0E-01	6,4E+01	3	3,3E-02	4	6,7E-07	1	1,0E-02	3	1,4E+02	4	5,0E-02	4	5,9E-04	4	8,3	0,8	low	I
57	919-86-8	L	I	Demeton-s-methyl	3,0E-01	1,5E+01	1	2,5E-03	3	1,7E-06	1	3,0E-04	4	4,0E+01	4	2,0E-01	4	7,8E+01	1	6,3	1,9	low	I
58	13684-56-5	S	H	Desmedipham	1,0E-01	1,1E+00	1	1,9E-06	1	3,7E-08	1	3,0E-02	2	9,6E+03	1	5,1E+01	2	1,7E+00	3	4,0	0,4	low	I
59	1014-69-3	S	H	Desmetryn	3,0E-01	4,3E+01	1	3,4E-03	3	1,7E-06	1	1,4E-03	4	1,4E+03	3	1,0E+02	1	2,2E+00	3	5,8	1,7	low	I
60	333-41-5	L	I	Diazinon	1,5E+00	8,4E+01	3	5,0E-03	3	9,9E-06	3	1,0E-03	4	1,0E+03	3	3,6E-01	4	2,1E-01	4	9,8	14,6	very high	IV
61	1918-00-9	S	H	Dicamba	6,0E-01	8,7E+01	3	7,2E-03	4	3,1E-06	2	3,0E-02	2	1,7E+03	3	1,0E+02	1	1,4E+02	1	7,3	4,4	moderate	II
62	1194-65-6	S	H	Dichlobenil	7,0E+00	5,3E+02	4	2,8E-01	4	1,4E-05	4	1,0E-02	3	3,2E+03	2	2,6E+01	2	5,0E+00	2	10,3	71,8	very high	IV

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		$LD50_{rat}$ mg/kg.bw		$LD50_{bee}$ µg/bee		$LC50_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
63	120-36-5	S	H	Dichlorprop	1,9E+00	4,4E+01	2	1,3E-04	1	1,6E-06	1	3,0E-02	2	8,0E+02	3	1,6E+01	3	2,8E+02	1	4,8	9,0	high	III
64	62-73-7	L	I	Dichlorvos	1,1E+00	1,5E+00	1	5,1E-02	4	7,6E-07	1	1,0E-03	4	5,6E+01	4	6,5E-02	4	2,3E-01	4	7,5	8,3	high	III
65	1085-98-9	S	F	Dichlofluanid	2,5E+00	1,1E+02	3	1,6E-03	3	7,9E-06	3	3,0E-01	1	5,0E+03	1	3,1E+01	2	3,0E-02	4	8,0	20,0	very high	IV
66	99-30-9	S	F	Dicloran	4,8E+00	1,1E+02	3	1,4E-02	4	2,4E-05	4	7,0E-02	1	4,0E+03	2	8,7E+01	2	1,6E+00	3	9,5	45,6	very high	IV
67	115-32-2	S	AC	Dicofol	6,0E-01	2,2E+02	4	2,0E-05	1	4,3E-06	2	2,0E-03	4	6,9E+02	3	1,2E+01	3	1,8E-01	4	8,0	4,8	moderate	II
68	87130-20-9	S	F	Diethofencarb	1,9E+00	1,3E+01	1	2,6E-03	3	9,6E-07	1	4,3E-01	1	5,0E+03	1	2,2E+01	2	1,3E+01	2	4,5	8,6	high	III
69	119446-68-3	S	F	Difenoconazole	3,0E-01	1,1E+02	4	4,4E-05	1	6,5E-06	3	1,0E-02	3	1,5E+03	3	1,0E+02	1	8,1E-01	3	8,0	2,4	moderate	II
70	83164-33-4	S	H	Diflufenican	2,0E-01	6,2E+01	3	1,1E-03	3	7,3E-06	3	2,0E-01	1	2,0E+03	2	6,7E+01	2	8,3E+01	1	7,5	1,5	low	I
71	34205-21-5	S	H	Dimefuron	9,4E-01	1,0E+02	3	1,4E-03	3	3,5E-06	2	2,0E-02	2	2,0E+03	2	5,0E+02	1	1,0E+03	1	6,5	6,1	high	III
72	60-51-5	S	I	Dimethoate	1,1E+00	6,8E+01	3	2,3E-03	3	1,6E-06	1	2,0E-03	4	1,5E+02	4	1,4E-01	4	6,2E+00	2	7,5	8,3	high	III
73	39300-45-3	S	F	Dinocap	4,4E-01	6,1E+01	2	5,2E-07	1	5,5E-06	3	6,0E-03	3	9,8E+02	3	3,6E+01	2	1,4E-02	4	7,5	3,3	moderate	II
74	2764-72-9	S	H	Diquat	7,0E-01	6,0E+01	2	5,1E-04	2	2,0E-06	1	2,0E-03	4	2,3E+02	3	5,0E+01	2	1,3E+01	2	5,8	4,0	moderate	II
75	3347-22-6	S	F	Dithianon	7,0E-01	1,0E+02	3	9,7E-04	3	3,8E-06	2	7,0E-03	3	6,4E+02	3	1,6E+01	3	6,0E-02	4	8,3	5,8	high	III
76	330-54-1	S	H	Diuron	3,8E+00	2,4E+02	4	2,7E-03	3	3,3E-06	2	1,0E-02	3	3,4E+03	2	2,2E+01	2	5,9E+00	2	7,8	29,1	very high	IV
77	534-52-1	S	H	DNOC	4,1E+00	4,2E+01	1	3,1E-04	2	6,3E-07	1	5,0E-03	4	2,5E+01	4	3,2E+00	3	7,0E+00	2	5,8	23,6	very high	IV
78	1593-77-7	L	H	Dodemorph	1,6E+00	1,1E+02	4	3,1E-05	1	9,3E-06	3	1,0E-02	3	4,5E+03	2	5,7E+01	2	2,2E+01	2	7,8	12,4	very high	IV
79	115-29-7	S	I	Endosulfan	7,5E-01	1,1E+01	1	2,8E-02	4	1,2E-06	1	6,0E-03	3	8,0E+01	4	7,8E+00	3	2,0E-03	4	7,0	5,3	moderate	II
80	129-67-9	S	H	Endothal-sodium	1,2E+00	5,8E+01	2	8,6E-04	3	3,5E-05	4	2,0E-03	4	5,1E+01	4	9,2E+00	3	1,6E+02	1	9,5	11,4	very high	IV
81	759-94-4	L	H	EPTC	4,7E+00	3,4E+01	1	3,6E-02	4	2,4E-06	2	7,0E-02	1	1,7E+03	3	1,9E+01	2	1,9E+01	2	6,5	30,6	very high	IV
82	16672-87-0	S	PGR	Ethephon	7,0E-01	5,8E+01	2	8,6E-04	3	3,0E-05	4	5,0E-02	1	4,0E+03	2	6,9E+01	2	3,0E+02	1	8,0	5,6	moderate	II
83	29973-13-5	L	I	Ethiofencarb	2,3E+00	3,0E+01	1	1,5E-04	1	1,3E-06	1	5,0E-02	1	2,0E+02	4	6,5E+00	3	1,3E+01	2	4,5	10,1	high	III
84	23947-60-6	S	F	Ethirimol	1,5E+00	5,9E+01	2	6,5E-04	2	2,1E-06	2	1,0E-01	1	6,3E+03	1	8,4E+01	2	2,0E+01	2	5,5	8,3	high	III
85	13194-48-4	L	I	Ethoprophos	4,0E+00	1,2E+02	4	5,3E-03	3	6,3E-05	4	3,0E-04	4	2,6E+01	4	1,5E+00	4	4,6E+00	2	11,0	44,0	very high	IV
86	80844-07-1	S	I	Etofenprox	1,0E-01	2,1E+02	4	1,6E-03	3	6,1E-05	4	3,0E-02	2	1,0E+04	1	1,3E+02	1	8,7E-01	3	9,3	0,9	low	I
87	2593-15-9	L	F	Etridiazole	3,0E-01	1,0E+02	3	1,9E-02	4	3,2E-05	4	3,0E-02	2	2,0E+03	2	1,0E+02	1	1,2E+00	3	9,5	2,9	moderate	II
88	38260-54-7	L	I	Etrimfos	1,5E+00	1,3E+01	1	7,3E-03	4	1,9E-06	1	1,0E-03	4	2,0E+03	2	1,0E-01	4	2,5E-01	4	7,0	10,5	high	III
89	22224-92-6	S	I	Fenamiphos	3,0E+00	6,1E+01	2	1,7E-04	2	2,5E-06	2	1,0E-04	4	1,5E+01	4	1,7E+00	4	1,0E-02	4	8,0	24,0	very high	IV
90	60168-88-9	S	F	Fenarimol	2,0E-01	2,2E+02	4	2,6E-03	3	2,7E-05	4	1,0E-02	3	2,5E+03	2	6,2E+01	2	9,1E-01	3	10,0	2,0	low	I
91	114369-43-6	S	F	Fenbuconazole	2,5E+00	1,0E+02	3	1,1E-02	4	1,5E-05	4	3,0E-02	2	2,0E+03	2	5,6E+01	2	6,8E-01	3	9,8	24,4	very high	IV
92	103112-35-2	S	H	Fenchlorazole-ethyl	4,0E+00	2,6E+02	4	2,0E-04	2	1,8E-05	4	1,5E-02	2	5,0E+03	1	2,0E+02	1	5,1E-01	3	8,8	35,0	very high	IV
93	122-14-5	L	I	Fenitrothion	5,0E-01	7,4E+01	3	3,7E-04	2	2,0E-06	1	5,0E-03	4	5,0E+02	3	1,8E-02	4	1,7E+00	3	7,0	3,5	moderate	II

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		LD50$_{rat}$ mg/kg.bw		LD50$_{bee}$ µg/bee		LC50$_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
94	74738-17-3	S	F	Fenpiclonil	2,0E+00	1,1E+02	4	2,3E-04	2	5,8E-06	3	1,3E-02	3	5,0E+03	1	5,5E+00	3	8,0E-01	3	8,5	17,0	very high	IV
95	39515-41-8	S	I	Fenpropathrin	2,0E-01	6,1E+01	2	1,2E-03	3	1,3E-05	4	3,0E-02	2	6,6E+01	4	5,0E-02	4	2,0E-03	4	10,0	2,0	low	I
96	67306-00-7	L	F	Fenpropidin	6,0E-01	1,1E+02	4	1,3E-06	1	1,1E-05	3	1,0E-03	4	1,4E+03	3	5,0E-01	4	1,9E+00	3	9,0	5,4	high	III
97	67306-03-0	L	F	Fenpropomorph	7,5E-01	1,0E+02	3	7,2E-04	3	9,9E-06	3	3,0E-03	4	3,5E+03	2	2,6E+01	2	3,2E+00	2	8,5	6,4	high	III
98	900-95-8	S	F	Fentin acetate	6,0E-01	4,4E+02	4	2,5E-02	4	5,4E-06	3	1,0E-03	4	1,3E+02	4	1,6E+01	3	3,2E-01	4	10,8	6,5	high	III
99	639-58-7	S	F	Fentin chloride	6,0E-01	3,1E+02	4	2,7E-01	4	2,8E-05	4	1,0E-03	4	1,4E+02	4	1,6E+01	3	1,1E-01	4	11,8	7,1	high	III
100	76-87-9	S	F	Fentin hydroxide	6,0E-01	4,6E+02	4	1,0E-02	4	2,1E-06	1	1,0E-03	4	1,1E+02	4	1,6E+01	3	4,2E-02	4	8,8	5,3	high	III
101	51630-58-1	L	I	Fenvalerate	2,0E-01	6,2E+01	3	1,1E-05	1	5,8E-06	3	2,0E-02	2	3,4E+03	2	3,6E-01	4	6,4E-04	4	8,0	1,6	low	I
102	79622-59-6	L	F	Fluazinam	8,0E-01	4,3E+02	4	8,3E-03	4	3,4E-05	4	1,0E-02	3	5,0E+03	1	2,0E+02	1	1,3E-01	4	10,3	8,2	high	III
103	113036-88-7	S	AC	Flucycloxuron	2,0E-01	1,1E+02	4	1,9E-05	1	1,2E-05	4	1,1E-02	3	5,0E+03	1	1,0E+02	1	1,1E+02	1	8,0	1,6	low	I
104	69377-81-7	S	H	Fluroxypyr	3,0E-01	1,0E+02	3	5,2E-03	3	2,1E-06	2	5,0E-01	1	5,0E+03	1	1,0E+02	1	1,0E+02	1	6,0	1,8	low	I
105	85509-19-9	S	F	Flusilazole	2,0E-01	6,1E+01	3	1,4E-04	2	3,0E-06	2	2,0E-03	4	1,1E+03	3	1,7E+02	1	1,5E+00	3	7,3	1,5	low	I
106	66332-96-5	S	F	Flutolanil	5,0E+00	6,1E+01	3	8,0E-05	1	2,9E-06	2	6,0E-02	1	1,0E+04	1	7,5E+01	2	2,4E+00	3	5,8	28,8	very high	IV
107	69409-94-5	L	I	Fluvalinate	2,0E-01	1,1E+02	4	7,4E-05	1	1,3E-05	4	5,0E-03	4	2,7E+02	3	4,7E+00	3	4,0E-03	4	10,0	2,0	low	I
108	944-22-9	L	I	Fonofos	1,7E+00	4,4E+01	2	9,0E-03	4	4,9E-06	3	2,0E-03	4	8,0E+00	4	3,3E+00	3	3,0E-02	4	9,8	16,6	very high	IV
109	2540-82-1	L	I	Formothion	5,0E-01	1,6E+01	1	5,9E-05	1	7,8E-07	1	2,0E-02	2	3,7E+02	3	1,8E-01	4	3,8E+01	1	4,5	2,3	moderate	II
110	39148-24-8	S	F	Fosetyl Al	2,8E+00	5,8E+01	2	8,9E-04	3	2,6E-05	4	1,0E+00	1	5,0E+03	1	2,0E+02	1	1,6E+02	1	7,5	20,6	very high	IV
111	57646-30-7	S	F	Furalaxyl	5,0E-01	5,9E+01	2	4,0E-04	2	2,1E-06	1	5,0E-02	1	9,4E+02	3	7,2E+00	3	3,3E+01	1	5,0	2,5	moderate	II
112	77-06-5	S	F	Gibberellic acid	5,0E-01	5,8E+01	2	8,7E-04	3	3,4E-05	4	5,0E+00	1	1,0E+04	1	2,2E+02	1	1,2E+02	1	7,5	3,8	moderate	II
113	1071-83-6	S	H	Glyphosate	1,2E+00	4,3E+01	2	6,0E-04	2	2,8E-08	1	3,0E-01	1	4,2E+03	2	3,9E+02	1	3,8E+01	1	4,3	5,1	high	III
114	39202-39-6	S	AF	Guazatine	2,0E-01	6,0E+01	2	3,5E-04	2	2,1E-06	2	6,0E-03	3	2,3E+02	3	5,4E+00	3	5,4E-01	3	7,0	1,4	low	I
115	69806-34-4	S	H	Haloxyfop	1,0E-01	6,1E+01	3	2,3E-04	2	2,8E-06	2	3,0E-04	4	3,9E+02	3	1,0E+02	1	5,5E+02	1	6,8	0,7	low	I
116	23560-59-0	L	I	Heptenophos	7,0E-01	2,7E+00	1	4,8E-03	3	4,1E-07	1	5,0E-03	4	9,6E+01	4	5,4E+00	3	9,3E+00	2	6,3	4,4	moderate	II
117	79983-71-4	S	F	Hexaconazole	1,0E-01	1,1E+02	4	2,0E-04	2	5,8E-06	3	5,0E-03	4	2,2E+03	2	1,0E+02	1	3,4E+00	2	8,3	0,8	low	I
118	51235-04-2	S	H	Hexazinone	3,7E+00	5,9E+01	2	7,1E-04	2	2,3E-06	2	1,0E-01	1	1,7E+03	3	1,5E+02	1	2,7E+02	1	5,5	20,4	very high	IV
119	35554-44-0	S	F	Imazalil	8,0E-01	1,1E+02	3	1,6E-04	2	5,5E-06	3	3,0E-02	2	9,2E+02	3	4,0E+01	2	2,1E+00	3	8,0	6,4	high	III
120	81405-85-8	S	H	Imazamethabenz-methyl	7,5E-01	6,1E+01	2	6,3E-05	1	2,8E-06	2	1,0E-02	3	5,0E+03	1	5,2E+01	2	2,8E+02	1	5,3	3,9	moderate	II
121	81334-34-1	S	H	Imazapyr	9,0E-01	5,8E+01	2	8,6E-04	3	3,5E-05	4	2,5E+00	1	5,0E+03	1	1,0E+02	1	1,1E+02	1	7,5	6,8	high	III
122	138261-41-3	S	I	Imidacloprid	1,0E-01	2,3E+02	4	1,2E-02	4	1,8E-03	4	6,0E-02	1	4,5E+02	3	8,1E-03	4	2,1E+02	1	10,3	1,0	low	I
123	36734-19-7	S	F	Iprodione	2,3E+00	8,8E+00	1	8,6E-06	1	3,1E-07	1	6,0E-02	1	3,5E+03	2	4,0E+02	1	3,1E+00	2	3,5	8,1	high	III
124	25311-71-1	L	I	Isofenphos	3,0E+00	6,1E+01	2	7,3E-05	1	3,4E-06	2	5,0E-04	4	2,0E+01	4	6,1E-01	4	1,8E+00	3	7,3	21,8	very high	IV

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		$LD50_{rat}$ mg/kg.bw		$LD50_{bee}$ µg/bee		$LC50_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
125	34123-59-6	S	H	Isoproturon	1,8E+00	1,7E+02	4	8,7E-03	4	6,3E-06	3	1,5E-02	3	1,8E+03	2	1,1E+02	1	9,0E+00	2	9,0	15,8	very high	IV
126	82558-50-7	S	H	Isoxaben	1,0E-01	6,2E+01	3	3,9E-05	1	3,2E-06	2	5,0E-02	1	1,0E+04	1	1,0E+02	1	1,0E+02	1	5,0	0,5	low	I
127	143390-89-0	S	F	Kresoxim-metil	2,5E-01	1,4E+02	4	2,0E-03	3	1,5E-05	4	4,0E-01	1	3,5E+03	2	2,0E+03	1	5,0E-01	3	9,3	2,3	low	I
128	91465-08-6	S	I	Lambda Cyhalothrin	1,1E+00	1,1E+02	4	9,4E-05	1	1,3E-05	4	5,0E-03	4	5,6E+01	4	4,0E-02	4	2,1E-04	4	10,5	11,6	very high	IV
129	2164-08-1	S	H	Lenacil	1,2E+00	6,1E+01	3	1,9E-04	2	2,3E-06	2	1,3E-01	1	1,0E+04	1	2,3E+01	2	1,1E+01	2	6,0	7,2	high	III
130	58-89-9	S	I	Lindane	3,0E+00	2,2E+02	4	5,6E-02	4	1,9E-05	4	3,0E-03	4	8,8E+01	4	2,0E-01	4	2,2E-02	4	12,0	36,0	very high	IV
131	330-55-2	S	H	Linuron	9,0E-01	1,6E+02	4	9,1E-03	4	6,4E-06	3	1,0E-02	3	4,0E+03	2	1,6E+01	3	8,9E-01	3	9,8	8,8	high	III
132	121-75-5	L	I	Malathion	1,7E+00	1,8E+01	1	8,4E-04	3	2,6E-07	1	5,0E-02	1	2,1E+03	2	7,3E-01	4	4,3E-01	4	5,8	9,8	high	III
133	8018-01-7	S	F	Mancozeb	2,0E+00	1,7E+01	1	4,6E-05	1	5,0E-09	1	6,0E-03	3	8,0E+03	1	2,6E+01	2	1,5E+00	3	4,3	8,5	high	III
134	12427-38-2	S	F	Maneb	2,5E+00	1,5E+00	1	1,9E-04	2	2,0E-07	1	3,0E-02	2	6,8E+03	1	1,2E+01	3	2,2E-01	4	5,0	12,5	very high	IV
135	94-74-6	S	H	MCPA	1,7E+00	1,9E+01	1	8,5E-05	1	1,9E-06	1	1,0E-02	3	7,0E+02	3	1,0E+02	1	9,7E+01	1	4,0	6,8	high	III
136	16484-77-8	S	H	Mecoprop-p	1,8E+00	1,6E+01	1	3,3E-05	1	5,9E-07	1	4,0E-02	1	1,1E+03	3	1,0E+02	1	1,5E+02	1	3,5	6,3	high	III
137	57837-19-1	S	F	Metalaxyl	3,8E-01	2,3E+02	4	6,2E-03	3	4,3E-05	4	3,0E-02	2	6,7E+02	3	2,7E+02	1	1,0E+02	1	9,3	3,5	moderate	II
138	108-62-3	S	M	Metaldehyde	4,5E-01	3,8E+01	2	3,4E-02	4	4,5E-06	3	5,0E-03	4	2,3E+02	4	1,6E+01	3	7,3E+00	2	9,3	4,2	moderate	II
139	18691-97-9	S	H	Methabenzthiazuron	2,0E+00	5,1E+02	4	2,7E-02	4	3,6E-06	2	4,0E-04	4	2,5E+03	2	8,0E-01	4	1,6E+01	2	9,0	18,0	very high	IV
140	10265-92-6	S	I	Methamydophos	6,0E-01	1,8E+01	1	1,9E-03	3	1,6E-06	1	3,0E-04	4	3,0E+01	4	8,6E-01	3	2,5E+01	1	6,0	3,6	moderate	II
141	950-37-8	L	I	Methidathion	5,0E-01	1,6E+01	1	1,8E-04	1	5,9E-07	1	1,0E-03	4	2,5E+01	4	2,3E-01	4	2,0E-03	4	6,0	3,0	moderate	II
142	2032-65-7	S	I	Methiocarb	5,0E-01	1,6E+02	4	5,9E-02	4	1,8E-05	4	2,0E-03	4	2,0E+01	4	1,1E+00	3	4,3E-01	4	11,8	5,9	high	III
143	16752-77-5	S	I	Methomyl	4,0E-01	1,5E+02	4	2,4E-02	4	4,0E-06	2	1,0E-02	3	1,7E+01	4	1,3E+00	3	9,0E-01	3	9,3	3,7	moderate	II
144	51218-45-2	L	H	Metolachlor	2,5E+00	2,2E+02	4	7,3E-03	4	2,0E-05	4	8,0E-02	1	2,8E+03	2	1,5E+02	1	2,0E+00	3	9,8	24,4	very high	IV
145	19937-59-8	S	H	Metoxuron	2,0E+00	5,7E+01	2	2,9E-03	3	4,4E-06	3	1,0E-02	3	3,2E+03	2	2,2E+01	2	2,0E+01	1	7,5	15,0	very high	IV
146	74223-64-6	S	H	Metsulfuron-methyl	1,0E-01	5,9E+01	2	5,3E-04	2	2,1E-06	2	1,0E-02	3	5,0E+03	1	2,6E+01	2	1,5E+02	1	5,8	0,6	low	I
147	7786-34-7	L	I	Mevinphos	3,5E-01	7,8E+00	1	1,1E-04	1	2,6E-08	1	2,0E-03	4	4,0E+00	4	7,0E-02	4	1,2E-02	4	6,0	2,1	low	I
148	1746-81-2	S	H	Monolinuron	9,0E-01	1,7E+02	4	2,3E-02	4	1,7E-05	4	5,0E-03	4	2,3E+03	2	1,4E+01	3	5,6E+01	1	10,5	9,5	high	III
149	88671-89-0	S	F	Myclobutanil	2,0E-01	6,1E+01	2	7,4E-04	2	2,9E-06	2	3,0E-02	2	1,6E+03	3	3,6E+02	1	3,3E+00	2	6,0	1,2	low	I
150	10552-74-6	S	F	Nitrothal-isopropyl	5,0E-01	9,7E+00	1	6,0E-02	4	7,3E-06	3	5,0E-02	1	6,4E+03	1	2,1E+01	2	7,0E-01	3	7,3	3,6	moderate	II
151	63284-71-9	S	F	Nuarimol	1,1E-01	1,1E+02	3	5,7E-04	2	4,3E-06	2	2,0E-02	2	1,3E+03	3	2,2E+01	2	5,6E+00	2	6,8	0,7	low	I
152	1113-02-6	L	I	Omethoate	8,0E-01	1,6E+01	1	6,4E-05	1	2,0E-06	1	3,0E-04	4	5,0E+01	4	8,3E-02	4	8,8E+00	2	5,5	4,4	moderate	II
153	19044-88-3	S	H	Oryzalin	1,7E+00	1,1E+02	4	2,2E-04	2	5,3E-06	3	1,0E-01	1	1,0E+04	1	1,1E+01	3	2,9E+00	2	7,8	13,2	very high	IV
154	23135-22-0	S	I	Oxamyl	1,5E+00	1,6E+01	1	5,2E-05	1	8,8E-07	1	3,0E-02	2	6,0E+00	4	4,5E+00	3	4,2E+00	2	4,8	7,1	high	III
155	301-12-2	L	I	Oxydemethon-methyl	4,0E-01	4,3E+00	1	2,1E-04	2	4,4E-07	1	3,0E-04	4	6,5E+01	4	5,4E-01	4	1,9E+00	3	6,3	2,5	moderate	II

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		$LD50_{rat}$ mg/kg.bw		$LD50_{bee}$ µg/bee		$LC50_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
156	298-00-0	L	I	Parathion-methyl	4,0E+00	8,5E+01	3	5,5E-03	4	3,6E-06	2	2,0E-04	4	1,4E+01	4	1,8E-01	4	2,7E+00	3	9,3	37,0	very high	IV
157	66246-88-6	S	F	Penconazole	1,5E-01	1,1E+02	4	7,3E-05	1	7,6E-06	3	3,0E-02	2	2,1E+03	2	5,3E+00	3	1,3E+00	3	8,0	1,2	low	I
158	66063-05-6	S	F	Pencycuron	3,0E+00	2,3E+02	4	7,3E-06	1	1,3E-05	4	2,0E-02	2	5,0E+03	1	1,3E+02	1	5,0E+00	2	8,0	24,0	very high	IV
159	40487-42-1	S	H	Pendimethalin	1,3E+00	2,8E+01	1	3,1E-04	2	7,9E-05	4	1,0E-01	1	1,1E+03	3	5,0E+01	2	1,4E-01	4	8,0	10,4	very high	IV
160	52645-53-1	L	I	Permethrin	2,0E-01	7,0E+01	3	3,7E-04	2	3,8E-05	4	5,0E-02	1	5,0E+02	3	4,0E-02	4	1,0E-03	4	9,5	1,9	low	I
161	2310-17-0	S	I	Phosalone	8,5E-01	1,7E+01	1	1,5E-05	1	8,8E-07	1	6,0E-03	3	1,2E+02	4	7,4E+00	3	1,1E-01	4	5,5	4,7	high	III
162	732-11-6	S	I	Phosmet	7,5E-01	1,6E+01	1	1,2E-04	1	5,7E-07	1	1,0E-02	3	1,1E+02	4	6,1E-01	4	7,0E-02	4	5,8	4,3	high	III
163	13171-21-6	L	I	Phosphamidon	3,0E-01	1,6E+01	1	6,2E-05	1	1,3E-06	1	2,0E-04	4	7,0E+00	4	3,2E-01	4	3,2E+00	2	5,5	1,7	low	I
164	14816-18-3	L	I	Phoxim	5,0E-01	1,3E+01	1	1,3E-02	4	4,7E-07	1	4,0E-03	4	2,0E+03	2	1,0E+02	1	2,2E-01	3	6,0	3,0	moderate	II
165	23103-98-2	S	I	Pirimicarb	6,0E-01	3,0E+02	4	1,6E-03	3	1,6E-06	1	2,0E-03	4	1,5E+02	4	1,8E+01	3	2,9E+01	1	7,5	4,5	high	III
166	29232-93-7	L	I	Pirimiphos-methyl	1,0E+00	5,9E+01	2	7,2E-04	2	4,6E-06	2	2,0E-02	2	2,0E+03	2	3,9E-01	4	6,4E-01	3	6,8	6,8	high	III
167	32809-16-8	S	F	Procymidone	7,5E-01	8,0E+01	3	1,0E-01	4	6,2E-06	3	1,5E-01	1	6,8E+03	1	1,1E+02	1	3,6E+00	2	7,8	5,8	high	III
168	122-42-9	S	H	Profam	3,5E+00	1,0E+01	1	2,0E-02	4	8,9E-07	1	1,0E-02	3	5,0E+03	1	1,6E+01	3	3,2E+01	1	5,5	19,3	very high	IV
169	41198-08-7	L	I	Profenofos	3,2E-01	6,2E+01	3	3,0E-05	1	4,1E-06	2	1,0E-02	3	3,6E+02	4	3,5E+00	3	8,0E-02	4	7,5	2,4	moderate	II
170	7287-19-6	S	H	Prometryn	9,0E-01	1,1E+02	4	5,6E-04	2	5,5E-06	3	3,0E-02	2	3,2E+03	2	1,9E+01	2	2,5E+00	3	8,3	7,4	high	III
171	1918-16-7	S	H	Propachlor	3,3E+00	2,2E+01	1	9,6E-03	4	3,5E-06	2	2,0E-02	2	1,5E+03	3	1,1E+01	3	1,7E-01	4	7,5	24,4	very high	IV
172	24579-73-5	S	F	Propamocarb	1,1E+00	5,8E+01	2	9,3E-04	3	8,4E-06	3	1,0E-01	1	8,6E+03	1	1,1E+02	1	1,6E+02	1	6,5	7,2	high	III
173	111479-05-1	S	H	Propaquizafop	1,5E-01	5,8E+01	2	3,3E-06	1	3,8E-06	2	3,0E-03	4	5,0E+03	1	2,0E+02	1	1,9E-01	4	6,0	0,9	low	I
174	139-40-2	S	H	Propazine	3,6E-01	1,0E+02	3	1,1E-03	3	4,4E-06	2	2,0E-02	2	5,0E+03	1	1,6E+01	3	1,8E+01	1	6,8	2,4	moderate	II
175	114-26-1	S	I	Propoxur	7,0E-01	4,2E+01	1	2,5E-05	1	1,9E-06	1	2,0E-02	2	9,5E+01	4	7,2E-01	4	6,2E+00	2	5,0	3,5	moderate	II
176	23950-58-5	S	H	Propyzamide	1,8E+00	2,0E+02	4	7,1E-02	4	1,8E-05	4	2,0E-02	2	5,6E+03	1	1,8E+01	2	5,4E+01	1	9,5	16,6	very high	IV
177	52888-80-9	L	H	Prosulfocarb	4,0E+00	6,2E+01	3	2,4E-05	1	4,1E-06	2	5,0E-03	4	1,8E+03	2	8,0E+01	2	1,7E+00	3	6,8	27,0	very high	IV
178	123312-89-0	S	I	Pymetrozine	3,0E-01	9,7E+01	3	3,4E-04	2	7,1E-08	1	3,0E-02	2	5,8E+03	1	1,2E+02	1	1,3E+02	1	4,8	1,4	low	I
179	13457-18-6	S	F	Pyrazophos	8,1E-01	1,4E+02	4	6,4E-04	2	7,9E-06	3	4,0E-03	4	4,4E+02	3	2,5E-01	4	1,6E-02	4	9,8	7,9	high	III
180	8003-34-7	L	I	Pyrethrins	4,0E-01	6,1E+01	3	4,0E-05	1	6,0E-06	3	4,0E-02	1	1,0E+03	3	2,1E-01	4	5,0E-03	4	8,0	3,2	moderate	II
181	96489-71-3	S	AC	Pyridaben	1,3E-01	1,0E+02	3	2,4E-03	3	4,6E-05	4	1,0E-02	3	8,2E+02	3	1,2E-01	4	3,0E-03	4	10,5	1,4	low	I
182	55512-33-9	S	H	Pyridate	7,5E-01	6,2E+01	3	5,7E-07	1	5,2E-06	3	3,6E-02	2	2,0E+03	2	1,7E+01	3	4,8E+01	1	7,0	5,3	high	III
183	88283-41-4	L	F	Pyrifenox	2,5E-01	1,1E+02	4	1,7E-03	3	1,0E-05	4	9,0E-02	1	2,9E+03	2	7,0E+01	2	6,6E+00	2	9,3	2,3	moderate	II
184	53112-28-0	S	F	Pyrimethanil	7,5E-01	5,9E+01	2	7,1E-04	2	2,6E-06	2	2,0E-01	1	4,2E+03	2	1,2E+02	1	1,0E+01	2	5,5	4,1	moderate	II
185	95737-68-1	S	I	Pyriproxyfen	3,0E-01	6,1E+01	2	7,8E-04	3	8,6E-06	3	7,0E-02	1	5,0E+03	1	1,1E+02	1	7,6E+00	2	6,8	2,0	low	I
186	90717-03-6	S	H	Quinmerac	4,0E-01	6,1E+01	2	2,9E-04	2	2,2E-06	1	8,0E-02	1	5,0E+03	1	4,3E+01	2	8,7E+01	1	4,3	1,7	low	I

	CAS#	Phys. State	Use	Name	Dose a.i.kg/ha	Pov days		LRTP -		iF kg/kg		ADI mg/kg.bw		$LD50_{rat}$ mg/kg.bw		$LD50_{bee}$ µg/bee		$LC50_{fish}$ mg/L		Hazard-Index	Pest-Score	Risk level	Class
187	76578-14-8	S	H	Quizalofop-ethyl	3,0E-01	6,0E+01	2	2,1E-04	1	3,5E-06	2	1,0E-02	3	1,2E+03	2	5,4E+01	2	2,8E+00	2	5,8	1,7	low	I
188	100646-51-3	S	H	Quizalofop-P-ethyl	1,3E-01	6,0E+01	2	2,1E-04	1	3,5E-06	2	1,0E-02	3	1,0E+03	3	5,1E+01	2	2,8E+00	2	6,0	0,8	low	I
189	122931-48-0	S	H	Rimsulfuron	1,0E-01	5,8E+01	2	9,4E-04	2	3,2E-05	4	1,0E-01	1	5,0E+03	1	1,0E+02	1	1,1E+02	1	7,0	0,7	low	I
190	74051-80-2	L	H	Sethoxydim	5,0E-01	6,2E+01	3	1,1E-05	1	3,7E-06	2	1,8E-01	1	3,2E+03	2	1,0E+01	3	3,8E+01	1	5,8	2,9	moderate	II
191	122-34-9	S	H	Simazine	2,6E+00	2,0E+02	4	3,5E-03	3	8,3E-06	3	5,0E-03	4	5,0E+03	1	2,3E+01	2	4,9E+01	1	8,5	22,1	very high	IV
192	128-04-1	L	F	Sodium dmdt-carbamate	1,0E-01	5,8E+01	2	8,6E-04	2	2,7E-05	4	2,0E-02	2	2,5E+03	2	5,1E+01	2	2,6E+00	3	8,3	0,8	low	I
193	107534-96-3	S	F	Tebuconazole	4,4E-01	1,1E+02	4	2,0E-04	1	5,2E-06	2	3,0E-02	1	1,7E+03	2	1,8E+02	1	5,9E+00	2	6,0	2,6	moderate	II
194	13071-79-9	L	I	Terbufos	1,2E+00	3,0E+01	1	3,1E-03	3	1,3E-05	3	2,0E-04	4	2,0E+00	4	3,2E-01	4	4,0E-03	4	9,0	10,8	high	III
195	886-50-0	S	H	Terbutryn	1,4E+00	1,1E+02	4	4,9E-04	2	6,3E-06	3	1,0E-01	1	2,4E+03	2	1,7E+01	3	3,0E+00	2	8,0	10,8	high	III
196	31895-21-3	S	I	Thiocyclam	5,0E-01	5,1E+01	1	1,3E-03	3	3,2E-06	2	1,3E-02	3	3,2E+02	3	8,0E+00	3	5,0E-02	4	7,3	3,6	moderate	II
197	59669-26-0	S	I	Thiodicarb	2,0E-01	4,2E+01	1	6,2E-02	4	5,0E-06	2	3,0E-02	1	6,6E+01	4	7,1E+00	4	1,2E+00	3	7,5	1,5	low	I
198	39196-18-4	S	I	Thiofanox	3,3E+00	6,0E+01	2	1,2E-03	2	3,3E-06	2	1,0E-04	4	8,0E+00	4	6,0E-02	4	1,3E-01	4	8,0	26,4	very high	IV
199	640-15-3	L	I	Thiometon	3,5E-01	1,6E+01	1	2,1E-04	1	6,8E-07	1	1,0E-03	4	1,2E+02	4	5,5E-01	4	8,0E+00	2	5,5	1,9	moderate	II
200	23564-05-8	S	F	Thiophanate-methyl	1,5E+00	1,6E+01	1	6,0E-05	1	8,2E-07	1	2,0E-02	2	6,0E+03	1	1,0E+02	1	1,1E+00	3	3,8	5,6	high	III
201	137-26-8	S	F	Thiram	2,9E+00	5,4E+01	2	4,7E-02	4	9,6E-06	3	1,0E-02	3	5,6E+02	3	1,3E+01	3	1,6E-01	4	9,3	26,8	very high	IV
202	57018-04-9	S	F	Tolclophos-methyl	3,0E+00	1,2E+02	4	1,9E-02	4	1,7E-05	4	5,0E-02	1	5,0E+03	1	1,0E+02	1	8,7E-01	3	9,5	28,5	very high	IV
203	731-27-1	S	F	Tolylfluanid	1,1E+00	9,9E+01	3	1,1E-02	4	2,5E-05	4	1,0E-01	1	5,0E+03	1	1,0E+02	1	6,0E-02	4	9,3	10,2	high	III
204	43121-43-3	S	F	Triadimefon	2,0E-01	1,0E+02	3	1,1E-03	2	3,7E-06	2	3,0E-02	1	6,0E+02	3	7,5E+01	2	6,9E+00	2	6,5	1,3	low	I
205	55219-65-3	S	F	Triadimenol	1,0E-01	6,1E+01	3	2,6E-04	2	2,2E-06	1	5,0E-02	1	9,0E+02	3	1,0E+02	1	1,5E+01	2	5,3	0,5	low	I
206	2303-17-5	L	H	Tri-allate	1,1E+00	3,1E+01	1	1,8E-02	4	1,1E-05	3	5,0E-03	4	2,2E+03	2	1,8E+01	3	1,2E+00	3	8,5	9,4	high	III
207	24017-47-8	L	I	Triazophos	6,0E-01	2,3E+02	4	2,2E-03	3	2,2E-05	4	1,0E-03	4	8,2E+01	4	5,5E-02	4	4,0E-01	4	11,5	6,9	high	III
208	52-68-6	S	I	Trichlorfon	6,0E-01	6,5E+00	1	9,3E-06	1	1,7E-07	1	1,0E-02	3	2,5E+02	4	6,0E-01	4	5,2E-01	4	5,8	3,5	moderate	II
209	55335-06-3	S	H	Triclopyr	2,0E-01	6,0E+01	2	6,3E-04	2	2,3E-06	1	5,0E-03	4	7,1E+02	3	6,1E+01	2	1,2E+02	1	5,5	1,1	low	I
210	68694-11-1	S	F	Triflumizole	5,0E-01	1,0E+02	3	2,3E-03	3	2,5E-05	4	4,0E-02	1	7,0E+02	3	2,0E+01	2	5,7E-01	3	9,3	4,6	high	III
211	1582-09-8	S	H	Trifluralin	1,3E+00	1,3E+02	4	1,2E-02	4	2,2E-05	4	2,0E-02	2	1,0E+04	1	1,0E+02	1	2,0E-02	4	10,0	12,5	very high	IV
212	26644-46-2	S	F	Triforine	3,5E-01	4,2E+02	4	1,8E-02	4	8,4E-05	4	2,0E-02	2	6,0E+03	1	3,0E+01	2	1,1E+02	1	9,5	3,3	moderate	II
213	83657-22-1	S	PGR	Uniconazole	1,5E+00	7,5E+01	3	8,6E-03	3	6,6E-06	3	2,0E-02	2	1,8E+03	2	2,0E+01	2	1,5E+01	2	8,0	12,0	very high	IV
214	2275-23-2	L	I	Vamidothion	5,0E-01	1,6E+01	1	6,4E-05	1	1,7E-06	1	5,0E-03	4	1,0E+02	4	6,0E-01	4	1,2E+02	1	5,3	2,6	moderate	II
215	50471-44-8	S	F	Vinclozolin	5,0E-01	1,0E+02	3	1,5E-03	3	5,4E-06	3	1,0E-02	3	1,0E+04	1	1,0E+02	1	3,2E+01	1	7,5	3,8	moderate	II
216	81-81-2	S	R	Warfarin	1,3E+00	6,0E+01	2	5,6E-04	2	2,2E-06	1	3,0E-04	4	1,0E+01	4	8,0E-01	4	6,5E+01	1	6,3	8,1	high	III
217	12122-67-7	S	F	Zineb	4,0E+00	1,2E+02	4	1,3E-02	4	2,0E-06	1	3,0E-02	1	5,0E+03	1	1,3E+01	3	2,0E+00	3	7,0	28,0	very high	IV

Chapter 6

General Conclusions and outlook

In this thesis, environmental assessment methodologies were advanced to facilitate the evaluation of the environmental performance of pesticides, specifically focusing on human intake and ecotoxicological impacts. Three principle strategies were pursued:

- Development and validation of fate and exposure models to predict pesticides residues in harvested greenhouse crops within the frame of life cycle impact assessment

- Experimental assessment of several active ingredients by a combination of field trials and chemical laboratory analyses and

- Development of a screening tool to provide a relative assessment of pesticide hazards to human health and the environment by combining measures of chemical toxicity with chemical release amounts and further fate and exposure characteristics.

Conclusions are brought here by answering to the different challenges and questions scheduled in the introduction (chapter 1.6).

The fate of pesticides is described by two models representing the system “pesticide - plant - environment” and describing the main transport and dissipation processes. These processes are dynamic, as a function of the elapsed time between pesticide application and crop harvest. The initial concentrations of substance in the soil, the air and the pesticide spray deposit on plants are determined by the distribution of pesticide in the system at spraying or irrigation. The initial distribution after spraying depends notably on the crop stage described by the leaf area index. Main transport processes are in form of advection and diffusion. Degradation of substances and plant growth are additional processes to be accounted for. Each transport is described by a transfer rate accounting for the process and for the equilibrium partitioning between the two exchanging phases or compartments. Partition coefficients describe the substance behaviour and distribution between different phases. These parameters show a high variation between substances. The most important parameter describing the partitioning between compartments is the octanol/water-partition coefficient (K_{ow}).

Half-life values and elapsed time between application and harvest determine the persistence of the substance. These parameters represent the most determining parameters and their influences on the dynamic evolution of the system are the easiest to interpret. Parameters linked with the system dynamics are important factors determining the fate and have an important influence on the human intake fraction of pesticides.

The first distribution of substance is given by the initial conditions of the system: the plant canopy and the losses of substances during application (wind drift, evaporation). The importance of the direct application on plants is high, particularly with pesticides applied during crop growth and just before harvest. For this reason the model needs to account for the plant stage and instant leaf area index at application time when spray application is considered. The residence time of the substance is a central factor to determine the relevant pathway (air, soil, spray deposit). The degradation in air is very fast for most pesticides, whereas the persistence of substance in soil may be very long. The half-life of substances deposited on plant is limited to a few days, but the transfer is fast from spray deposit to the inner plant, where degradation has been shown to be much faster. Consequently the direct spray application is an important source for accumulation in plant. It concerns particularly substances rapidly transported into the plant tissue (high K_{ow}) instead of being degraded as deposit on the plant surface.

Washing eatable parts of crops with water can contribute significantly to the reduction of pesticide residues and thus substantially reduce the human intake fraction. Including processing factors in fate and exposure models is shown to be of great importance. The wash-off fraction of pesticides from plant surfaces due to washing with cold tap water was tested in this thesis on four different active ingredients. Wash-off fractions varied significantly (22-69%) and could not be correlated to any physical-chemical properties like water solubility or the octanol/water-partition coefficient (K_{ow}) of the substances analysed. Washing the final agricultural product directly after harvest could furthermore reduce intake fractions of pesticides as residues on the plant surface which potentially tend to move into the plant would be removed at the earliest possible time. At this point it has to be mentioned that most active ingredients are applied using surfactants or emulsifiers (leaf wetting agents) favouring a penetration and making it easier for the pesticide to enter the inner parts of the plant. This issue has not been addressed in any fate and exposure model yet but could be of importance. Risk assessment methodologies for pesticides generally take only the active ingredient into account.

The modelling of pesticides transfer from deposit through the cuticular waxes and membrane offer new possibilities to model pesticide fate in agricultural systems and to account for the contribution of direct application to the occurrence of residues. Particularly the description and quantification of the substance mobility in the cuticular membrane represents an essential factor for the evaluation of pesticide fate and a potential improvement for environmental multimedia models.

The dynamic behaviour first affects the initial distribution of substance between the air, the soil and the deposit on plant surface as a function of the dynamic development of the crop, including the growth and the leaf area index evolution. However, the dynamic behaviour principally relates to the time interval between application and harvest. The initial transport processes, during the first days after the application distribute the substance in the different system compartments. Once residues in each plant compartment have reached a maximum amount, a dissipation phase occurs up to the moment of harvest. The duration of these determining periods, from application to maximum residues and from maximum residues to harvest, is determinant for the level of residues. These processes directly depend on the half-lives of the substance in the initial compartment (soil, plant surface) and inside the plant. It also depends on the transfer rates between the compartments. The consideration of this dynamic behaviour is an essential factor that makes the modelling of pesticides residues distinct from other applications of multimedia models. The models are based on initial amounts of substance in the source compartments, on transfer rates linking the compartments and on a dynamic modelling of the system, as a function of the time interval between application and harvest. Each compartment is described by a linear differential equation defining the variation in accumulated mass and its dissipation. The capacity to express each process by the determining factors is the major challenge in developing the models.

Most important pathways for substance accumulation in plants are identified. The spray deposit is an important source, particularly when the application takes place shortly before harvest. Due to the higher persistence in ground, the soil is logically determinant for early applied pesticides, for substances with a low degradation rate. The contribution of substance from the air is mostly negligible due to relatively fast degradation. The evolution of each subsystem is characterised by a maximum accumulated mass. The capacity to quantify this maximal accumulated mass and the time to reach it is a major contribution for the understanding of the model system. This point corresponds to equilibrium, when the flux of transfer from the source compartment is equal to the flux of dissipation from the receiving plant compartment.

Direct soil application of pesticides was shown to be a viable alternative to the standard spray application. Uptake and persistence was evaluated by a new developed dynamic root uptake model for pesticides aiming at the estimation of time dependent contaminant concentrations in fruits (edible part of tomato crops). Concentrations in whole tomato fruits measured after foliar spray application were higher than those detected in whole fruits treated by soil application throughout the entire dissipation study. Concentrations in fruits after spray application exceeded those in fruit after soil application by up to a factor of five indicating that the use of drip irrigation systems for the application of systemic pesticides would have advantages over spray applications. It would minimize worker and consumer exposure to the pesticide, result in a uniform application, and prevent runoff of pesticide by spray drift into the environment. However, peeled tomatoes treated by spray application show lower concentrations of active ingredient compared to tomatoes treated by drip-irrigation. From these results a possible advantage for the spray application can be drawn as peeling tomatoes treated by drip-irrigation would not minimize residual concentrations of pesticides.

In order to determine the most environmentally friendly active ingredient prior to application, thus leading to better management and decision-making about pesticide use, a new ranking method was presented. The chemical ranking and scoring method entitled PestScreen has been developed as a screening tool to provide a relative assessment of pesticide hazards to human health and the environment. The method was developed to serve as an analytical tool in screening and identification of pesticides of environmental concern used in agriculture. It incorporates both the toxic effects of pesticides and their fate and exposure characteristics in different compartments of the environment. This is done by combining measures of chemical toxicity pertaining to both human health and the environment with chemical release amounts and information on overall environmental persistence, long-range transport potential and human population intake fractions. Each hazard measure is scored and weighted and finally combined with the pesticide application dose to provide a single final indicator of relative concern (PestScore).

According to these answers, the objectives of the study have been achieved: identification and description of main processes in environment – plant exchanges, building of models to assess the residue concentration at harvest in agricultural commodities, understanding of the functioning of the system “pesticide - plant - environment” and characterisation of pesticides used in greenhouse cropping systems. The methodology for the evaluation of pesticide fate in agricultural commodities is improved by the consideration of dynamic processes, of agricultural conditions and of direct applications on plants. This opens new perspectives in the frame of life cycle assessment in agriculture, in particular concerning the effective relevance of pesticides in agricultural products on a toxicological point of view.

There is a specific need to improve the description of determinant transfers between environment and vegetation. Particularly, knowledge is continuously improved concerning the pesticides mobility in cuticular membrane and the substance partitioning between the different media from the formulation deposit to the plant inner and from the root zone to upper parts of plants. The present results have shown that the soil may be an important source for accumulation, particularly on a long time perspective when degradation rates are low. A better knowledge should be obtained for the balance between the accumulation to the plant and the losses from the agricultural soil to other environmental compartments. Data on evaporation from soil and runoff from plant surfaces are still scarce and highly uncertain.

The quality of data should be a permanent survey. Particularly, half-life data are determinant for the functioning of the present models. Based on empirical information of 41 active ingredients on degradation half-lives in soil and degradation half-lives on plant surfaces derived from field experiments (including two pesticides analyzed in this thesis), an estimation routine for degradation half-lives on vegetation was developed.

Furthermore, the estimation of pesticide half-life within plants has been improved by presenting a generic estimation routine for substance specific half-lives based on experimental field data. However, this relationship suggested is not without uncertainties and is based only on the two pesticides analyzed in this thesis. More case studies need to be carried out for different types of plant protection products. This would improve knowledge on the relevance of fate and effects of different active substances in the frame of LCIA. Rules for decision support based on LCA could then be validated and defined more specifically, e.g. per substance class or per group of pesticide.

Concerning the pesticides ranking methodology (PestScreen), the results presented in this study could be improved by combining the current approach with artificial neural networks (ANN). ANN are systems of elementary computing units that model the information-processing abilities of biological neural networks. These, biologically-inspired methods of computing are thought to be the next major advancement in the computing industry. The self-organizing map (SOM) is an unsupervised artificial neural network which consists of computing units called artificial neurons. SOM is based on data mining, which means that the information is extracted from a large database to discover hidden facts contained in large databases. It is considered a future step in comparison to the classic statistical tools. The main difference is that data mining techniques build the models automatically while classical statistical tools need to be wielded by a trained statistician with a clear (or possibly preconceived) idea about what is looking for. Another positive aspect is that SOM owns a clustering procedure, which has been shown to be equivalent or superior to some other cluster analysis methods. The weights associated to each neuron in a two-dimensional lattice are adjusted to cluster the original information. The map can also be divided into so many c-planes (component planes) as data variables, representing the variable contribution to each neuron in the map. SOM, as well as other ANN techniques, could be successfully applied to characterize environmental performance of pollutants in particular areas. Likewise, SOM could be successfully applied to pesticides in order to rank these for the use in comparative environmental risk assessment.

Appendix

Publication list (peer reviewed)

Frischer, M.E., Danforth, J.M., Foy, T.F. and **Juraske, R.** Bioluminescent Bacteria as Indicators of Chemical Contamination of Coastal Waters. *Journal of Environmental Quality* 34: 1328-1336., 2005

Juraske, R., Antón A., Castells F., and Huijbregts, M.A.J. Human intake fractions of pesticides via greenhouse tomato consumption: Comparing model estimates with measurements for captan. *Chemosphere* 67: 1102-1107., 2007

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Juraske, R., Antón A., Castells F. Estimating half-lives of pesticides in/on vegetation for use in fate and exposure models. *Chemosphere (accepted for publication)*

Juraske, R., Castells F., Vijay, A., Muñoz, P. and Antón A. Comparing uptake and persistence of imidacloprid in tomatoes treated by soil chemigation and foliar spray application: Measurements and model estimates *(submitted)*

Rosenbaum R.K., Bachmann T.M., Hauschild M.Z., Huijbregts M.A.J., Jolliet O., **Juraske R.**, Köhler A., Larsen H.F., MacLeod M., Margni M., McKone T.E., Payet J., Schuhmacher M., Russel A., van de Meent D. USEtox - The UNEP/SETAC-consensus model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in Life Cycle Impact Assessment *(submitted)*

Ocampo-Duque, W., **Juraske, R.**, Kumar, V., Nadal, M., Schuhmacher, M., Domingo, JL. A screening ecological risk based model to assess the impact of hazardous substances in river systems based on self organizing maps and fuzzy reasoning. *(submitted)*

Contributions to conferences

Juraske, R., Antón A., Castells F., and Huijbregts, M.A.J., PestScreen: Screening, scoring and ranking pesticides by life-cycle impact assessment approach. LCM 2007, Zürich, Switzerland, 2007

Juraske, R., Antón A., Castells F., Estimating half-lives of pesticides for use in fate and exposure models. SETAC Europe 17th annual meeting, Porto, Portugal, 2007

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