Health Impact Assessment of Pesticide Use in Europe

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To my beloved mom,
To Nicole, my love and partner in life,
To Elias & Emily

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Abbreviations and Acronyms

6^{th} EAP	Sixth Environment Action Programme
ADI	Acceptable Daily Intake
AERU	Agriculture and Environment Research Unit
BfR	Bundesinstitut für Risikobewertung
BMJ	Bundesministeriums der Justiz
BoD	Burden of Disease
BVL	Bundesamt für Verbraucherschutz und Lebensmittelsicherheit
CAC	Codex Alimentarius Commission
CAS-RN	Chemical Abstracts Service Registry Number
CBA	Cost-Benefit Analysis
CEA	Cost-Effectiveness Analysis
CF	Characterization Factor
DALY	Disability-Adjusted Life Year
DRF	Dose-Response Relationship
dynamiCROP	Dynamic Assessment Model for Human Health Impacts due to Crop Uptake of Organic Pollutants
EC	European Commission
EEA	European Environment Agency
EFSA	European Food Safety Authority
ERF	Exposure-Response Relationship
EU	European Union
FAI	Fruit Area Index
FAO	Food and Agriculture Organization of the United Nations
GAP	Good Agricultural Practice
HBCDD	Hexabromocyclododecane
hF	Harvest Fraction
IER	Institute of Energy Economics and the Rational Use of Energy
iF	Human Intake Fraction
ILSI	Research Foundation Risk Science Institute
IPA	Impact Pathway Approach

ISO	International Organization for Standardization
LAI	Leaf Area Index
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
LWK	Landwirtschaftskammer Nordrhein-Westfalen
MoA	Mode of Action
MRL	Maximum Residue Level
NOEL	No-Observed Effect Level
NRC	National Research Council
OCSEH	Office of Chemical Safety and Environmental Health
OECD	Organisation for Economic Co-operation and Development
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD/F	Polychlorinated Dibenzo-*p*-Dioxin and Polychlorinated Dibenzofuran
PFOS	Perfluorooctanesulfonic Acid
PHI	Minimum Pre-harvest Interval (between pesticide application and crop harvest)
POP	Persistent Organic Pollutant
PRC	Pesticide Residues Committee
QSAR	Quantitative Structure-Activity Relationship
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SETAC	Society of Environmental Toxicology and Chemistry
U.S.	United States of America
U.S. EPA	United States Environmental Protection Agency
UBA	Umweltbundesamt
UNEP	United Nations Environment Programme
USDA	United States Department of Agriculture
USEtox	UNEP/SETAC Model for the Comparative Assessment of Chemicals Released to Air, Water and Soil and Their Toxic Effects on the Human Population and Ecosystems
VBA	Visual Basic for Applications
WHO	World Health Organization
YLD	Years Lived with a Disability
YOLL	Years of Life Lost

Abstract

Technology assessments in Europe have mainly focused on air quality management with respect to energy conversion and road transport. However, other environmental media must also be considered to arrive at an integrated perspective for developing strategies towards more sustainability and an improved human welfare. Consequently, bioaccumulation of pollutants in the environment, in food crops and in animal food products leads to human ingestion exposure that must be accounted for. In addition, growing crops for use as energy, biofuels and non-energy raw materials becomes more and more important in the context of current policy. Unfortunately, only little is known about how the health of the general population is affected by current agriculture in Europe, especially with respect to the use of pesticides.

Over the last three decades, European policy has developed towards a large legislation body regulating the marketing and use of pesticides as well as their residues in drinking water and various food items. Nonetheless, residues are still reported to reach levels where they can harm humans or the environment. Especially effects of pesticides on human health have lead to a continuously concerned general public. Existing regulations are therefore under constant revision by steadily evaluating the negative consequences of pesticide application based on continuously required scientific support. Thereby, evaluating exposure to pesticides and related health effects must build upon a deterministic understanding of the pathways from substance application via loss to the environment and uptake into the different food crops to finally human intake. However, current assessment tools are still challenged by the inherent complexity of plant uptake and translocation mechanisms as well as by an insufficient understanding of substance-specific chemical transformation, post-harvest food processing and health effects.

The present work, hence, aims at improving existing health impact assessments of pesticide use by contrasting pathways of human exposure to pesticides. Main challenges were to consider characteristics of different food crops, to characterize individual pesticide-crop combinations and to simplify a complex dynamic model for incorporation into existing assessment tools to also account for the pesticide fraction that directly reaches the target crops. To address these challenges, a new operational modeling approach was developed for quantifying health impacts from exposure to pesticide residues in multiple directly treated food crops based on transparent matrix algebra. From analyzing its functioning and uncertainty, the system was parameterized for use in existing models, thereby keeping crops and substances disaggregated.

In a case study, the new approach was applied to estimate health impacts and related damage costs caused by the five most extensively used pesticides in each of 25 European countries in 2003. Results indicate a high variation of impacts between countries as a function of the amount applied and substance toxicity. Total health impacts amount to 1672 DALY (disability-adjusted life years), to which the fraction reaching the target crops and the fraction lost to the environment during application contribute with 97% and 3%, respectively. Spain with 485, Italy with 442 and France with 370 DALY show the highest impacts per country. If translated into costs, damages amount to 67 million Euro in Europe in 2003. Results demonstrate the importance of considering pesticide residues in treated food crops for estimating overall human health impacts as integral part of evaluating current pesticide use in Europe.

Zusammenfassung

Technikbewertung in Europa war bisher hauptsächlich fokussiert auf Luftreinhaltemaßnahmen im Rahmen der Energieumwandlung und des Straßenverkehrs. Jedoch müssen für einen ganzheitlichen Ansatz zur Erreichung von mehr Nachhaltigkeit und eines verbesserten Gemeinwohls auch weitere Umweltmedien berücksichtigt werden. Diesbezüglich führt die Schadstoffanreicherung in der Umwelt, in Nahrungspflanzen und tierischen Produkten zur menschlichen Exposition über die Nahrungsaufnahme. Auch der wachsende Kulturpflanzenanbau zur Energie-, Biokraftstoff- und Rohmaterialien-Produktion spielt eine wichtige Rolle für die aktuelle Politik. Leider ist bisher nur wenig darüber bekannt, wie sich die heutige Landwirtschaft auf die menschliche Gesundheit auswirkt, insbesondere bezüglich der Nutzung von Pestiziden.

In den letzten drei Jahrzehnten wurden in Europa Richtlinien zur Regulierung von Vermarktung und Anwendung von Pestiziden als auch zur Kontrolle von Rückständen in Trinkwasser und Nahrungsmitteln erarbeitet. Trotzdem finden sich Rückstandsmengen, die auf Mensch und Umwelt schädlich wirken können. Insbesondere Gesundheitsschäden führten zu einer kontinuierlich besorgten Bevölkerung. Bestehende Regulierungen unterliegen deshalb der ständigen Überprüfung hinsichtlich negativer Auswirkungen des Pestizideinsatzes auf Basis wissenschaftlicher Erkenntnisse. Dabei ist eine deterministische Betrachtungsweise der gesamten Wirkungskette vom Pestizideinsatz über den Transport in der Umwelt und in Nahrungspflanzen bis zur Aufnahme durch den Menschen entscheidend für die Abschätzung von Gesundheitsbelastungen. Bisherige Bewertungsmodelle haben jedoch bis heute sowohl mit der Komplexität von Schadstoffflüssen in Pflanzen als auch mit unzureichenden Kenntnissen bezüglich chemischen Stoffumbaus, Nahrungsmittelverarbeitung und Gesundheitseffekten zu kämpfen.

Die vorliegende Arbeit soll durch den Vergleich von menschlichen Expositionspfaden gegenüber Pestiziden bestehende Methoden zur Bewertung des Pestizideinsatzes verbessern. Besondere Herausforderungen waren die Betrachtung verschiedener Nutzpflanzen, die Charakterisierung einzelner Pestizid/Pflanze-Kombinationen und die Einbindung des Ansatzes in bestehende Bewertungsmodelle zur Berücksichtigung der Rückstände in Nahrungspflanzen. Zur Bewältigung dieser Herausforderungen wurde ein neues Bewertungsmodell zur Quantifizierung von Gesundheitsschäden durch Pestizidrückstände in Nahrungspflanzen auf Basis eines Matrix-Algebra Ansatzes entwickelt. Das Modellsystem wurde mittels Funktional- und Unsicherheitenanalyse parametrisiert, um in ganzheitlichen Bewertungsmodellen verwendet zu werden.

In einer Fallstudie wurde der vorliegende Ansatz zur Abschätzung von Gesundheitsschäden und damit verbundener Kosten durch die fünf am meisten eingesetzten Pestizide in jeweils 25 europäischen Ländern im Jahr 2003 angewendet. Die Ergebnisse zeigen hohe länderspezifische Unterschiede als Funktion von Einsatzmenge und Toxizität. Insgesamt belaufen sich die Schäden auf 1672 DALY ('disability-adjusted life years'), zu denen der die Nahrungspflanzen erreichende Pestizidanteil mit 97% beiträgt. Spanien mit 485, Italien mit 442 und Frankreich mit 370 DALY weisen die höchsten Schäden auf. Die Schadenskosten durch Pestizideinsatz in Europa im Jahr 2003 belaufen sich auf 67 Millionen Euro. Die Ergebnisse verdeutlichen, dass die Berücksichtigung von Rückständen in Pflanzen wichtig ist für die Abschätzung von Gesundheitsschäden als integralem Bestandteil zur Bewertung des Pestizideinsatzes in Europa.

1. Introduction

1.1. Background and context

In the last decades, technology assessment at the European level has mainly focused on air quality management, exposure of humans towards air contaminants and related emission reduction strategies, primarily with respect to energy conversion and use as well as with respect to road transport (EC European Commission, 1999, 2001, 2005a, 2008b, 2010, 2011b). However, other media like agricultural and natural soil, marine, fresh- and groundwater must also be considered in the assessment of technological systems in order to arrive at an integrated perspective for developing strategies towards more sustainability, efficiency and an improved human welfare. Consequently, the bioaccumulation of many different pollutants in the environment, in crops grown for human consumption and finally in animal food products leads to human exposure via ingestion that must be taken into account. In addition, with respect to agricultural crop production, growing crops for energy use from biomass burning and for biofuel use from biomass conversion becomes more and more important in the context of current policy (EC European Commission, 2009a), as well as the use of agricultural products as sustainable non-energy raw materials for the production of e. g. pharmaceuticals, bioplastics and fine chemicals (EC European Commission, 2011a). Unfortunately, only little is known about how the health of the general population is affected by current agriculture in Europe, especially with respect to the use of pesticides.

With more than 50,000 commercial formulations of several hundred active ingredients currently on the market, pesticides are widely used in agricultural practice all around the world (Covello and Merkhoher, 1993; Alloway et al., 1996). The generic term *pesticide* is in this context defined in EC European Commission (2009b, Art. 2.1) as a product "consisting of or containing active substances, safeners or synergists" that is used to protect plants or plant products against all harmful plants and organisms or to influence the life processes of plants or preserve plant products. Since in the present study impacts related to the active substances or active ingredients are discussed, the term pesticide is used to exclusively refer to chemical compounds[1] describing the biologically active part of a pesticide formulation.

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[1] Chemical compounds are pure chemical substances consisting of two or more different elements that are chemically combined and, hence, can be decomposed into their individual elements only by chemical reactions (Wilbraham et al., 2007). Terms like *chemicals*, *substances* and *pollutants* are used in the present work as synonyms for the considered chemical compounds.

The usage of pesticides and, thus, their dispersion and fate in the environment has mainly occurred in the last seventy years and they have become relatively ubiquitous pollutants, especially in technologically advanced countries, such as the United States (U.S.) and most countries of the European Union (EU). As a result, pesticides – along with other organic and inorganic pollutants – can be found in human and animal tissues, in different agricultural soils and adjacent areas, in groundwater, in rivers and lakes, in drinking water and in various items of the food chain (Arias-Estévez et al., 2008; Hamilton and Crossley, 2004; Margni et al., 2002; ILSI Research Foundation Risk Science Institute, 1999). However, the transport of pesticides in the atmosphere, in the oceans and in the marine food chain has resulted in their wider global distribution. Hence, concentrations of several pesticides can even be found in the Arctic snows (Herbert et al., 2005; Hoferkamp et al., 2010), in Antarctic penguins (Geisz et al., 2008) and last but not least in the atmosphere all over the world including the polar regions (Li et al., 2005; Hung et al., 2010). Therefore, environmental policy at the national and international level is important for regulating the use of pesticides, thereby affecting exposure and related risks to humans and the environment.

The sustainable use of pesticides is one of the seven thematic strategies of European environmental policy and, hence, belongs to the key mechanisms for delivering the objectives set out in the Sixth Environmental Action Programme adopted by the European Parliament and the Council for the period 2002-2012 (EC European Commission, 2002). Each strategy examines the links between environmental impacts and sectoral policies, proposes strategic objectives and explores short- and medium-term measures where appropriate, thus, helping to meet the EU's global commitments (EC European Commission, 2007a). The thematic strategy on the sustainable use of pesticides was adopted by the European Commission on 12 July 2006 (EC European Commission, 2006c) and is accompanied by a legislative proposal to create an overall coherent and consistent policy framework for pesticide use (EC European Commission, 2006a) as well as by a detailed impact assessment (EC European Commission, 2006b). However, especially effects of pesticides on human health have lead to a continuous concern of the general public (EFSA European Food Safety Authority, 2006; Chalak et al., 2008; Karabelas et al., 2009), although damages on the environment are reported to exceed effects on human health (Brock et al., 2009; Pretty, 2005). Moreover, the use of pesticides has been perceived as one of the most risky activities pursued by human societies (Epp et al., 2010; Slovic, 2010). Hence, current health policy is under constant revision with focus on improving the sustainability of pesticide use (EC European Commission, 2007a) by steadily evaluating and managing related benefits and damages at both the farm level and the society level based on continuously required scientific support.

1.2. State and trends of pesticide management in Europe

Regulating potentially harmful substances, in particular pesticides (Hellweg and Geisler, 2003; WHO World Health Organization, 2005; Mackova et al., 2006), on the one hand helps to sufficiently protect agricultural crops and on the other hand – together with agri-environmental policies[2] – helps to reduce the negative externalities of agricultural production due to harmful effects on human health and unacceptable effects on the environment (Baylis et al., 2008). In the EU, a large legislation body regulates the marketing and use of pesticides as well as their residues in drinking water and various processed and unprocessed food items. Existing policies and legislation on pesticides were first introduced at EU level in 1979 (EC European Commission, 2007a) and have evolved considerably over the years, culminating in the Regulation 1107/2009/EC (EC European Commission, 2009b) that replaced Council Directive 91/414/EEC on the placing of plant protection products on the market (EC European Commission, 1991) in 2011.

However, although marketing and use of pesticides in the EU are subject to a uniform body of legislation, the compulsory authorization of product formulations containing any regulated active ingredient is in the responsibility of national authorities. In Germany, as an example, the use, sale, monitoring and authorization of pesticides are regulated by the ´Pflanzenschutzgesetz' (Plant Protection Act) (BMJ Bundesministeriums der Justiz, 2009) with the Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (Federal Office of Consumer Protection and Food Safety, BVL) as competent authority, which, for the authorization procedure, collaborates with the following evaluation authorities: the Bundesinstitut für Risikobewertung (Federal Institute for Risk Assessment, BfR), the Julius Kühn Institute and the Umweltbundesamt (Federal Environmental Agency, UBA). After authorization of a pesticide, its application is surveyed by means of control and monitoring programs, whereby, in case of unexpected effects, the BVL can change the authorization or, if necessary, even withdraw it. In contrast to the procedure that an active ingredient undergoes at the European legislation level in order to be registered as a pesticide, the national authorization (a) ensures that each pesticide is authorized for a particular range of crops only, since not all pesticides are used on all crops (USDA United States Department of Agriculture, 2011), and (b) recommends application amounts, minimum pre-harvest intervals (PHI) for application, application frequencies and other substance-specific aspects to prevent applicants from misuse and thereby from creating additional impacts in humans and non-target organisms. These recommendations are commonly referred to as good agricultural practice (GAP) (Kroes et al., 2002) according to the definition of the FAO Food and Agriculture Organization of the United Nations (2003a).

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[2] Agri-environmental policies in the EU and in the U.S. are "examples of payments for environmental services that pay farmers to reduce the negative externalities of agricultural production, while serving as a means to transfer public funds to farmers" (Baylis et al., 2008, p. 753).

Since pesticides are used before and after harvesting crops to protect these from infestation by pests and plant diseases, a possible consequence is the presence of residues in products produced from treated crops. Hence, in addition to authorization of marketing and use of pesticides also their maximum allowed residues in drinking water and various food products are subject to European regulation to ensure that such residues are not found in food or feed at levels presenting an unacceptable risk to humans. In the EU, Regulation 396/2005/EC on maximum residue levels (MRLs) of pesticides in or on food and feed of plant and animal origin is applicable (EC European Commission, 2005b). Based on that, MRLs undergo a common EU assessment, thereby ensuring that all consumer classes, including babies, children and other vulnerable groups, are sufficiently protected.

However, since some human health effects do not show a threshold, i. e. they are assumed to be linearly related to the dose of a triggering chemical (Krewitt et al., 2002; Huijbregts et al., 2005), MRLs are on the one hand not suitable for estimating actual risks that humans face with respect to effects with lacking 'safety' levels or thresholds. In addition, food is randomly observed to ensure that residues do not exceed MRLs without any knowledge about which pesticides have been applied, at what dose and time before harvest. Finally, MRLs are based on extreme values mostly set according to lower limits of analytical detection rather than based on related risks for humans (EC European Commission, 2008a). On the other hand, a 2009 summary report from the Standing Committee on the Food Chain and Animal Health states that for 10 commonly used pesticides the existing MRLs should be lowered, because at their current levels the acceptable daily intake (ADI) for these pesticides may be exceeded (Flynn, 2011). In fact, pesticide residues exceeding official MRLs have also been reported elsewhere (PRC Pesticide Residues Committee, 2007; FAO Food and Agriculture Organization of the United Nations, 2009; Claeys et al., 2011).

These drawbacks make it difficult (a) to accurately compare existing MRLs with residues in agricultural crops that have been either measured or predicted by using modeling approaches as in the present study and (b) to allow for deriving a related potential or actual harm to human health. Scientific support is, hence, required to provide more reliable understanding of the complex behavior of pesticides in the plant-environment system finally leading to actual residues that humans are exposed to.

1.3. Problem setting of assessing pesticides

Despite the existing regulatory restrictions and despite an expensive authorization process that pushes prices up, the actual consumption and use of pesticides in the EU has not decreased over the last 15 years, although it is evident that pesticides are designed to be harmful to at least a certain range of organisms according to their intrinsic mode of action (MoA) (Coats and Yamamoto, 2003; Alavanja et al., 2004; Bassil et al., 2007; Brock et al., 2009). Moreover, the amount of food and feed samples with pesticide residues exceeding maximum regulatory limits remains constantly in the vicinity of 5% (EC European Commission, 2007a). Finally, pesticides may negatively affect human health even below existing MRLs as already discussed in the previous section.

For pesticides, generally all human exposure pathways are relevant including inhalation exposure of more volatile pesticides (Lippmann, 2009), exposure via ingestion of drinking water (EEA European Environment Agency, 1999; Li et al., 2007) as well as dermal and inhalation exposure in the context of occupational exposure e. g. during the application procedure of pesticides (Krüse and Verberk, 2008; Lu et al., 2008; Ramos et al., 2010; WHO World Health Organization, 2006). However, by far the most important exposure pathway for the general public is the ingestion of residues from consuming food crops to which the pesticides have been directly applied (Margni et al., 2002; Hamilton and Crossley, 2004). So far, human exposure towards pesticides in food products has not adequately been considered in impact assessments contributing to current European policy. In this context, Humbert et al. (2007) and Juraske et al. (2009b) demonstrated that pesticide residues in directly treated crops are of particular importance compared to inhalation and ingestion exposure caused by the pesticide fraction that is lost to beyond the field boundaries during the application process. In addition to improved analytical methods, the application of models simulating the crop-specific plant-environment system in a dynamic way is required for a better understanding of the functioning of the system and its underlying processes and parameters.

Despite the findings of Humbert et al. (2007) and Juraske et al. (2009b), no currently applied model in impact assessment of chemicals considers both pathways, ingestion exposure from residues in directly treated food crops and exposure from the pesticide fraction lost to the environment during application, which is due to the intrinsically different nature of assessing these pathways. Whereas for the latter pathway, steady state assumptions are usually sufficient, plant uptake and translocation of pesticides in directly treated crops requires a dynamic assessments (Rein et al., 2011). In addition, addressing exposure towards food crop residues introduces additional complexity due to distinct crop characteristics, which require crop-specific modeling (Trapp and Kulhanek, 2006). As a result, most impact modeling frameworks addressing a wide range of organic chemicals are on the one hand restricted to only assess exposure to the pesticide fraction lost to beyond the treated field under steady state conditions, whereas on the other hand existing crop-specific dynamic plant uptake models are restricted to assess exposure towards pesticide residues in a single food crop only. The different pathways that a pesticide undergoes after its application to a target food crop with respect to the exposure of the general public are summarized in Figure 1.1.

Regarding the scope of the individual pesticide pathways with respect to subsequent human intake, the overall applied amount is separated as follows: (a) The fraction

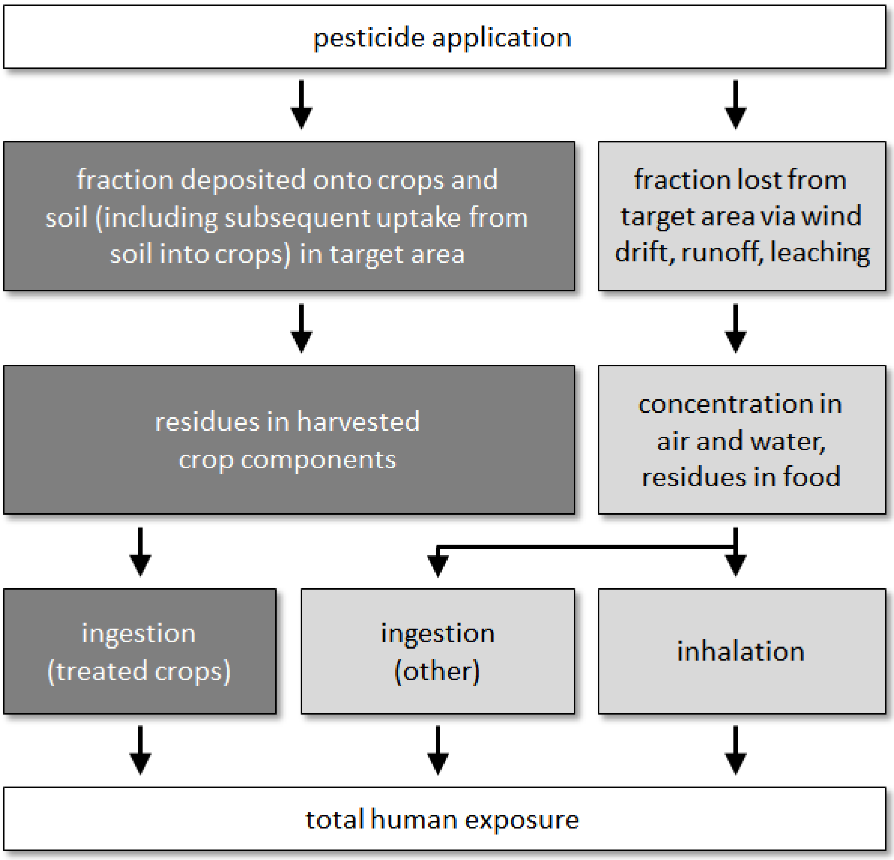

Figure 1.1.: Graphical representation of the environmental pathways that pesticides undergo from initial application to food crops until human exposure with ingestion of pesticide residues from food crop consumption as predominant human exposure pathway.

directly reaching the target crops in a defined area, such as an agricultural field, along with the fraction reaching the soil below the target crops in the same defined area are relevant for estimating pesticide residues in the target crops that humans are exposed to via consuming these crops. (b) The remaining fraction that does not deposit directly, but is lost to beyond the defined area via e. g. wind drift together with the fraction deposited onto soil that undergoes surface run off or leaching, i. e. the amount that leaves the defined area towards fresh- or groundwater, are relevant for estimating human exposure to air via inhalation and processed food grown outside the treated area via ingestion.

In spite of the wide range of available impact assessment tools, no framework adequately addresses all these human exposure pathways with respect to pesticides. Consequently, a modeling approach is required that is able to compare exposure to residues in directly treated food crops with exposure to the fraction lost to beyond the field boundaries, both initiated by the same pesticide application. In addition, the required approach needs to assess human exposure to residues in crop dynamically and must distinguish between different crop types to account for plant-specific characteristics and uptake mechanisms. Finally, the dynamic assessment tool needs to be available for spatially explicit steady state models in a way that also residues in directly treated food crops can be calculated and evaluated via linking the initial conditions of the dynamic model to the steady state assessment of spatial impact assessment tools. This can only be achieved by fully parameterizing the dynamic model into a regression that can finally be used in steady state frameworks, of which the latter need to be spatially explicit. More specifically, translocation and conversion processes in air at various spatial scales play a crucial role for the multimedia fate of most organic substances (Leip and Lammel, 2004; Shatalov et al., 2005; Lammel and Zetsch, 2007; Hollander et al., 2008) and, hence, require special attention for the air pathway. The important role of environmental media in contact with air, in particular water and soil as described in Ilyina et al. (2006); Lammel et al. (2007) and Ruzicková et al. (2007) as well as vegetation as stated in Barber et al. (2004); Schuhmacher et al. (2006) and Harmens et al. (2007) indicates the need for a special focus on exchange processes between air and other media, in particular with plants. For exchange processes with plants as well as for translocation processes within plants, in addition, species-specific characteristics play a significant role according to Trapp and Kulhanek (2006); Wang and Liu (2007) and Fan et al. (2009), which requires to embed a plant-specific assessment that covers most of the crops consumed by humans into a spatial framework to combine local dynamics in plant uptake with related spatial processes, such as volatilization of certain chemicals to air and subsequent atmospheric transport.

Environmental problems have become of economic concern due to a constantly growing population and related scarcity of natural resources like land area for cultivating food crops. Since many environmental problems can negatively influence the welfare of a society as a whole or at least the welfare of some member groups of a society (Bowles and Webster, 1995; Markandya and Tamborra, 2005), negative effects on welfare have an economically measurable value. However, many of these negative effects arising from decisions within the economic market affect members of a society not directly involved in the decision. Hence, negative externalities occur leading to social costs that are not accounted for on the related market products. More precisely, when the consumption of a food product leads to a negative effect from pesticide ingestion in a person that was not involved in the decision of applying pesticides on the corresponding food crop, such a negative externality occurs that can be expressed in terms of external or damage costs and that must be accounted for in the price of the marketed food product. Thus, assessing human exposure from relevant pathways needs to be embedded into an impact assessment also covering the valuation of health impacts by transforming the latter into monetary values.

So far, available studies on damage costs related to pesticide use disregarded exposure to residues in directly treated crops, e. g. Pimentel et al. (1992); Davison et al. (1996); Waibel and Fleischer (1998); Bailey et al. (1999); Pretty et al. (2000, 2001); Tegtmeier and Duffy (2004); Pimentel (2005); Rabl (2007) and finally Leach and Mumford (2008). By ignoring exposure towards pesticide residues in treated food crops it is likely that these studies underestimate human health damages caused by pesticide use.

In summary, no existing impact assessment approach covers the entire impact pathway including a damage cost assessment, no existing model covers all relevant pathways with respect to human exposure to pesticides, and no existing dynamic model covers all crop types relevant for human exposure to pesticide residues from food crop consumption. Hence, there is a pressing need for a consistent assessment framework that meets the requirements for addressing plant uptake of pesticides into multiple food crops, which is available as a parameterized version for use in existing spatial assessment tools to also address pesticide residues in treated food crops, and which finally allows to estimate and monetize human health impacts from pesticide use in Europe via different exposure pathways.

1.4. Scope and objectives

It is the main goal of the present study to develop a new consistent, operational modeling framework that follows the entire impact pathway from the application of currently marketed pesticides to agricultural food crops via different environmental fate and human exposure pathways to finally quantify and valuate related human health impacts at the European scale. Thereby, the specific dynamic characteristics of the ingestion exposure pathway following the uptake and translocation of pesticides in food crops will be addressed by designing a fully dynamic plant uptake model.

The dynamic modeling framework will then be parameterized for use in spatial impact assessment tools, which is a particular challenge, since on their side “most individual environmental models are not designed for interaction with other models” (Covello and Merkhoher, 1993, p. 116). In the end, both exposure pathways relevant for the general public will be fully addressed, i. e. human exposure to pesticide residues in different directly treated food crops as well as human exposure to the pesticide fractions lost to beyond field boundaries via wind drift in air, run off from soil to fresh water and leaching towards the groundwater table.

Human health effects caused by pesticide intake will in a next step be evaluated and incorporated into a transparent health impact assessment framework to finally arrive at the damage level for estimating damage costs from the application of pesticides at the European level. Finally, the overall methodology will be tested in a case study, where human health damage costs caused by the use of pesticides in different European countries will be quantified.

1.5. Outline of the present study

The present study consists of 5 main chapters starting with Chapter 1 setting the background and context, stating the problem with respect to current legislation and management of pesticide use in Europe and defining the needs and objectives of this work.

What follows in Chapter 2 is a detailed introduction into the newly developed matrix-based dynamic modeling framework termed dynamiCROP for assessing pesticide uptake into field crops and the estimation of related human exposure towards pesticide residues based upon a comprehensive review of existing state-of-the-art plant uptake modeling tools. In the same chapter, a newly introduced procedure to account for residues in multiple food crops is presented along with a method to obtain – with the help of existing steady state assessment models – human exposure via inhalation and ingestion caused by the fraction of applied pesticides that is lost to beyond the field boundaries estimated by the new dynamiCROP model. As a final step, the framework is explained how to arrive at human toxicity characterization factors as basis for estimating related pesticide health impacts for both exposure pathways and for developing pesticide substitution scenarios.

An extensive analysis of the functioning of the new dynamiCROP model system together with an assessment of sensitivities and uncertainties of input variables based on matrix-algebra and an evaluation of model output against independent experimental data are presented in Chapter 3. Based on the findings of the model analysis, evaluation and uncertainty propagation, a parameterized model version for each studied food crop is provided in the same chapter for use in spatially explicit model frameworks to be applied in the frame of health impact assessment of pesticides.

In Chapter 4, the developed methodology is applied in a case study for estimating human health impacts and related damage costs from pesticide application data in EU25 countries in 2003. After introducing the overall assessment framework to quantify damages from pesticide application based on the Impact Pathway Approach (IPA), results of the case study are described in detail, followed by a results discussion with focus on implications for policy makers and practitioners.

Finally, overall conclusions of the present study along with recommendations for future research are summarized in Chapter 5.

2. Dynamic modeling of substance uptake into field crops and assessment of health damages with focus on ingestion exposure with dynamiCROP

2.1. Summary

Impact assessments, such as life cycle impact assessment (LCIA), have been used as tools to characterize potential toxic impacts on human health and the environment attributable to pesticide use (Humbert et al., 2007; Juraske et al., 2009b; Margni et al., 2002). These assessments thereby build upon substance-specific characterization factors (CF) combining pesticide exposure and toxicity potentials to represent contributions of pesticides to overall human health and environmental impacts. Human health impacts of pesticides, however, are still poorly represented in existing approaches, since only effects from the fractions lost to beyond the considered crop field domain during and after application are considered, thereby disregarding ingestion exposure from residues in field crops to which the pesticides are directly applied.

While in case of the pesticide fractions lost from the field environmental media like air and soil serve as emission target compartments, in case of residues in target crops the cultivated food crop itself receives the applied mass. As a first attempt to account for effects caused by residues in target crops, recent studies compared measured residues with the fractions lost from the field for calculating human intake fractions (iF) in fruits and vegetables (Pennington et al., 2005; Rosenbaum et al., 2008) and concluded that ingestion of pesticide residues from consuming directly treated food crops and their products is the most important human exposure route. As a result, detailed exchange processes between environmental media and vegetation have been introduced in multimedia models designed for LCIA or other health impact assessments, traditionally considering steady-state conditions. However, for pesticide residues and related impacts, steady-state is usually not reached during the short time period from substance application to ultimate crop harvest, which is why the evolution of residues needs to be assessed dynamically (Rein et al., 2011).

By taking advantage of latest developments based on reviewing the state of the art in in crop-specific plant uptake modeling (Section 2.2), an innovative dynamic model to estimate pesticide residues in food crops, dynamiCROP, is proposed in the following. For describing plant uptake and translocation mechanisms, wheat is used as example crop for explaining all relevant pesticide fate and exposure mechanisms due to its worldwide importance with respect to human consumption (Section 2.3). The model is used to demonstrate the analysis of uptake and translocation of pesticides in wheat after foliar spray application and subsequent intake by humans. Based on the evolution of residues in edible parts of harvested wheat, it will be predicted that between 22 mg and 2.1 g per kg applied pesticide are taken in by humans via consumption of processed wheat products like bread. Model results are compared with experimentally derived concentrations of six pesticides in wheat ears. In addition, model results are compared with inhalation and ingestion intake caused by the amount lost from the field domain and estimated with the help of an existing steady state model to demonstrate the importance of considering residues in treated food crops.

As a next step, the model is adapted to include the assessment of six major crop archetypes covering a large fraction of the worldwide consumption (Section 2.4). Model estimates correspond well with observed pesticide residues for 12 substance-crop combinations, showing standard errors between a factor 1.5 and 19. To arrive at related human health impacts after exposure to pesticides, human intake fractions, effect and characterization factors are calculated for 726 substance-crop combinations and different application times (Section 2.5). Intake fractions typically range from 10^{-2} to $10^{-8}\,\mathrm{kg_{intake}\,kg_{applied}^{-1}}$. Human health impacts vary up to 9 orders of magnitude between crops and 10 orders of magnitude between pesticides, stressing the importance of considering interactions between specific crop-environments and pesticides. Time between application and harvest, degradation half-life in plants and residence time in soil are driving the evolution of pesticide masses. It will finally be demonstrated that toxicity potentials can be reduced up to 99% by defining adequate pesticide substitutions.

2.2. State of the art in plant uptake modeling of pesticides

2.2.1. Introduction and background

Wheat is the most important staple food for humans worldwide. With a production of 680 million tons in 2009 wheat contributes with 30% to the world's average crop consumption (FAO Food and Agriculture Organization of the United Nations, 2011). Furthermore, wheat is grown on more arable land than any other commercial crop (Curtis et al., 2002) with an ever increasing demand due to a continuously growing global population. Since expansion of arable land is limited, cropping intensity and crop yield must be increased (FAO Food and Agriculture Organization of the United Nations, 2003b). Pesticides are widely used to control weeds, insects, fungi and other unwanted pests potentially damaging high wheat crop yield levels and quality of wheat products (Hamilton and Crossley, 2004). However, pesticides may also reach nontarget areas and humans via wind drift, surface runoff, leaching and by-stander exposure (Felsot et al., 2010). More importantly, residues reaching wheat grains may lead to risks for humans from consumption of wheat-based food products. The general public is, hence, continuously concerned about pesticide residues in wheat and other crops (EFSA European Food Safety Authority, 2006), entailing that pesticide use is subject to steady observation.

For most wheat products, maximum residue levels of pesticides are available to ensure product safety. However, MRLs are not well suited for use in Life Cycle Assessment (LCA) or economic assessments for several reasons: (a) Food is randomly observed to ensure that residues do not exceed MRLs. Observations are usually done without knowledge whether the studied pesticide has been applied, at what dose and time before harvest. (b) MRLs are based on extreme values, whereas LCA and economic assessments require more realistic average residues to enable comparison with other averaged impacts (Pennington et al., 2006). (c) MRLs available for wheat and its processed commodities have mostly been set according to lower limits of analytical detection rather than based on related risks (EC European Commission, 2008a), thereby indicating that even levels below official MRLs may cause negative health effects due to e. g. the assumption of linear dose-response relationships for particular effects (Krewitt et al., 2002; Huijbregts et al., 2005). This complicates to derive related potential or actual harms to humans. Therefore, scientific support is required to provide better understanding of the complex behavior of pesticides in the wheat-environment system finally leading to residues that humans are exposed to (Charles et al., 2006). In this context, Humbert et al. (2007) and Juraske et al. (2009b) demonstrate that exposure towards residues in consumed food crops that were directly sprayed is particularly important compared to inhalation or ingestion exposure from pesticide amounts lost to the environment during application.

In addition to improved analytical methods, models that dynamically simulate crop-specific plant-environment systems are required to better understand system functioning, underlying processes and parameter influences. The present chapter aims at assessing the mechanistic principles of pesticide uptake into wheat after foliar spray and subsequent translocation into grains for estimating residues relevant for human consumption. To define the scope, existing models and state of the art knowledge regarding pesticide behavior in crops have been reviewed as presented in the following.

2.2.2. Review of crop-specific plant uptake models

Models have been developed to give deeper insights into specifics of plant-environment systems. In the 1990s, rather generic mathematical models emerged, mainly focusing on uptake mechanisms of organic chemicals. Some tools specialized on root uptake from soil (Behrendt et al., 1995; Matthies and Behrendt, 1995; Sicbaldi et al., 1997; Chiou et al., 2001), others on leaf uptake from air (Riederer, 1995; Trapp and Mc Farlane, 1995), and yet others on both pathways (Trapp et al., 1990; Paterson and Mackay, 1995;

Hung and Mackay, 1997). Soon, crop-specific models evolved, thereby striving towards best estimates for characterizing particular crop-environment systems. In Table 2.1, crop-specific uptake models reviewed as basis for developing the present framework are summarized.

Table 2.1.: Comparison of existing crop-specific modeling approaches for pesticide uptake into food crops from the environment.

Crops	Model specificities	Model scope	References
bean	dynamic over time; crop-specific regression for root concentration factor	assumed constant volume of plant components; no explicit fruit compartment considered; no sensitivity or uncertainty study; tested for twelve carbamates	Trapp and Pussemier (1991)
generic fruit tree	steady state; explicit thick root, fine root system (only equilibrium with soil) and fruit compartments	assumed constant soil concentration; root uptake only; no uncertainty propagation, but sensitivity study of key parameters; tested for apple, pear, plum trees; tested for seven PAHs and two dioxins on apple, pear and plum trees	Trapp et al. (2003)
apple tree	steady state; explicit thick root, fine root system (only equilibrium with soil) and fruit compartments	assumed constant soil concentration; no uncertainty propagation, but sensitivity study of key parameters; not tested against independent data	Trapp (2007)
potato and carrot	dynamic over time; explicit thick root, fine root system (only equilibrium with soil) compartments	developed for investigating PAHs, not pesticides; assumed constant soil concentration; tested in laboratory with plant tissue slices; tested for four PAHs	Trapp et al. (2007)
generic cereal	dynamic over time; first attempt of predicting residues in wheat; two compartments dynamic analysis (based on analytical matrix algebra)	requires further understanding of dynamic solution for more than two compartments; no explicit fruit compartment considered; no consecutive transfer from soil via root to stem; tested for six substances on wheat	Charles (2004)

(continued on next page)

Table 2.1 (continued)

Crops	Model specificities	Model scope	References
tomato	dynamic over time; explicit fruit compartment	no explicit thick root compartment considered; no root uptake from soil considered; explicit solution only for fruit compartment; no sensitivity or uncertainty analysis; tested for substance captan	Juraske et al. (2007)
tomato	dynamic over time; explicit thick root and fruit compartments	no leave uptake from air considered in root model (leave model see Juraske et al., 2007); no sensitivity or uncertainty analysis; tested for substance imidacloprid	Juraske et al. (2009a)
potato	dynamic over time; explicit stem tuber compartment; time-dependent soil migration	no leave uptake from air considered; no sensitivity or uncertainty analysis; tested for substance chlorpyrifos	Juraske et al. (2011)
wheat and carrot	dynamic over time and steady state; explicit fruit compartment; multi-cascade model to simulate multiple applications and background concentrations	no explicit air compartment considered; analytical solution limited to unidirectional transfers, i. e. no backflows allowed; no uncertainty propagation, but sensitivity study of key parameters; not tested against independent data	Rein et al. (2011)
sweet pepper	dynamic over time; explicit fruit compartment; multi-cascade model to simulate multiple applications	no explicit air compartment considered; no deposition from air considered (neglected); analytical solution limited to unidirectional transfers, i. e. no backflows allowed; sensitivity study of key parameters; tested for substance methomyl	Legind et al. (2011)

(continued on next page)

Table 2.1 (continued)

Crops	Model specificities	Model scope	References
soybean and spinach	dynamic over time; explicit fruit compartment	no root uptake from soil considered; exposed water solution as source medium, thus, no consecutive transfer from air via leaves, stem to fruits; no sensitivity or uncertainty analysis; tested for six substances	Fujisawa et al. (2002a)
radish	dynamic over time; explicit root hairs, peel and core compartments	exposed water solution as source medium; no sensitivity or uncertainty analysis; tested for substances furametpyr and pyriproxifen	Fujisawa et al. (2002b)
mango tree	dynamic over time; explicit fruit compartment	no consecutive transfer from soil via root to stem; no sensitivity or uncertainty analysis; tested for substance paclobutrazol	Paraíba (2007)
rice	dynamic over time; based on fugacities	no distinction between different plant components (single compartment representing whole plant); no sensitivity or uncertainty analysis; tested for substance carbofuran	Paraíba et al. (2007); Contreras et al. (2008)
potato	dynamic over time; explicit thick root compartment	no advection into plant due to transpiration considered; no explicit leaf compartment considered; no sensitivity or uncertainty analysis; not tested against independent data	Paraíba and Kataguiri (2008)

An early crop-specific model was designed for root uptake into beans by Trapp and Pussemier (1991), using correlation factors between concentrations in different compartments. Trapp and co-authors further formulated generalized models (Trapp and Mc Farlane, 1995; Trapp et al., 2003), before crop-specific approaches followed for apple trees (Trapp, 2007) and potatoes/carrots (Trapp et al., 2007). Findings from Trapp et al. (2007) regarding uptake and transfer through roots and tubers are considered in a recent potato model from Juraske et al. (2011). Charles (2004), in contrast, focuses on atmospheric deposition onto leaves for modeling pesticide translocation in cereals. The mass balance is solved with matrix algebra and includes plant surface deposit as compartment for specifically modeling transport through cuticles, which is considered an important uptake pathway (Schreiber and Schönherr, 2009). However, Charles' approach is limited with respect to descriptions of roots and transfers into grains. Considering the relevance of degradation, for which we assume first order kinetics in line with e. g. Boesten et al. (2006), Juraske et al. (2008) and Thomas et al. (2011) provide relationships to extrapolate degradation half-lives in plant tissue and on plant surfaces as a function of degradation in soil. These relationships are tested by Juraske et al. (2009a) for pesticide uptake into tomatoes. Fujisawa et al. (2002a) build their leaf uptake model on a generic single compartment system from Trapp and Mc Farlane (1995) and designed it for uptake into soybeans and spinach. Paraíba and co-authors developed models for uptake into mango trees (Paraíba, 2007), potatoes (Paraíba and Kataguiri, 2008) and rice (Contreras et al., 2008), of which models for mango tree and potato build upon concepts by Trapp et al. (2003) for fruit trees and Trapp et al. (2007) for potatoes/carrots, respectively. The model by Contreras et al. (2008) is based on fugacities, which is not in line with most other reviewed approaches. In contrast to exponential growth assumed in all other reviewed models, Rein et al. (2011) and Legind et al. (2011) introduce logistic plant growth in their matrix-based frameworks along with considering multiple substance applications. Whereas Legind et al. (2011) focus on sweet pepper, Rein et al. (2011) assess uptake of an industrial solvent into wheat from foliar application and into carrot from soil as constant source. In both studies, soil, roots, stem, leaves and fruits are considered as compartments. However, air as explicit compartment and feedback from backflow, reverse or bidirectional processes are omitted in support of a diagonalized system that is solved analytically.

All in all, no reviewed crop-specific uptake model accounts for all compartments, pathways and characteristics considered relevant in the present study for assessing pesticide uptake into wheat. Whereas models by Trapp and co-authors are not designed for direct pesticide spray, models by Charles and Juraske focus on the dynamics after spray application. However, Charles (2004) does not cover all relevant wheat components, most importantly the protected grain. Wheat grains are included in Rein et al. (2011), but air and plant surface deposit for addressing bidirectional plant-atmosphere exchange are unconsidered. Moreover, the intermittent character of rain affecting deposition processes is not addressed by any reviewed study. Thus, an innovative and appropriate approach for predicting residues of neutral organic pesticides in wheat is newly developed in the present study. Thereby, it will be taken advantage of latest developments on (a) root and stem modeling by Trapp (2007) and Trapp et al. (2007), (b) extrapolated degradation half-lives from Juraske et al. (2008) and Thomas et al. (2011), wherever half-lives in wheat are not available, (c) the initial crop model from Charles (2004) including plant surface deposit compartments for plant-atmosphere exchange, and (d) logistic wheat growth as well as an explicitly considered wheat grain compartment from Rein et al. (2011). Additionally, the transfer through a hull protecting the wheat grain, a more complex growth function for wheat leaves, and the intermittent character of rain described by Jolliet and Hauschild (2005) as influencing atmospheric deposition is newly introduced.

The next section focuses on three specific aims. (1) Describing the system's compartmental setup including considered physical processes. (2) Analyzing relations describing exchange between individual wheat components, including a consistent approach for modeling pesticide transfer into roots, leaf and grain surface deposits, and the subsequent transfer to wheat grains. (3) Comparing model results with measured residues in wheat and modeled intake from losses to beyond the field boundaries.

2.3. Modeling framework for assessing pesticide uptake into wheat

2.3.1. Introduction and background

Exposure towards pesticides occurs from the consumption of crops containing residues from the sprayed amount that directly reaches the target, or from the inhalation and ingestion of the factions lost via air and soil towards outside the target field. For assessing human health impacts caused by pesticides directly sprayed onto wheat, the Impact Pathway Approach according to Bickel et al. (2005) is followed. This bottom-up analysis pursues a pesticides' pathway from application via environmental transport to exposure and finally impacts on humans, thereby linking substance releases to health impacts. First, the system is described by means of a consistent approach of rate coefficients characterizing pesticide translocation and dissipation within and between compartments, followed by describing underlying physical processes and plant growth. Further, the subsequent exposure assessment is described and the experimental setup used for evaluating modeled residues in wheat. Finally, an example of how the model is applied to six pesticides is given and results are compared with experimental data and results for other exposure pathways.

2.3.2. Compartmental system and mass balance

The multimedia plant uptake model setup for wheat is shown in Figure 2.1 with environmental compartments (atmospheric ground layer, root-zone soil layer) and vegetation compartments (leaf and fruit surface deposit, leaf, fruit, stem, and thick root). Since protected grains are explicitly taken into account for substance accumulation, model output can directly be compared with measured pesticide residues. Depending on application technique (foliar spray, soil application, etc.), atmospheric ground layer, root-zone soil layer and leaf/fruit surface deposit are compartments potentially receiving a fraction of

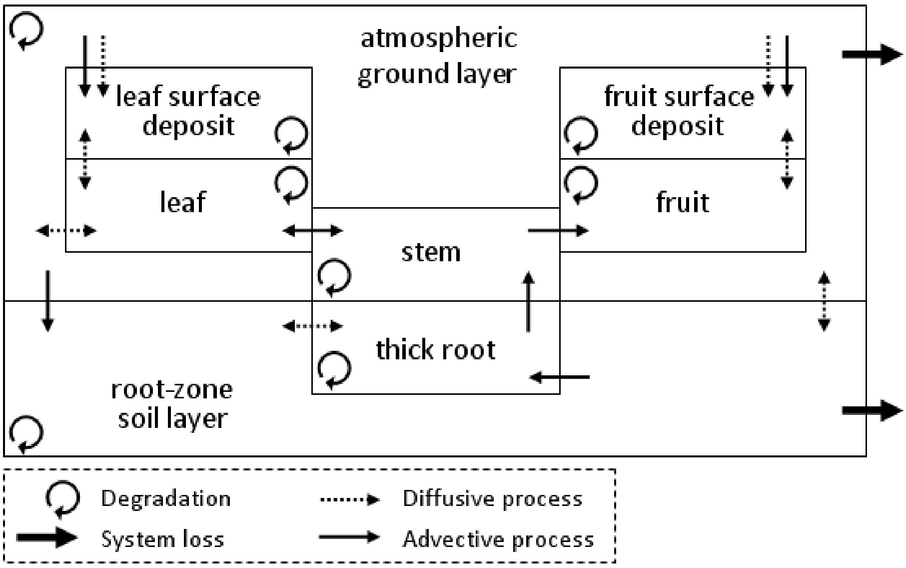

Figure 2.1.: Graphical representation of model setup consisting of environmental compartments (atmospheric ground layer, root-zone soil layer), wheat crop components (leaf and fruit surface deposit, leaf, fruit, stem, and thick root) and processes within/between compartments.

applied pesticides, thereby defining initial mass distribution. Pesticides can bioaccumulate in each compartment as a function of initial mass distribution and plant-internal translocation processes via xylem and phloem. When sprayed onto wheat, three components are directly exposed, namely leaves, grains and stem, while the fraction reaching the soil can be taken up through roots. Environmental compartments and their characteristics are considered to remain constant, whereas plant components evolve over time. Substance transformation within and translocation between compartments is described using first-order rate coefficients, which aggregate underlying physical processes including degradation, diffusive and advective transfers. All considered physical processes are given in Table 2.2.

Table 2.2.: Intramedia dissipation and intermedia mass transfer processes considered in dynamiCROP (including system losses, i. e. transport beyond the model domain).[a]

Compartment/Interface	Physical process(es)
all compartments	– bulk degradation
atmospheric ground layer	– advection (wind drift; system loss)

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Table 2.2 (continued)

Compartment/Interface	Physical process(es)
atmospheric ground layer – root-zone soil layer/paddy water layer	– diffusion (dry gas deposition) – dry particle/wet gas/particle deposition – volatilization
atmospheric ground layer – leaf/fruit surface deposit	– diffusion (dry gas deposition) – dry particle/wet gas/particle deposition – volatilization
atmospheric ground layer – leaf interior	– diffusion through stomata
root-zone soil layer – paddy water layer	– diffusion – sedimentation – adsorption – resuspension
root-zone soil layer – (surface) water	– run off (system loss)
root-zone soil layer – sub-surface soil layer	– leaching (system loss)
root-zone soil layer – thick root	– diffusion – advection (from soil to thick root)
paddy water layer – (surface) water	– advection (outflow; system loss)
paddy water layer – stem	– diffusion
leaf/fruit surface deposit – leaf interior	– diffusion
leaf interior – stem	– advection via phloem
fruit interior – stem	– advection via xylem (from stem to fruit)
stem – thick root	– advection via xylem and phloem

[a] The described processes go beyond the domain of modeling wheat and cover the full list of considered processes for all crops described in Section 2.4. Processes not considered are washoff and volatilization from vegetation surface as well as advection from stem towards roots via phloem, since these processes are considered negligible (see main text).

Rate coefficients form the basis for analytically solving the system's mass balance by means of matrix algebra. All coefficients describing intermedia transport and loss from the model domain are formulated in Table 2.3. Note that also processes are listed that are not relevant for wheat, but for other crops considered in the subsequent section discussing the extension of the dynamiCROP model to assess pesticide uptake into multiple crop types (see Section 2.4).

Table 2.3.: Rate coefficients for intermedia mass transfer processes (including system losses, i. e. processes towards compartments not included in the model domain) considered in dynamiCROP as input for the matrix of transfer rate coefficients as shown in Figure 2.2. All processes are further described in Appendix A and underling input data are given in Appendix B.

Transfer rate	Equation of rate coefficient [d^{-1}]	Equation
Atmospheric ground layer to root-zone soil layer/paddy water layer	$k_{\mathrm{ts/pw}\leftarrow\mathrm{a}} = \left(k_{\mathrm{a,dep,dry}} + \Delta k_{\mathrm{a,dep,wet,int}}\right) \cdot \mathrm{e}^{-(\mathrm{LAI}+\mathrm{FAI})\cdot c_{\mathrm{cap}}}$	A.20
Atmospheric ground layer to vegetation leaf surface deposit	$k_{\mathrm{vld}\leftarrow\mathrm{a}} = \left(k_{\mathrm{a,dep,dry}} + \Delta k_{\mathrm{a,dep,wet,int}}\right) \cdot \left(1 - \mathrm{e}^{\mathrm{LAI}\cdot c_{\mathrm{cap}}}\right)$	A.20
Atmospheric ground layer to vegetation fruit surface deposit	$k_{\mathrm{vfd}\leftarrow\mathrm{a}} = \left(k_{\mathrm{a,dep,dry}} + \Delta k_{\mathrm{a,dep,wet,int}}\right) \cdot \left(1 - \mathrm{e}^{\mathrm{FAI}\cdot c_{\mathrm{cap}}}\right)$	A.20
Atmospheric ground layer to vegetation leaf (interior)	$k_{\mathrm{vl}\leftarrow\mathrm{a}} = \frac{A_{\mathrm{vl}}\cdot\varphi_{\mathrm{a/vl}}}{K_{\mathrm{a/w}}\cdot V_{\mathrm{a}}}$	A.26
Root-zone soil layer to atmospheric ground layer	$k_{\mathrm{a}\leftarrow\mathrm{ts}} = \frac{A_{\mathrm{ts}}\cdot fc_{\mathrm{L\,to\,m^3}}\cdot\varphi_{\mathrm{a/ts}}}{K_{\mathrm{ts/a}}\cdot M_{\mathrm{ts}}}$	A.29
Root-zone soil layer to freshwater body	$k_{\mathrm{fb}\leftarrow\mathrm{ts}} = \frac{(fc_{\mathrm{ts,paq}}+fc_{\mathrm{ts,ps}}\cdot \mathit{fr\_M}_{\mathrm{ts,run,ps}})\cdot p_{\mathrm{rain}}\cdot \mathit{fr\_p}_{\mathrm{rain,run}}}{h_{\mathrm{ts}}}$	A.34
Root-zone soil layer to saturated subsoil (groundwater layer)	$k_{\mathrm{us}\leftarrow\mathrm{ts}} = \frac{fc_{\mathrm{ts,paq}}\cdot\left(p_{\mathrm{rain}}\cdot \mathit{fr\_p}_{\mathrm{rain,leach}}\cdot \mathit{fr\_V}_{\mathrm{ts,paq}}-\varphi_{\mathrm{ts}}\right)}{h_{\mathrm{ts}}}$	A.37
Root-zone soil layer to paddy water layer	$k_{\mathrm{pw}\leftarrow\mathrm{ts}} = \frac{A_{\mathrm{pw}}\cdot\left(p_{\mathrm{ts,resus}}+\varphi_{\mathrm{ts,diff}}\right)}{V_{\mathrm{ts}}}$	A.39
Root-zone soil layer to vegetation thick root	$k_{\mathrm{vr}\leftarrow\mathrm{ts}} = \frac{\left(A_{\mathrm{vr}}\cdot fc_{\mathrm{L\,to\,m^3}}\cdot\varphi_{\mathrm{vr}}+Q_{\mathrm{xyl}}\right)\cdot K_{\mathrm{w/ts}}}{M_{\mathrm{ts}}}$	A.44

(continued on next page)

Table 2.3 (continued)

Transfer rate	Equation of rate coefficient [d^{-1}]	Equation
Root-zone soil layer to root crop thick root	$k_{\mathrm{vr}\leftarrow\mathrm{ts}} = \frac{fc_{\mathrm{D,vr,tis}} \cdot D_{\mathrm{vr,tis}} \cdot M_{\mathrm{vr}}}{{r_{\mathrm{vr}}}^2 \cdot \rho_{\mathrm{vr}} \cdot K_{\mathrm{ts/w}} \cdot M_{\mathrm{ts}}}$	A.46
Paddy water layer to atmospheric ground layer	$k_{\mathrm{a}\leftarrow\mathrm{pw}} = \frac{A_{\mathrm{a}} \cdot fr\_m_{\mathrm{pw,paq}} \cdot \varphi_{\mathrm{a/pw}}}{V_{\mathrm{pw}}}$	A.47
Paddy water layer to freshwater body	$k_{\mathrm{fb}\leftarrow\mathrm{pw}} = \frac{p_{\mathrm{pw,fb}}}{h_{\mathrm{pw}}}$	A.51
Paddy water layer to root-zone soil layer	$k_{\mathrm{ts}\leftarrow\mathrm{pw}} = \frac{A_{\mathrm{ts}} \cdot \left(p_{\mathrm{pw,ps}} \cdot fr\_m_{\mathrm{pw,ps}} + p_{\mathrm{pw,ts}} + \varphi_{\mathrm{pw/ts,paq}} \cdot (1 - fr\_m_{\mathrm{pw,ps}})\right)}{V_{\mathrm{pw}}}$	A.52
Paddy water layer to vegetation stem	$k_{\mathrm{vs}\leftarrow\mathrm{pw}} = \frac{A_{\mathrm{vs,pw}} \cdot \varphi_{\mathrm{vs,pw}}}{V_{\mathrm{pw}}}$	A.54
Vegetation leaf surface deposit to vegetation leaf (interior)	$k_{\mathrm{vl}\leftarrow\mathrm{vld}} = \frac{A_{\mathrm{vl}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{vld}}} = k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}}$	A.55
Vegetation fruit surface deposit to vegetation fruit (interior)	$k_{\mathrm{vf}\leftarrow\mathrm{led}} = \left(\frac{2}{k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}}} + \frac{K_{\mathrm{lem/cut}} \cdot M_{\mathrm{lem}}}{A_{\mathrm{lem}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}}\right)^{-1}$	A.60
Vegetation leaf (interior) to atmospheric ground layer	$k_{\mathrm{a}\leftarrow\mathrm{vl}} = \frac{A_{\mathrm{vl}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{a/vl}} \cdot K_{\mathrm{a/w}}}{K_{\mathrm{vl/w}} \cdot M_{\mathrm{vl}}}$	A.61
Vegetation leaf (interior) to vegetation leaf surface deposit	$k_{\mathrm{vld}\leftarrow\mathrm{vl}} = \frac{A_{\mathrm{vl}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}}{K_{\mathrm{vl/cut}} \cdot M_{\mathrm{vl}}}$	A.65
Vegetation leaf (interior) to vegetation stem	$k_{\mathrm{vs}\leftarrow\mathrm{vl}} = \frac{Q_{\mathrm{vf,phlo}}}{K_{\mathrm{vl/w}} \cdot M_{\mathrm{vl}}}$	A.67
Vegetation fruit (interior) to vegetation fruit surface deposit	$k_{\mathrm{led}\leftarrow\mathrm{vf}} = \left(\frac{K_{\mathrm{vf/cut}} \cdot (M_{\mathrm{vf}} + M_{\mathrm{lem}})}{A_{\mathrm{vf}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}} + \frac{1}{k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}}}\right)^{-1}$	A.69
Vegetation stem to paddy water layer	$k_{\mathrm{pw}\leftarrow\mathrm{vs}} = \frac{A_{\mathrm{vs,pw}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{vs,ps}}}{K_{\mathrm{vs/w}} \cdot M_{\mathrm{vs}}}$	A.70
Vegetation stem to vegetation leaf (interior)	$k_{\mathrm{vl}\leftarrow\mathrm{vs}} = \frac{Q_{\mathrm{vl,xyl}}}{K_{\mathrm{vs/w}} \cdot M_{\mathrm{vs}}}$	A.75

(continued on next page)

Table 2.3 (continued)

Transfer rate	Equation of rate coefficient [d^{-1}]	Equation
Vegetation stem to vegetation fruit (interior)	$k_{\mathrm{vf}\leftarrow\mathrm{vs}} = \frac{Q_{\mathrm{vf,xyl}}+Q_{\mathrm{vf,phlo}}}{K_{\mathrm{vs/w}}\cdot M_{\mathrm{vs}}}$	A.80
Vegetation thick root to root-zone soil layer	$k_{\mathrm{ts}\leftarrow\mathrm{vr}} = \frac{A_{\mathrm{vr}}\cdot fc_{\mathrm{L\,to\,m^3}}\cdot\varphi_{\mathrm{vr}}}{K_{\mathrm{vr/w}}\cdot M_{\mathrm{vr}}}$	A.82
Root crop root to root-zone soil layer	$k_{\mathrm{ts}\leftarrow\mathrm{vr}} = \frac{fc_{\mathrm{D,vr,tis}}\cdot D_{\mathrm{vr,tis}}\cdot M_{\mathrm{ts}}}{r_{\mathrm{vr}}{}^2\cdot\rho_{\mathrm{w}}\cdot K_{\mathrm{vr/w}}\cdot M_{\mathrm{vr}}}$	A.88
Vegetation thick root to vegetation stem	$k_{\mathrm{vs}\leftarrow\mathrm{vr}} = \frac{Q_{\mathrm{xyl}}}{K_{\mathrm{vr/w}}\cdot M_{\mathrm{vr}}}$	A.89

Where A area [m^2]; LAI and FAI area index of vegetation leaf and fruit, respectively [m^2 m^{-2}]; c_{cap} substance capture coefficient [–]; $fc_{\mathrm{D,vr,tis}}$ correction factor for radial diffusion model [–]; $fc_{\mathrm{L\,to\,m^3}}$ conversion factor of 1,000 L per 1 m^3; fc_{paq} correction factor between aqueous and bulk phase of compartments [L·L^{-1}]; fc_{ps} correction factor between solid and bulk phase of compartments [L·L^{-1}]; *fr_M* mass of compartment or phase related fraction [kg·kg^{-1}]; *fr_m* mass of substance in compartment or phase related fraction [kg·kg^{-1}]; *fr_p* advection velocity related fraction [m·d^{-1} per m·d^{-1}]; *fr_V* volume related fraction [m^3·m^{-3}]; h vertical dimension (height or depths) [m]; k rate coefficient [d^{-1}]; Δk equivalent rate coefficient [d^{-1}]; K partition coefficient [kg·m^{-3} per kg·m^{-3}, kg·kg^{-1} per kg·L^{-1}, kg·kg^{-1} per L·kg^{-1}, or kg·kg^{-1} per kg·m^{-3}]; M mass of compartment or phase [kg]; p advection process velocity [m·d^{-1}]; φ diffusion process velocity [m·d^{-1}]; Q volume related flow rate [L·d^{-1}]; r mean radius [m]; V volume [m^3].

Indices: a, fb, pw, ts, us, vf, vl, vld, vr, vs, w denote the compartments atmospheric ground layer, freshwater body, paddy water layer, root-zone soil layer, saturated subsoil layer, vegetation fruit, leaf, leaf surface deposit, thick root, stem, and water; cut, cuw, led, lem, paq, ps denote the compartment phases/components cuticle, cuticle wax, fruit lemma deposit, fruit lemma, aqueous phase and solid phase; dep, dry, int, leach, phlo, rain, resus, run, wet, xyl denote processes related to deposition, dry deposition, intermittent or interval periods, leaching, phloem flow, rain, resuspension, run off, wet deposition and xylem flow, respectively. A complete list of indices is found in the Appendix (Section B.3).

When assuming pulse inputs from single pesticide applications, one mathematically arrives at a homogeneous system consisting of n compartments potentially receiving substance masses from adjacent compartments and atmospheric ground layer, root-zone soil layer, leaf and fruit surface deposit as source compartments potentially receiving a fraction of initially applied substance. System dynamics are described by an $n \times n$ matrix $\mathbf{K}$ with line and column indices indicating receiving and source compartments, respectively. The mass balance is described by a set of ordinary first-order linear differential equations that is expressed in vector-matrix notation:

$$\frac{\mathrm{d}\vec{m}(t)}{\mathrm{d}t} = \mathbf{K}\,\vec{m}(t) \tag{2.1}$$

where $\vec{m} \in \mathbb{R}^n$ [kg] is the vector of substance masses in compartments, t [d] is time, and $\mathbf{K} \in \mathbb{R}^{n \times n}$ is the square matrix containing first-order rate coefficients k [d^{-1}]. Each off-diagonal element of $\mathbf{K}$, i.e. $k_{i \leftarrow j}$ with $i \neq j,\ i, j \in \{1, \ldots, n\}$, contains a single transfer rate coefficient from compartment j to compartment i. In contrast, each main diagonal element $k_{i \leftarrow j}$ with $i = j,\ i, j \in \{1, \ldots, n\}$, contains the bulk removal rate coefficient in compartment i, $k_{i,\text{loss}}$, plus the sum of transfer rate coefficients from compartment i to adjacent compartments j. Bulk removal refers to the sum of degradation and advective losses from the system domain. For any compartment $i \in \{1, \ldots, n\}$, the differential equation, hence, reads:

$$\frac{\mathrm{d}m_i(t)}{\mathrm{d}t} = -\left(k_{i,\text{loss}} + \sum_{l=1,\, l \neq i}^{n} k_{l \leftarrow i}\right) m_i(t) + \sum_{j=1,\, j \neq i}^{n} k_{i \leftarrow j} m_j(t) \tag{2.2}$$

In the wheat system, the number of compartments equals $n = 8$ with the related populated K matrix presented in Figure 2.2.

$$\begin{array}{c|cc|cccccc|}
 & \text{a} & \text{ts} & \text{vld} & \text{vlf} & \text{vl} & \text{vf} & \text{vs} & \text{vr} \\
\hline
\text{a} & -k_{\text{a}} & k_{\text{a}\leftarrow\text{ts}} & & & k_{\text{a}\leftarrow\text{vl}} & & & \\
\text{ts} & k_{\text{ts}\leftarrow\text{a}} & -k_{\text{ts}} & & & & & & k_{\text{ts}\leftarrow\text{vr}} \\
\hline
\text{vld} & k_{\text{vld}\leftarrow\text{a}} & & -k_{\text{vld}} & & k_{\text{vld}\leftarrow\text{vl}} & & & \\
\text{vfd} & k_{\text{vfd}\leftarrow\text{a}} & & & -k_{\text{vfd}} & & k_{\text{vfd}\leftarrow\text{vf}} & & \\
\text{vl} & k_{\text{vl}\leftarrow\text{a}} & & k_{\text{vl}\leftarrow\text{vld}} & & -k_{\text{vl}} & & k_{\text{vl}\leftarrow\text{vs}} & \\
\text{vf} & & & & k_{\text{vf}\leftarrow\text{vfd}} & & -k_{\text{vf}} & k_{\text{vf}\leftarrow\text{vs}} & \\
\text{vs} & & & & & k_{\text{vs}\leftarrow\text{vl}} & & -k_{\text{vs}} & k_{\text{vs}\leftarrow\text{vr}} \\
\text{vr} & & k_{\text{vr}\leftarrow\text{ts}} & & & & & & -k_{\text{vr}} \\
\hline
\end{array}$$

Figure 2.2.: Matrix of constant transfer rate coefficients as derived from the underlying physical processes. Column (input/source) and row (receiving) compartments are described as follows: a (atmospheric ground layer), ts (root-zone soil layer), vld and vfd (vegetation leaf and fruit surface deposits), vl and vf (vegetation leaf and fruit interior), vs (vegetation stem) and vr (vegetation thick root). Coefficients are described in the text.

Analytical matrix algebra is applied to solve the system of differential equations. The common solution of the system in Eq. 2.1 for direct pesticide application, i.e. pulse release with $\vec{m}_0 = \vec{m}(0)$ for $t = 0$, builds upon the matrix exponential of $\mathbf{K}$:

$$\vec{m}(t) = \mathrm{e}^{\mathbf{K}t}\, \vec{m}(0) \tag{2.3}$$

Matrix exponentials are obtained by using Matlab functionality called from the spreadsheet via Visual Basic for Applications (VBA). A full description of the steps involved in solving the mass balance is given in Section 3.2.

2.3.3. Plant growth

Wheat development can be accounted for by a logistic growth function with initial exponential part and slackening growth towards crop ripening (Patil et al., 2010). Logistic growth is applied for root, stem, and grains according to Rein et al. (2011), from which the wheat mass $M(t)$ [kg] at time t [d] is derived:

$$M(t) = \frac{M_{\max}}{1 + \frac{M_{\max} - M_0}{M_0} \times \mathrm{e}^{-k_{\text{wheat}} \times t}} \tag{2.4}$$

where $M_{\max}$ [kg] is the maximum mass, $M_0 \in [0, M_{\max}]$ [kg] is the initial mass and k_{wheat} [d^{-1}] is the logistic growth rate coefficient. To consider the effect of growth dilution, Eq. 2.4 is directly solved for k_{wheat} with $0 < M_0$, $M(t) \leq M_{\max}$:

$$k_{\text{wheat}} = \frac{\ln\left(\frac{M(t)}{M_0}\right) - \ln\left(\frac{M_{\max} - M(t)}{M_{\max} - M_0}\right)}{t} \tag{2.5}$$

The interdependency between k_{wheat} and $M_{\max}$ in Eq. 2.4 requires fitting both parameters simultaneously based on measured masses for at least three different days after plant emergence. Wheat masses measured by Cao (2001) per unit area of $1\,\mathrm{m}^2$ at days 0, 140 and 169 of respectively 0.15, 1.14 and 1.36 kg yield values for $M_{\max} = 1.75\,\mathrm{kg}$ and $k_{\text{wheat}} = 0.021\,\mathrm{d}^{-1}$. Wheat leaves do not follow logistic growth (Patil et al., 2010). In contrast, leaf growth is described by a curve obtained from the development of leaf area index LAI [$\mathrm{m}^2\,\mathrm{m}^{-2}$]. Wheat LAI shows exponential increase at the beginning and exponential decrease at the end of a plant's life cycle. LAI development was fitted based on measured values for winter wheat under temperate seasonal climate and loess soil conditions by Lenz (2007). The corresponding growth curve of LAI(t) as a function of time t [d] after crop emergence reads:

$$\mathrm{LAI}(t) = -0.0015 \times t^2 + 0.34 \times t - 13.8 \tag{2.6}$$

2.3.4. Environmental fate processes

An overview of the conceptual framework behind the rate coefficients presented in Table 2.3 and Figure 2.2 is given in the following, whereas detailed information regarding the specific rate coefficients as applied in the present work is given in Appendices A and B.

Initial capture and distribution

Physical processes behind rate coefficients in Eq. 2.2 are described in the following. From pesticide foliar application initial distributions between compartments are defined, i. e. initial mass conditions at time $t = 0$. According to Hauschild (2000) and Juraske et al. (2007), considered losses via wind drift and deposition onto plant surface and soil must sum up to 100% applied mass fr_m_{applied} [$\mathrm{kg\,kg^{-1}}$]. Consequently, the fraction reaching wheat $fr\_m_{\mathrm{dep,wheat}}$ [$\mathrm{kg\,kg^{-1}}$] is obtained as:

$$fr\_m_{\mathrm{dep,wheat}} = fr\_m_{\mathrm{applied}} - (fr\_m_{\mathrm{drift,air}} + fr\_m_{\mathrm{dep,soil}}) \tag{2.7}$$

where $fr\_m_{\mathrm{dep,wheat}}$ exclusively refers to leaf surface, if pesticides are applied before grain emergence. Overall fractions lost to air $fr\_m_{\mathrm{drift,air}}$ [$\mathrm{kg\,kg^{-1}}$] are fixed to 16.5% and refer to 10% volatilization from plant surface (Charles, 2004) and 6.5% wind drift for foliar spray application according to reported values for field crops by van de Zande et al. (2007). Based on wheat growth stage and capture efficacy, fractions reaching the soil via deposition $fr\_m_{\mathrm{dep,soil}}$ [$\mathrm{kg\,kg^{-1}}$] are described as:

$$fr\_m_{\mathrm{dep,soil}} = \begin{cases} \mathrm{e}^{-c_{\mathrm{cap}} \times (\mathrm{LAI} + \mathrm{FAI})} & \text{for } t_{\mathrm{vf}} \leq t_{\mathrm{app}} \\ \mathrm{e}^{-c_{\mathrm{cap}} \times \mathrm{LAI}} & \text{for } t_{\mathrm{vf}} > t_{\mathrm{app}} \end{cases} \tag{2.8}$$

where c_{cap} [$\mathrm{kg\,m^{-2}}$ per $\mathrm{kg\,m^{-2}}$] is the substance capture coefficient, LAI [$\mathrm{m^2_{leaf}\,m^{-2}_{soil}}$] is leaf area index and FAI [$\mathrm{m^2_{fruit}\,m^{-2}_{soil}}$] is fruit area index. Two cases are distinguished: (i) Pesticides are applied before grains evolve, i. e. time between plant emergence and grain appearance t_{vf} [d] is smaller or equal to time from plant emergence to pesticide application t_{app} [d]. (ii) Pesticides are applied after grains evolve, i. e. $t_{\mathrm{vf}} > t_{\mathrm{app}}$. In Eq. 2.8, values for LAI and FAI depend on the plant life cycle with the FAI curve following logistic growth of wheat grains and the LAI curve following a quadratic growth function as described above.

Degradation

After application, pesticides are considered to undergo degradation in all compartments. Photochemical oxidation, photolysis, hydrolysis and metabolism may all contribute to overall degradation. However, data describing such contributions are rarely, if at all, available for pesticides. They can instead be summed up to a bulk degradation rate coefficient k_{deg} [$\mathrm{d^{-1}}$] as a function of the degradation half-life $t_{1/2}$ [d] in the respective compartment according to $k_{\mathrm{deg}} = \ln(2)/t_{1/2}$, i. e. assuming first order kinetics in line with e. g. Boesten et al. (2006).

Diffusive transfer across boundaries

Diffusion describing mass exchange across compartment boundaries is based on Fick's first law of diffusion postulating mass flux from high to low concentrations proportional to the concentration gradient (Fick, 1995). Transfer rate coefficients from compartment i to j, $k_{j\leftarrow i,\mathrm{diff}}$ [d^{-1}], are calculated accordingly:

$$k_{j\leftarrow i,\mathrm{diff}} = -\frac{A_{ij}}{V_i} \times \frac{D}{\Delta l} \times K_{ij} \tag{2.9}$$

where A [m^2] is the compartments' exchange area, V [m^3] is the volume, D [$\mathrm{m}^2\,\mathrm{d}^{-1}$] is the diffusion coefficient, Δl [m] is the boundary diffusion path length, and $K_{ij} = K_{i\mathrm{w}}/K_{j\mathrm{w}}$ [$\mathrm{L\,kg}^{-1}$] is the quotient of partition coefficients between compartments i, j and water. The ratio $D/\Delta l$ is commonly referred to as conductance, φ [$\mathrm{m\,d}^{-1}$], permeability, or diffusion velocity, depending on the context (Trapp, 2007). Partition coefficients between wheat compartments i and water $K_{i\mathrm{w}}$ [$\mathrm{L\,kg}^{-1}$] are calculated as a function of compartment phase composition (Trapp and Mc Farlane, 1995):

$$K_{i\mathrm{w}} = \left(\mathit{fr\_V}_{i,\mathrm{paq}} + \mathit{fr\_V}_{i,\mathrm{pli}} \times \frac{\rho_{\mathrm{water}}}{\rho_{\mathrm{octanol}}} \times K_{\mathrm{ow}}{}^{\mathit{fc}} \right) \times \frac{\rho_i}{\rho_{\mathrm{water}}} \tag{2.10}$$

where $\mathit{fr\_V}_{i,\mathrm{paq}}$ [$\mathrm{L\,kg}^{-1}$] is the volumetric water fraction, $\mathit{fr\_V}_{i,\mathrm{pli}}$ [$\mathrm{L\,kg}^{-1}$] is the volumetric lipid fraction, ρ [$\mathrm{kg\,L}^{-1}$] is the density of compartment i, water or n-octanol, and K_{ow} [$\mathrm{kg\,m}^{-3}$ per $\mathrm{kg\,m}^{-3}$] is the octanol-water partition coefficient. Ratio $\rho_{\mathrm{water}}/\rho_{\mathrm{octanol}} = 1.22$ corrects for different densities between water and n-octanol. Dimensionless exponents $\mathit{fc} = 0.77$ for limiting uptake into roots and $\mathit{fc} = 0.95$ for limiting translocation into aerial wheat compartments correct for different lipophilicities between plant lipids and n-octanol (Briggs et al., 1982, 1983). Although Briggs' exponents seem to be restricted to uptake of rather neutral chemicals into root and stem, Trapp (2007) considers their use for calculating partition coefficients between various plant compartments and water for chemicals with a wide range in K_{ow} based on findings of a sensitivity study. Whenever more than one boundary layer or phase is relevant, conductance is calculated in series or in parallel, respectively, according to pathway specifics as will be demonstrated for diffusion into wheat grains. At maturity, the grain (caryopsis) is enclosed within fibrous, modified leaves (bracts), namely lemma at dorsal and palea at ventral position, together forming a protecting hull around the grain (Kulp and Ponte Jr., 2000). For diffusive pesticide transport from grain surface deposit, hence, conductance through the leaf-like lemma and its surface is considered in addition to conductance through the grain surface, summarized in a single transfer rate coefficient between grain surface deposit and actual grain $k_{\mathrm{vf}\leftarrow\mathrm{vfd}}$ [d^{-1}]:

$$k_{\mathrm{vf}\leftarrow\mathrm{vfd}} = \left(\frac{1}{k_{\mathrm{l}\leftarrow\mathrm{l,surf}}} + \frac{1}{k_{\mathrm{g,surf}\leftarrow\mathrm{l}}} + \frac{1}{k_{\mathrm{g}\leftarrow\mathrm{g,surf}}} \right)^{-1} \tag{2.11}$$

where $k_{\mathrm{l} \leftarrow \mathrm{l,surf}}$ [d^{-1}] is the transfer rate coefficient from outer lemma surface to lemma interior, $k_{\mathrm{g,surf} \leftarrow \mathrm{l}}$ [d^{-1}] is the subsequent rate coefficient from lemma interior to actual grain surface and $k_{\mathrm{g} \leftarrow \mathrm{g,surf}}$ [d^{-1}] finally is the rate coefficient from grain surface to inner grain. Sometimes, conductance data are not available, but calculated as a function of limiting boundaries and diffusing substances like for cuticular transfers. Cuticles are extracellular, solid-state polymer membranes composed of two chemically distinct fractions, namely polymer matrix membranes and transport-limiting cuticular waxes (Schreiber and Schönherr, 2009). Cuticles protect from uncontrolled water loss and often represent the major barrier into plants for sprayed pesticides (Schreiber, 2005). According to Riederer and Müller (2006), conductance through cuticles depends on solute mobility (desorption rate coefficient) in the limiting skin k_{cut} [d^{-1}] and partition coefficient between cuticular wax and deposited surface residue K_{cuw} [$\mathrm{kg\,m}^{-3}$ per $\mathrm{kg\,m}^{-3}$]. The transfer rate coefficient from leaf surface deposit to leaf interior is described accordingly:

$$k_{\mathrm{vl} \leftarrow \mathrm{vld}} = k_{\mathrm{cut}} \times K_{\mathrm{cuw}} \tag{2.12}$$

Schönherr and Schreiber (2004) express k_{cut} as linear function of substance molecular weight MW [$\mathrm{g\,mol}^{-1}$], solute size selectivity of cuticular membranes SL_{cut} [$\mathrm{mol\,g}^{-1}$], and mobility of a hypothetical substance with zero molar volume $k_{\mathrm{cut,V0}}$ [d^{-1}]:

$$\log k_{\mathrm{cut}} = \mathrm{MW} \times SL_{\mathrm{cut}} \times \log k_{\mathrm{cut,V0}} \tag{2.13}$$

Values for SL_{cut} and $k_{\mathrm{cut,V0}}$ are given in Fantke et al. (2011a). K_{cuw} is described by Popp et al. (2005) as a function of K_{ow}:

$$\log K_{\mathrm{cuw}} = 1.03 \times \log K_{\mathrm{ow}} - 0.92 \tag{2.14}$$

Advective transfer and translocation

Advection, i. e. co-transport of pesticides in a flowing medium, addresses transport via xylem and phloem in wheat as well as system loss via runoff and leaching from root-zone soil layer to surface water and saturated subsoil, respectively. The general equation for advective transfer from compartment i to j, $k_{j \leftarrow i,\mathrm{adv}}$ [d^{-1}], reads:

$$k_{j \leftarrow i,\mathrm{adv}} = \frac{A_{ij} \times p_{ij,\mathrm{adv}} \times fc_{\mathrm{L\,to\,m3}}}{K_{i\mathrm{w}} \times M_i} = \frac{Q_{ij,\mathrm{adv}}}{K_{i\mathrm{w}} \times M_i} \tag{2.15}$$

where A [m^2] is the connecting area shared by both compartments, p [$\mathrm{m\,d}^{-1}$] is the advective transfer rate, constant factor $fc_{\mathrm{L\,to\,m3}}$ [$\mathrm{L\,m}^{-3}$] corrects for different volume units, $K_{i\mathrm{w}}$ [$\mathrm{L\,kg}^{-1}$] is the partition coefficient between compartment i and water, M [kg] is the compartment mass, and Q [$\mathrm{L\,d}^{-1}$] is the volume-related flow rate. Advection in wheat follows acropetal transpiration in xylem originating in roots as well as basipetal assimilation in phloem loaded in leaves, both leading to accumulation in sink organs like wheat grains. Movement in xylem is driven by hydrostatic pressures generated by osmotic pressure in root cells and transpiration rate of wheat as a function of plant development stage and active growth (Orcutt and Nilsen, 2000). Hydrostatic pressure in phloem is generated from loading sugars and other solutes in leaves and post-phloem translocation into roots and grains. Pesticide transport in both xylem and phloem has been adopted from Trapp (2007).

2.3.5. Experimental setup

Experimental procedures help to test the accuracy of modeled data and to identify limitations and the applicability of models (Schwartz, 2000). Experiments were conducted on residues in wheat grains by Cao (2001) and Charles (2004) in Changins-Nyon, Switzerland. Measured data from these studies are used to assess the two main phases regarding environmental fate addressed in the presented model, namely initial pesticide distribution and subsequent dissipation into wheat. However, distribution of pesticides directly after application is an important source of uncertainty. Whereas the model considers constant climate conditions and good agricultural practice, possible high losses during the first hours after application are partly related to varying application pattern and climatic conditions in the field experiments.

Cao (2001) and Charles (2004) applied four fungicides (chlorothalonil, cyproconazole, prochloraz, tebuconazole) and two insecticides (deltamethrin, pirimicarb) as late treatment on wheat 30 days before harvest. A 30 days period has been chosen, because realistic application conditions, such as an application of individual fungicides to wheat 67 days before harvest, cannot be represented in experimental setups due to lower analytical detection limits. Hence, the present setup is designed only for the evaluation of modeled residues. Pesticide characteristics and applied amounts that were also adopted in the corresponding model simulation runs are summarized in Table 2.4.

All pesticides were applied at high concentration levels and first samples were analyzed shortly (6 hours) after application to avoid measuring inconsiderable concentrations. Residues in wheat ears were measured regularly between application and harvest time. Measurements of initial concentrations and residues in harvest were then compared with modeled initial concentrations and residues, respectively.

Table 2.4.: Physicochemical properties (MW, molecular weight; Kow, octanol-water partition coefficient; Kaw, air-water partition coefficient; $t_{1/2,\mathrm{soil}}$, degradation half-life in bulk soil; $t_{1/2,\mathrm{wheat}}$, degradation half-life in wheat) and substance mass applied via foliar spray (experiments and modeling) m_{applied} for six selected pesticides.

substance	MW[a] [g mol^{-1}]	log Kow[a] [–]	log Kaw[a] [–]	$t_{1/2,\mathrm{soil}}$[a] [d]	$t_{1/2,\mathrm{wheat}}$[a] [d]	m_{applied}[b] [g ha^{-1}]
prochloraz	376.7	4.3	−6.2	120	5	300
tebuconazole	307.8	3.7	−8.3	62	8[c]	250
chlorothalonil	265.9	2.9	−4.9	22	8.2	1500
cyproconazole	291.8	3.1	−7.5	142	16	80
deltamethrin	505.2	4.6	−5.4	13	6	7.5
pirimicarb	238.4	1.7	−6.9	86	6.5	75

[a] AERU Agriculture and Environment Research Unit (2011); [b] Cao (2001), Charles (2004);
[c] Cabras et al. (1997)

2.3.6. Comparison with measured residues

Modeled pesticide concentrations in wheat grains have been compared with concentrations measured by Cao (2001) and Charles (2004). Distribution at time of substance application is of particular interest; the filled symbols in Figure 2.3 compare modeled initial concentrations in grains at time $t = 0$ with experimentally derived concentrations 6 hours after application. Modeled initial concentrations are close, but slightly lower than measured concentrations, i. e. between 7.5% (chlorothalonil) and 58% (cyproconazole). To consider pesticide evolution in grains, blank symbols in Figure 2.3 compare modeled with measured concentrations at 1, 7, 24 and 30 days after application with final concentrations after 30 d listed in Table 2.5.

The accuracy of the model to predict concentrations is estimated by calculating the coefficient of determination R^2 as well as the standard error SE, also known as standard deviation of the log of residuals, between measured and modeled concentrations as discussed in Hamburg and Young (1994) and as defined in Eq. 2.18. Coefficients of determination R^2 are 0.86 for cyproconazole, 0.88 for prochloraz, 0.91 for chlorothalonil, deltamethrin and tebuconazole, and 0.92 for pirimicarb. Standard errors SE amount to 0.16 for chlorothalonil, 0.17 for pirimicarb, 0.24 for prochloraz, 0.30 for tebuconazole, 0.31 for deltamethrin, and 0.32 for cyproconazole. Overall, modeled and measured concentrations fit very well and deviated from less than a factor 1.5 for chlorothalonil to a maximum factor 3 for tebuconazole. The evaluation of residues demonstrates that the

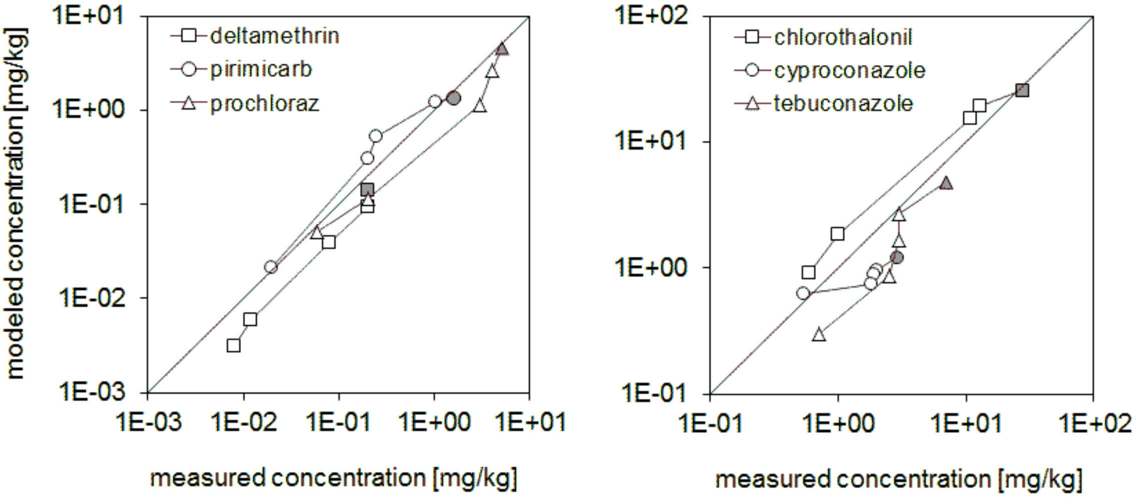


Figure 2.3.: Modeled versus measured concentrations of six pesticides in wheat grains at time $t = 0$ (filled symbols) as well as 1, 7, 24, and 30 days after pesticide application (blank symbols).

model allows us to recognize trends of different pesticides applied to wheat over their full concentration ranges, thereby accounting for the complex interactions between different compartments. Main sources of uncertainty in the model are related to (a) estimated physicochemical properties of pesticides, (b) wheat crop characteristics and development, and (c) the mathematical description of the fate processes by means of rate coefficients, which is due to the limitation of using first-order kinetics (Barber et al., 2004). Uncertainties in the modeling approach are further discussed in Chapter 3. Main sources of uncertainty in the experimental approach, in contrast, are related to (a) limitations in detecting pesticides in residues, (b) statistical uncertainty, and (c) specifics in time and location of the measurements.

2.3.7. Evolution and distribution of masses

Mass evolution in all considered compartments is shown in Figure 2.4 for the six selected pesticides with their physicochemical properties and applied masses given in Table 2.4. Masses in atmospheric ground layer quickly decrease due to very short degradation half-lives for all pesticides. In contrast, masses in root-zone soil layer decrease much slower and start to be predominant in the system for chlorothalonil (c), pirimicarb (f) and deltamethrin (e) after 5, 8 and 24 days, respectively. This results from the overall residence times in soil, incorporating both removals by degradation and translocation (MacLeod and McKone, 2008). Related to a reduced overall residence time in soil, cyproconazole (d), prochloraz (a) and tebuconazole (b) show a different behavior with masses

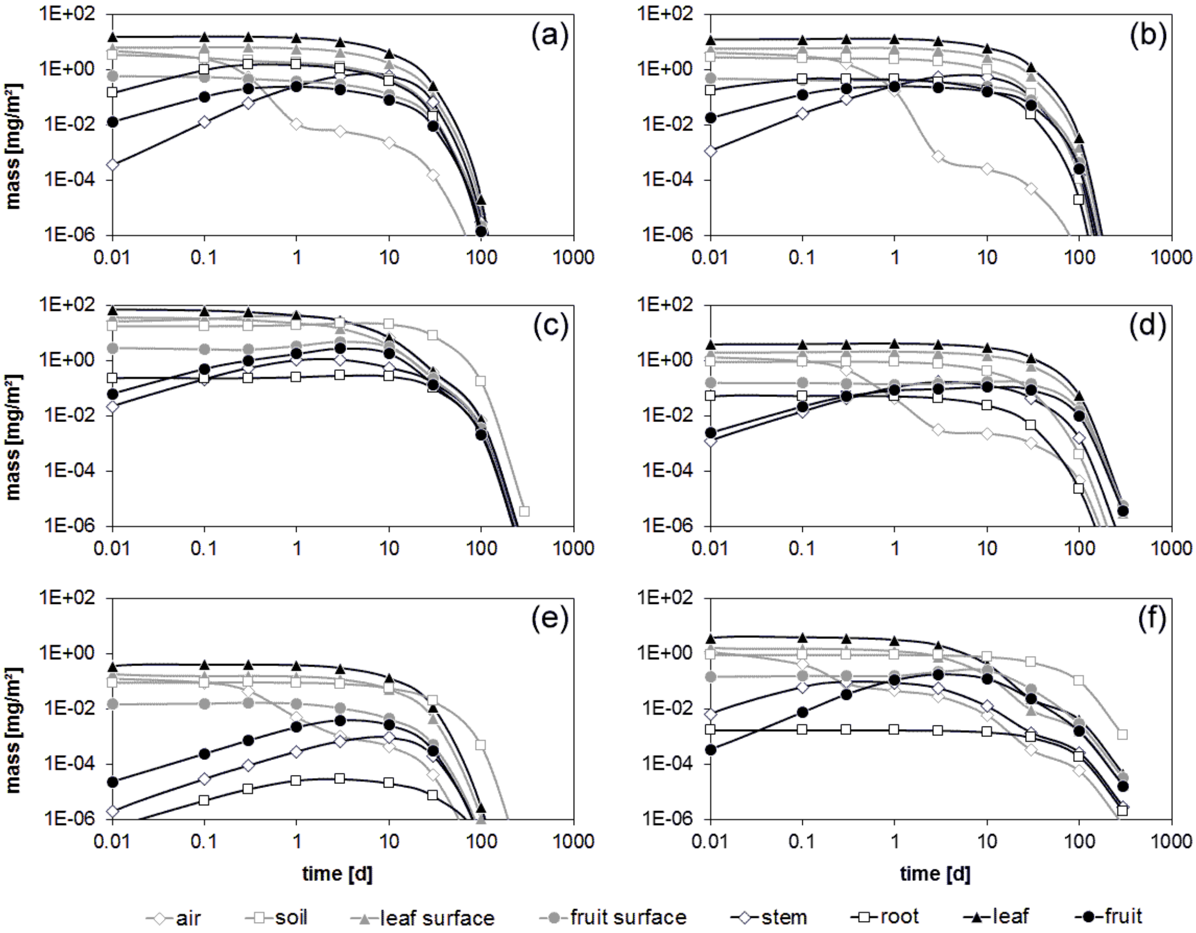


Figure 2.4.: Evolution of masses [$\text{mg}_{\text{pesticide}}\ \text{m}^{-2}_{\text{compartment}}$] of prochloraz (a), tebuconazole (b), chlorothalonil (c), cyproconazole (d), deltamethrin (e), and pirimicarb (f) in the wheat-environment system after spray application.

in leaves being predominant at least until harvest 67 days after application, which represents realistic application conditions for wheat. All pesticides start entering the fruit compartment (wheat grains) quickly after application and accumulate for some days, before degradation starts to mainly influencing the further mass evolution, thereby leading to a mass decrease in grains until harvest. Initial substance distribution, transfer velocities between compartments, and degradation influence mass distributions over time. Degradation is finally responsible for the overall exponential mass decrease in the long-term, leading to low residues in harvest after 67 days for prochloraz and deltamethrin that have short half-lives in plant of 5 and 6 days, respectively, and to higher residues for cyproconazole with a longer half-life in plant of 16 days, comparing the evolution of masses of the six selected pesticides in wheat grains from application to harvest). Similar trends of pesticide mass evolutions are obtained by Juraske et al. (2007) for captan spayed onto tomatoes, Paraíba (2007) for mango trees treated with paclobutrazol via soil application, Juraske et al. (2009a) for tomatoes treated with imidacloprid via foliar and soil application, Juraske et al. (2011) for chlorpyrifos sprayed onto potatoes, and Legind et al. (2011) for sweet peppers treated with methomyl via drip irrigation. In the present approach, residual masses in wheat grains at harvest time range from $0.01\,\mu\mathrm{g\,m^{-2}}$ for deltamethrin to $0.03\,\mathrm{mg\,m^{-2}}$ for cyproconazole. Corresponding concentrations in harvested grains are calculated from pesticide mass in grains at harvest time divided by the mass of harvested grains and range from $10^4\,\mathrm{mg\,kg^{-1}}$ for deltamethrin to $0.09\,\mathrm{mg\,kg^{-1}}$ for cyproconazole. Provided that assumed time from application to harvest of 67 days and application amounts are in line with good agricultural practice, modeled residues can be compared with official MRLs. All modeled residues are below MRLs set by the European Commission (EC European Commission, 2008a), although the residue for cyproconazole is close to the MRL of $0.01\,\mathrm{mg\,kg^{-1}}$ for wheat.

2.3.8. Exposure to residues in harvested wheat

Human exposure from consumption of food crops builds upon fractions of applied pesticides that end up as residues in harvest. Pesticide residues in harvested wheat grains expressed relative to initially applied pesticide mass yields the harvest fraction hF $[\mathrm{kg_{in\,harvest}\,kg_{applied}^{-1}}]$:

$$\mathrm{hF}(t) = \frac{m_{\mathrm{residue}}(t)}{m_{\mathrm{applied}} + m_{\mathrm{background}}} \tag{2.16}$$

where $m_{\mathrm{residue}}(t)$ $[\mathrm{kg\,m^{-2}}]$ is the residual mass in grains at harvest time t, m_{applied} $[\mathrm{kg\,m^{-2}}]$ is the total applied mass and $m_{\mathrm{background}}$ $[\mathrm{kg\,m^{-2}}]$ is the background mass from previous applications. Processing of harvested crop components, hereafter referred to as food processing, may lead to significant reduction of pesticide residues and plays an important role for wheat and other cereals. According to Saka et al. (2008), the food processing factor relates residues in processed products $[\mathrm{kg_{residue,proc}\,kg_{product}^{-1}}]$ to residues in harvested, unprocessed wheat $[\mathrm{kg_{residue,unproc}\,kg_{harvest}^{-1}}]$ and can finally be expressed as kg pesticide in consumed food per kg pesticide in harvest. Sharma et al. (2005) and Uygun et al. (2005) found between 53% and 82% reduction of residues in processed wheat due to bread making based on empirical data, from which an average food processing factor of 0.33 is derived. The fraction of harvested wheat that is finally consumed after food processing is expressed as intake fraction, iF $[\mathrm{kg_{ingested}\,kg_{applied}^{-1}}]$, which is defined as mass fraction of applied pesticide that is ultimately consumed by humans (Bennett et al., 2002). Assuming that 100% of harvested grains are consumed yields:

$$\mathrm{iF}(t) = \mathrm{hF}(t) \times \mathrm{PF_{food}} \tag{2.17}$$

where $\mathrm{iF}(t)$ [$\mathrm{kg_{ingested}\,kg^{-1}_{applied}}$] is the total population intake fraction, $\mathrm{hF}(t)$ [$\mathrm{kg_{in\,harvest}}$ $\mathrm{kg^{-1}_{applied}}$] is the harvest fraction, both referring to harvest time t, and $\mathrm{PF_{food}}$ [$\mathrm{kg_{ingested}}$ $\mathrm{kg^{-1}_{in\,harvest}}$] is the constant food processing factor.

2.3.9. Harvest fractions and human intake fractions

Table 2.5 presents modeled harvest fractions 67 days after substance application for the six selected pesticides, representing the fractions of applied pesticide masses that are found in harvested grains for ultimate intake by humans via consumption. Harvest fractions range over more than three orders of magnitude, from $1.8\times10^{-6}\,\mathrm{kg_{in\,harvest}\,kg^{-1}_{applied}}$ for deltamethrin to $6.5\times10^{-3}\,\mathrm{kg_{in\,harvest}\,kg^{-1}_{applied}}$ for cyproconazole. This reflects the high variability of physicochemical properties among pesticides and the determining influence of these properties on the final residue in wheat grains after translocation and degradation in the modeled system. Since harvest fractions are normalized for the total applied substance mass, the behavior of pesticides can be compared independently of the applied amounts. Considering the observed variation between harvest fractions and applied pesticide masses, the uncertainty on applied quantities is a factor of secondary significance. Table 2.5 presents modeled intake fractions for the six selected pesticides, thereby accounting for a mean food processing factor of 0.33 for bread making from wheat grains based on empirical data. Intake fractions range from $5.9\times10^{-7}\,\mathrm{kg_{ingested}\,kg^{-1}_{applied}}$ for deltamethrin to $2.1\times10^{-3}\,\mathrm{kg_{ingested}\,kg^{-1}_{applied}}$ for cyproconazole.

Table 2.5.: Measured and modeled residues [$\mathrm{mg\,kg^{-1}}$] in wheat grains 30 days after pesticide application (day chosen for comparison between model and experimental results only), modeled actual hF [$\mathrm{kg\,kg^{-1}}$] 67 days after application (realistic conditions for wheat), and related modeled iF [$\mathrm{kg\,kg^{-1}}$] for six selected pesticides. Modeled iF from residues in wheat are compared with iF due to inhalation and ingestion from the fraction lost from the field via air.

substance	residues		hF	$\mathrm{iF_{direct\,spray}}$	$\mathrm{iF_{field-loss,air}}$	
	measured	modeled		food crops	inhalation	ingestion
prochloraz	0.06	0.05	6.7×10^{-6}	2.2×10^{-6}	9.1×10^{-8}	6.0×10^{-7}
tebuconazole	0.71	0.30	2.8×10^{-4}	9.2×10^{-5}	2.9×10^{-7}	8.5×10^{-6}
chlorothalonil	0.66	0.75	1.1×10^{-4}	3.5×10^{-5}	5.5×10^{-7}	1.6×10^{-5}
cyproconazole	0.54	0.62	6.5×10^{-3}	2.1×10^{-3}	2.6×10^{-7}	1.4×10^{-5}
deltamethrin	0.008	0.003	1.8×10^{-6}	5.9×10^{-7}	2.3×10^{-8}	1.8×10^{-7}
pirimicarb	0.02	0.02	5.0×10^{-4}	1.7×10^{-4}	6.9×10^{-8}	5.6×10^{-7}

2.3.10. Exposure to pesticide fractions lost beyond field boundaries

Exposure towards pesticides is not limited to consumption of directly treated food crops. Instead, there is a fraction that is lost to air beyond the field boundaries via wind drift during and after application and a fraction that is lost to freshwater via run off and to groundwater via leaching, both initiated by the fraction that deposits onto soil during application. For demonstration purposes, the fraction lost to air beyond the field boundaries is compared with exposure from consumption of treated wheat. Intake fractions via inhalation and ingestion exposure from the fraction lost to air are estimated assuming multimedia steady-state transfers by applying the Impact 2002 model, which is fully described in Pennington et al. (2005). The pesticide mass lost to air is estimated by means of the dynamiCROP model and serves as 'emission' input for the Impact 2002 model. From there, the entire multimedia fate and exposure assessment is conducted in Impact 2002 with human intake fractions for both exposure pathways inhalation and ingestion caused by 'emission to air' as result.

2.3.11. Comparison of different exposure pathways

In addition to pesticide intake via consumption of sprayed wheat, intake fractions via inhalation and ingestion from the fraction that is lost to air during and after pesticide application is estimated. Intake fractions from the mass applied that is lost to air obtained by means of the Impact 2002 model range from $2.3 \times 10^{-8}\,\mathrm{kg_{ingested}\,kg_{applied}^{-1}}$ for inhalation of deltamethrin to $1.6 \times 10^{-5}\,\mathrm{kg_{ingested}\,kg_{applied}^{-1}}$ for ingestion of chlorothalonil (Table 2.5). In comparison to intake fractions caused by consumption of residues in treated wheat, intake fractions caused by the fractions lost to air are up to four orders magnitude lower. In summary, results from assessing harvest and intake fractions indicate that (a) different pesticides accumulate differently in edible wheat grains, (b) ingestion of residues from treated wheat is highly dependent on physicochemical properties of applied pesticides, and (c) consumption of food crops directly treated with pesticides is the predominant exposure pathway compared to inhalation or ingestion exposure caused by the fraction lost to air, which is in line with findings from Humbert et al. (2007) and Juraske et al. (2009b).

2.3.12. Conclusions

Results of the assessment of six pesticides applied to wheat obtained with the newly developed model indicate that dynamic plant uptake modeling can be used to simulate the behavior of neutral organic pesticides in the wheat-environment system and is a valuable tool to predict human intake as a function of harvest time, initial conditions and rate coefficients. The structure of the mass balance underlying the newly developed model allows for covering pesticide application to several input compartments, deposition onto wheat and soil, diffusive and advective transfer processes between compartments including losses beyond the model domain via e. g. wind drift, runoff or leaching, as well as substance degradation. Future studies can take advantage of the way the model is analytically solved and considers environmental and crop-related compartments. A high level of detail in describing environmental fate processes along with a large number of input parameters requires to study related uncertainties and the functioning of the modeled system as will be discussed in Chapter 3. Nevertheless, since pesticides residue levels in wheat for human consumption substantially vary with substance properties, results of this model constitute an important input for the comparative assessment of pesticides and for decision making. In addition, human exposure to residues in wheat constitutes the predominant pathway compared to exposure caused by the fraction lost to air during and after pesticide application. However, the presented approach is so far limited to assess wheat only. Hence, the model is adapted to also assess other crops and environmental conditions as described in the following section.

2.4. Modeling framework for assessing pesticide uptake into multiple crops

2.4.1. Introduction and background

Pesticide uptake and translocation mechanisms vary considerably between crop species and may indicate significant differences in related health impacts (Trapp and Kulhanek, 2006). Consequently, differing crop-specific characteristics need to be considered as provided for individual crop species by recently developed plant uptake models (Fantke et al., 2011a; Juraske et al., 2007, 2011; Trapp, 2007; Rein et al., 2011). In Section 2.2, a wide range of crop-specific uptake models assessing environmental fate of pesticides after direct application was compared, concluding that none of the existing tools is able to contrast various crops consumed by humans. Since this implies a major drawback in characterizing human toxicity, the present section aims at introducing a consistent approach for answering the following questions: (i) What are the most important crop types to be assessed with respect to human vegetal consumption? (ii) How can these crop archetypes be contrasted to identify crop type-specific fate pathways for modeling subsequent residues in food crops? To answer these questions, the new dynamic assessment model for wheat as described in Section 2.3 is extended to assess uptake of pesticides into multiple crop types. Six food crops covering a large fraction of the worldwide consumption of vegetal origin were selected, thereby representing the most important crop archetypes. Finally, residues in the six crop types have been evaluated against measured pesticide concentrations.

2.4.2. Selection of crops

Six characteristic plant species are introduced representing the most relevant crop archetypes with respect to human vegetal food based on a systematic criteria approach. Selection criteria are human consumption quantity, share on crop archetype, crop characteristics (cropping practice, plant phenotype, and harvested components), availability of knowledge from other models and experimental data for comparison with modeled residues. Human consumption is analyzed based on global FAO statistics of 159 food crops (FAO Food and Agriculture Organization of the United Nations, 2011). Table 2.6 summarizes the criteria analysis and lists selected crop species accounting for 45% of the global vegetal consumption in 2007 (FAO Food and Agriculture Organization of the United Nations, 2011). These crops cover the most important archetypes, that is, cereals (wheat), paddy cereals (paddy rice rice), herbaceous fruits and vegetables (tomato), fruit trees (apple), leafy vegetables (lettuce), as well as roots and tubers (potato). Based on these archetypes, the model framework can be easily adapted to assess additional crop species of interest.

Table 2.6.: Selected crops and represented archetypes according to a set of systematic criteria Including share of crop on human consumption of archetype (φ_{crop}) and share of archetype on total human vegetal consumption ($\varphi_{\text{archetype}}$).

crop	archetype	consumption share		characteristics
		φ_{crop}	$\varphi_{\text{archetype}}$	
wheat	cereals	68%	24%	grasslike
paddy rice	paddy cereals	97%	13%	grasslike, paddy water
tomato	vegetables	15%	26%	herbaceous
apple	fruit trees	13%	17%	treelike, perennial
lettuce	leafy crops	14%	2%	high adsorption, leaves harvested
potato	roots/tubers	51%	18%	roots or stem harvested

2.4.3. Crop characteristics

Initial deposition of pesticides on plant surfaces directly after application depends on the crop-specific leaf area index representing leaf growth stage, and furthermore the pesticide capture coefficient being a measure of a crop's capture efficacy (Gyldenkaerne et al., 1999). While the latter can be seen as a fixed value, crop growth and related LAI development are time-dependent. Logistic crop development is applied for all studied crops, describing an initial exponential growth that finally saturates at some maximum level (Fantke et al., 2011a; Rein et al., 2011). However, evolution of leaf area follows a more complex behavior. Crop-specific LAI curves based on experimental data are applied for wheat (Lenz, 2007), paddy rice (Chen et al., 2006), tomato (Antón Vallejo, 2004), apple (Gong et al., 2006), lettuce (Carranza et al., 2009) and potato (Eremeev et al., 2008) as shown in Figure 2.5.

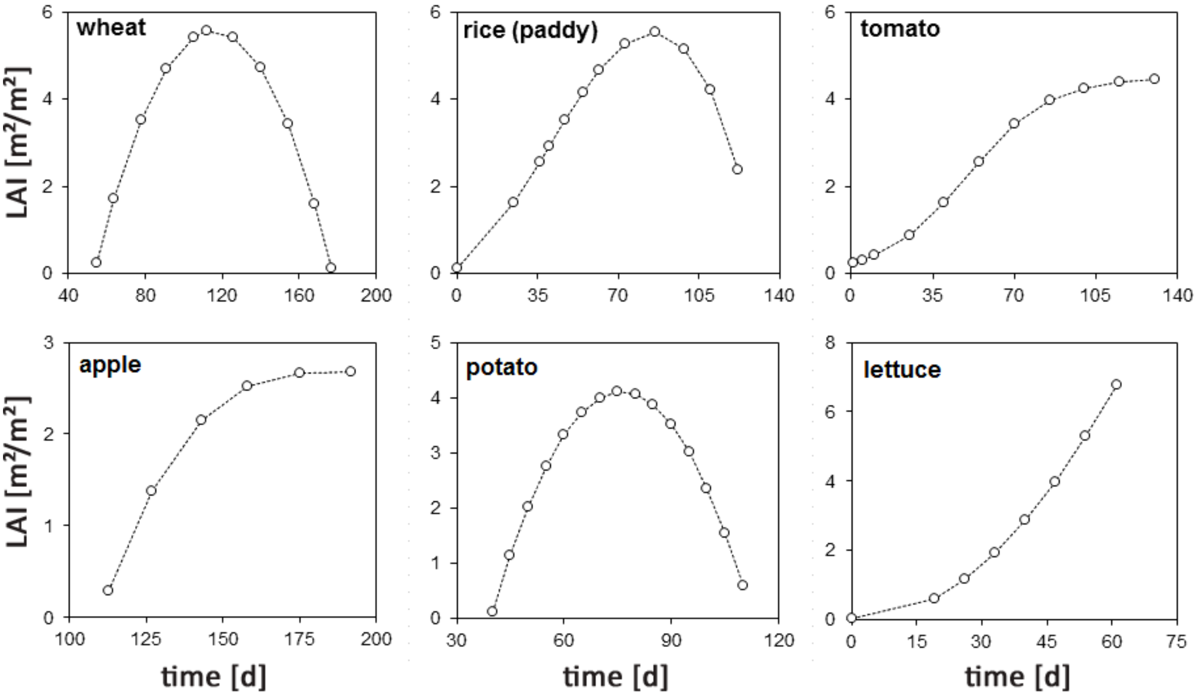


Figure 2.5.: LAI curves from literature representing leaf development as applied for each of the six studied crops. The time is given in days after planting except for apples (being a perennial crop) for which the time is given in days of the year.

After a pesticide is applied to a crop, a certain fraction of the initial dose has the potential for drifting from the agricultural site. In most cases, drift mainly depends on application method, pesticide formulation, environmental conditions and crop type (Wolters et al., 2008). Typical crop type- and application method-specific drift values are applied as loss fractions. Finally, in order to evaluate the effect of food processing on the magnitude of pesticide residues in the studied crops, food processing factors for washing, peeling, cooking, juicing, and baking are adopted from Table 2.8.

All other relevant crop-specific input data for assessing pesticide behavior in the selected crop types are provided in Table 2.7.

Table 2.7.: Crop characteristics relevant as model input for six selected food crops.

crop-specific model input	unit	wheat	rice	tomato	apple	lettuce	potato
time from planting to harvest	[d]	181(1)	128(2)	114(3)	259*(4)	84**	159(5)
substance capture coefficient	[-]	0.50(6)	0.50(6)	0.45(3)	0.50(6)	0.34**	0.40(5)
transpiration coefficient	[L kg^{-1}]	500(7)	300(7)	162(8)	333(9)	681**	550(10)
root to shoot ratio	[kg kg^{-1}]	0.50(11)	0.10(12)	0.10(8)	0.23(4)	0.09(13)	0.47(5)
leaf fraction of aerial plant	[kg kg^{-1}]	0.12(11)	0.15(14)	0.33(3)	0.22(15)	0.88(16)	0.50(5)
fruit fraction of aerial plant	[kg kg^{-1}]	0.44(11)	0.50(12)	0.36(8)	0.22(17)	—	—
stem fraction of aerial plant	[kg kg^{-1}]	0.44(11)	0.35(14)	0.31(8)	0.56(15)	0.12(16)	0.50(5)
mean height of stem	[m]	1.00(11)	1.20(12)	2.10(3)	5.00(17)	0.18**	0.70(5)
water content of leaf	[L kg^{-1}]	0.80(17)	0.80(17)	0.87(3)	0.80(17)	0.96**	0.80(17)
water content of fruit	[L kg^{-1}]	0.13(11)	0.30(12)	0.87(8)	0.84(17)	—	—
water content of stem	[L kg^{-1}]	0.80(11)	0.80(11)	0.80(8)	0.38(17)	0.96**	0.80(11)
water content of stem tuber	[L kg^{-1}]	—	—	—	—	—	0.78(18)
water content of root	[L kg^{-1}]	0.89(17)	0.89(17)	0.88(8)	0.89(17)	0.91**	0.89(17)
leaf area index at harvest	[m^2 m^{-2}]	4.10(1)	4.50(1)	3.11(3)	2.35(1)	6.52**	3.89(5)

*Apple trees are perennial crops; hence, planting refers to the beginning of the calendar year. **experimental study at the Institute of Agriculture and Food Research and Technology, Barcelona, Spain in 2011 (unpublished). (1)Fantke et al. (2011b); (2)Capri and Karpouzas (2008); (3)Juraske et al. (2007); (4)Jackson (2003); (5)Juraske et al. (2011); (6)Gyldenkaerne et al. (1999); (7)Cohen (1996); (8)Juraske et al. (2009a); (9)Pincebourde et al. (2006); (10)Keller et al. (1997); (11)Fantke et al. (2011a); (12)Yoshida (1981); (13)Rowse (1974); (14)Srivastava and Yoshida (1990); (15)Kikuchi et al. (1996); (16)Santos Filho et al. (2009); (17)Trapp (2007); (18)Trapp et al. (2007).

2.4.4. Multicrop model evaluation

Internal model consistency was continuously examined by checking the underlying mass balance, that is, ensuring that the sum of elimination and biodistribution pathways at any time equals the total pesticide mass applied. Second, modeled residues are evaluated by analyzing whether model simulations adequately represent collected experimental data from the literature for all considered crops. The measure used to estimate model prediction quality compared with experiments is again the standard error, also known as standard deviation of the log of residuals between n observed/experimentally derived concentrations, x_{e}, and modeled/simulated residues, x_{m} as defined in Section 2.3.6 and calculated according to:

$$\mathrm{SE} = \sqrt{\frac{1}{n} \times \sum\nolimits_{i=1}^{n} \Big(\log(x_{\mathrm{e}}) - \log(x_{\mathrm{m}})\Big)_i^2} \tag{2.18}$$

A standard error of, for example, 0.5 implies a deviation between modeled and experimental data of approximately a factor $10^{\mathrm{Student's}\, t \times 0.5}$. For a Student's t-value of ~2, one would then arrive at a factor 10 deviation. Third, model sensitivity was as a first attempt studied to determine the influence of the most important parameters on output variability. A full sensitivity and uncertainty analysis is in addition given in Chapter 3.

2.4.5. Pesticide residues in multiple crops

Modeled residues are compared with measured concentrations of eleven different pesticides applied to the six selected crops as shown in Figure 2.6. Experimentally derived maximum concentrations are reported to range from 29 $\mathrm{mg\,kg^{-1}}$ in apples at the day of application to 0.01 $\mathrm{mg\,kg^{-1}}$ in potato tubers measured 15 days after the tested pesticide was applied, demonstrating a variability of 3 orders of magnitude between crops. Measurements and model estimates correspond well with total crop-specific standard errors ranging between 0.08 (factor 1.5 deviation) for fenitrothion applied to lettuce and 0.64 (factor 19) for propisochlor sprayed on rice with an overall standard error of 0.33 (factor 4.5) over all 12 substance-crop combinations. A higher accuracy of prediction is observed in crops where the final commodity stands in direct contact with the applied pesticide (apple, lettuce, tomato, and wheat). In comparison, crops in which the pesticide has to pass an additional medium like paddy water (rice) or soil (potato) in order to reach the harvested good, on average showed higher uncertainties.

2.4.6. Conclusions

Results of assessing the environmental fate behavior of pesticides applied to six major crop archetypes obtained with the extended multicrop model indicate that dynamic plant uptake modeling helps to understand the behavior of neutral organic pesticides in various crop-environment systems. The flexible structure of the underlying mass balance allows for adjusting the number of considered compartments according to the characteristics of each crop-environment system. More specifically, paddy rice requires an additional compartment accounting for paddy water, whereas lettuce and potato do not include fruit or fruit surface deposit compartments. Since pesticides residue levels in the different crops are not only a function of substance properties, but also of crop characteristics, results of the multicrop model constitute an important potential for

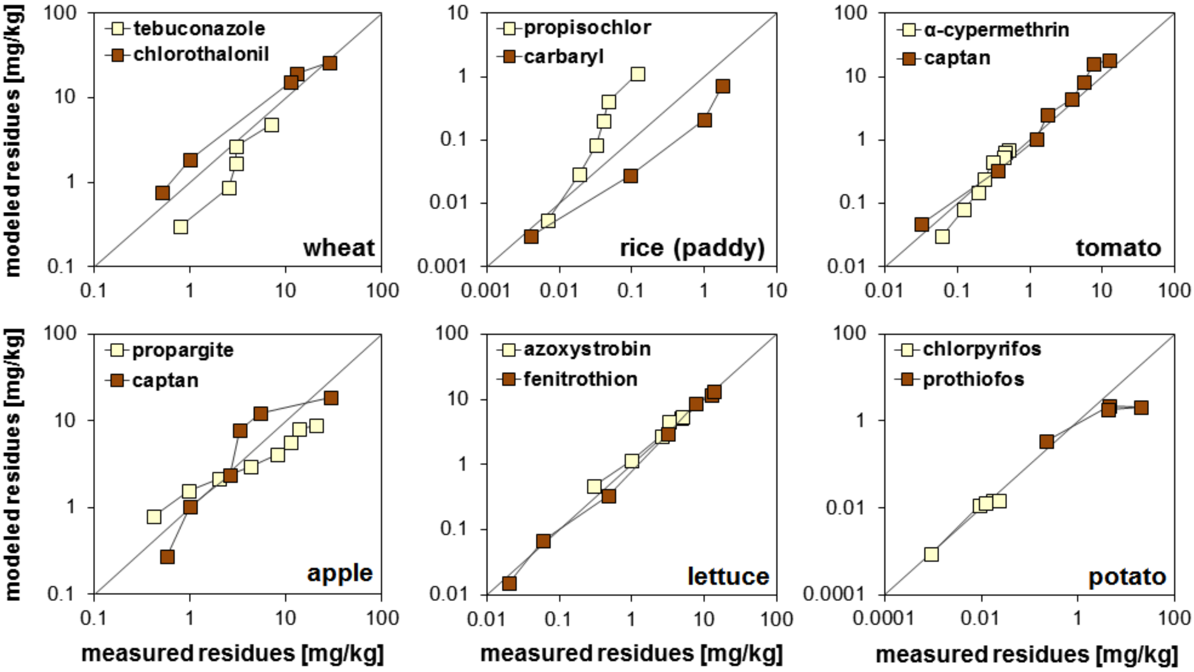


Figure 2.6.: Measured and modeled pesticide residues in plant components harvested for human consumption for each of the six studied crops.

decision making with respect to identifying the contribution of individual crop types to the overall human exposure to pesticides. Hence, the multicrop model is extended to assess human intake and related health impacts from the consumption of different crop types.

2.5. Human exposure and health impact assessment

2.5.1. Introduction and background

Many pesticides taken up by humans via e. g. consuming treated food crops can negatively affect human health via a wide range of health endpoints (Hamilton and Crossley, 2004; Sanborn et al., 2004, 2007; Lippmann, 2009). Hence, the present section aims at introducing a consistent approach for answering the following questions: (i) How can human intake of pesticides via ingestion of different food crops and related health impacts be characterized and evaluated in a transparent, consistent and concise way? (ii) What are the differences between crop-specific characterization factors from direct pesticide application to different food crops and generic characterization factors from the fractions lost to beyond the field boundaries during and after application? (iii) What is the influence of crop characteristics, substance properties and application times on the dynamic behavior of pesticides in crops? (vi) How can substitution of pesticides be evaluated and their health impacts compared on a similar functional basis for different crops? To answer these questions, the multicrop assessment model described in Section 2.4 is extended to also include human exposure and impact assessment. For each archetype, substance-specific human ingestion intake fractions are calculated and evaluated. In addition, the influence of crop and substance characteristics as well as the time between application and harvest on pesticide characterization is discussed. Finally, crop-specific characterization factors are provided – differentiated according to human cancer and non-cancer effect information – along with generic characterization factors to also account for the pesticide fractions lost from the field. The latter have been calculated by means of applying the USEtox model. All characterization factors factors can finally be used to evaluate human health impacts and related damage costs due to the application of pesticides.

2.5.2. Exposure and impact assessment framework

For human impacts, the general impact assessment cause-effect chain was followed by linking applied pesticide masses to health impacts via environmental fate, exposure and effects (Udo de Haes et al., 2002). The human-toxicological population impact score, $\mathrm{IS}_{i,x}(t)$ [$\mathrm{DALY\,ha^{-1}}$], caused by intake of pesticide i applied to crop x that is harvested at time t is expressed as the product of the characterization factor for human toxicity, $\mathrm{CF}_{i,x}(t)$ [$\mathrm{DALY\,kg_{applied}^{-1}}$] with the total mass of pesticide applied, $m_{\mathrm{applied},i,x}(t)$ [$\mathrm{kg_{applied}\,ha^{-1}}$]:

$$\mathrm{IS}_{\mathrm{total},x} = \sum_{i=1}^{n} \mathrm{IS}_{i,x}(t) = \sum_{i=1}^{n} \mathrm{CF}_{i,x}(t) \times m_{\mathrm{applied},i,x}(t) \tag{2.19}$$

with $\mathrm{IS}_{\mathrm{total},x}$ as total impact score per crop, expressed in DALY (disability adjusted life years as measure for overall population health impacts) per hectare. One determines the characterization factor by multiplying the human effect factor for pesticide i, EF_i [$\mathrm{DALY\,kg_{intake}^{-1}}$], with the total population intake fraction of the pesticide via consumption of crop x, $\mathrm{iF}_{i,x}(t)$ [$\mathrm{kg_{intake}\,kg_{applied}^{-1}}$]:

$$\mathrm{CF}_{i,x}(t) = \mathrm{EF}_i \times \mathrm{iF}_{i,x}(t) = \beta_i \times \mathrm{SF} \times \mathrm{iF}_{i,x}(t) \tag{2.20}$$

Effects Factors. The effect factor EF_i consists of a dose-response slope factor β_i [$\mathrm{incidence\ risk\ kg_{intake}^{-1}}$] and a severity factor SF [$\mathrm{DALY\,incidence^{-1}}$] for distinguishing between cancer and noncancer effects. Severity factors of 11.5 and 2.7 DALY per incidence for cancer and non-cancer effects, respectively, are based on global human health statistics (Huijbregts et al., 2005) and are intended for comparative purposes rather than estimating absolute damages. However, although in the present study absolute damages will be finally estimated, severity factors estimated according to Huijbregts et al. (2005) will be used due to the lack of other effect information. Slope factors relating potential risks of pesticides in humans to their quantities ingested via food crop consumption are derived from the chronic lifetime dose of pesticide i affecting 50% of a population, $\mathrm{ED50}_i$ [$\mathrm{risk\,kg}_{\mathrm{intake}}^{-1}\,\mathrm{person}^{-1}$]. For noncarcinogenic effects, chronic ED50 values are only rarely available. Hence, assuming linear dose-response relationships, $\mathrm{ED50}_{i,s}$ is estimated from no-observed effect levels of exposed animal species s, $\mathrm{NOEL}_{i,s}$ [$\mathrm{mg\,kg}_{\mathrm{applied}}^{-1}\,\mathrm{d}^{-1}$]:

$$\beta_i = \frac{fc_{\mathrm{ED50}}}{\mathrm{ED50}_i} = fc_{\mathrm{ED50}} \times \left(\frac{\mathrm{NOEL}_{i,s} \times fc_{\mathrm{NOEL}} \times \mathrm{BW} \times \mathrm{LT} \times fc_{\mathrm{d\,to\,yr}}}{fc_s \times fc_{\mathrm{time}} \times fc_{\mathrm{mg\,to\,kg}}} \right)^{-1} \tag{2.21}$$

$\mathrm{BW} = 70$ $\mathrm{kg\,person}^{-1}$ denotes average body weight, $\mathrm{LT} = 70$ years is the average human lifetime, $fc_{\mathrm{d\,to\,yr}} = 365$ $\mathrm{d\,yr}^{-1}$ corrects for number of days per year, $fc_{\mathrm{mg\,to\,kg}} = 106$ $\mathrm{mg\,kg}^{-1}$ corrects for mg per kg, and fc [–] denotes an extrapolation factor. $fc_{\mathrm{ED50}} = 0.5$ accounts for the human response level corresponding to ED50, $fc_{\mathrm{NOEL}} = 9$ is the NOEL to ED50 extrapolation factor, fc_s corrects for interspecies differences between the studied animal and humans, and fc_{time} accounts for differences in exposure time (Huijbregts et al., 2005, 2010). Extrapolation factors correcting for differences between studied receptor species and humans are $fc_s = 4.1$ for rat, $fc_s = 7.3$ for mouse, $fc_s = 1.5$ for dog, $fc_s = 2.4$ for rabbit and $fc_s = 1.9$ for monkey.5 Extrapolation factors correcting for differences between exposure duration of the study and chronic exposure are $fc_{\mathrm{time}} = 5$ for subacute exposure and $fc_{\mathrm{time}} = 2$ for subchronic exposure.

Intake Fractions. Human intake fractions describing the mass fractions of applied pesticides that are ultimately taken in by the human population via food ingestion builds upon Eqs. 2.16 and 2.17, but is defined crop-specifically as follows:

$$\mathrm{iF}_{i,x}(t) = \frac{m_{\mathrm{intake},i,x}(t)}{m_{\mathrm{applied},i,x}} = \mathrm{hF}_{i,x}(t) \times \mathrm{PF}_{\mathrm{food},x} \tag{2.22}$$

with $m_{\mathrm{intake},i,x}(t)$ [$\mathrm{kg}_{\mathrm{intake}}\,\mathrm{ha}^{-1}$] as mass of pesticide i taken in via ingestion of crop x, $\mathrm{hF}_{i,x}(t)$ [$\mathrm{kg}_{\mathrm{in\,harvest}}\,\mathrm{kg}_{\mathrm{applied}}^{-1}$] as mass fraction of applied pesticide that is found as residue in crops at harvest time t [d], and finally PF_x [$\mathrm{kg}_{\mathrm{intake}}\,\mathrm{kg}_{\mathrm{in\,harvest}}^{-1}$] as crop-specific food processing factor accounting for reduction in pesticide residues between harvest and final consumption. Food processing factors for different processing steps are listed in Table 2.8 for all selected crop archetypes.

Table 2.8.: Food processing factors (min–max range in parentheses) as applied for different crops or crop types aggregated over (a) all considered substances and (b) all crops belonging to a specific crop type.

Crop(s)	$fc_{\text{processing}}$ [–]	Processing step	Reference
Cereals[1]	0.3313 (0.28–0.53)	bread making	Wilkin and Fishwick (1981); Sharma et al. (2005); Uygun et al. (2005)
Rice	0.3175 (0.14–0.78)	parboiling & cooking	Cogburn et al. (1990); Holland et al. (1994); Saka et al. (2008)
Maize	0.34 (0.23–0.40)	cooking	FAO (1992); Lalah and Wandiga (2002); Kaushik et al. (2009)
Vegetables[2]	0.3217 (0.09–0.49)	cooking	Kontou et al. (2004); Boulaid et al. (2005); Caldas et al. (2006)
Leaf vegetables[3]	0.36 (0.21–0.65)	washing	Holland et al. (1994); Schattenberg III et al. (1996); Paradjikovic et al. (2004)
Root vegetables[4]	0.05 (0.01–0.19)	peeling & cooking	Holland et al. (1994); Kaushik et al. (2009); Keikotlhaile et al. (2010)
Fruits with peel[5]	0.1567 (0.01–0.65)	peeling	Toker and Bayindirli (2003); Caldas et al. (2006); Rawn et al. (2008)
Fruits/vegetables[6]	0.3492 (0.05–0.69)	juicing	Holland et al. (1994); Burchat et al. (1998); Kaushik et al. (2009)
Fruits peel-less[7]	0.4928 (0.16–0.91)	washing	Mergnat et al. (1995); Teixeira et al. (2004); Lentza-Rizos et al. (2006)

(continued on next page)

Table 2.8 (continued)

Crop(s)	$fc_{\text{processing}}$ [–]	Processing step	Reference
Various crops	0.4512 (0.16–0.65)	long-term storage	Holland et al. (1994); Kaushik et al. (2009); Juraske et al. (2011)
Others[8]	0.4733 (0.12–0.84)	washing	Juraske et al. (2007); Kaushik et al. (2009); Keikotlhaile et al. (2010)

[1] All grain cereals common in Europe, but rice and maize. [2] Vegetables that are usually cooked (including spinach) and not allocated elsewhere in this table. [3] Leafy vegetables usually consumed raw, e. g. lettuce. [4] Vegetables of which any underground part is usually cooked, e. g. carrot (taproot), sweet potato (tuberous root), ginger (stem rhizome), potato (stem tuber); onion (bulb). [5] Fruits that are usually peeled, e. g. banana and mango. [6] Fruits and vegetables that are used to produced any kind of juice, e. g. apple and tomato. [7] Fruits that are usually eaten unpeeled, e. g. apple and grapes. [8] All field crops that are not allocated elsewhere in this table; washing is assumed to be default processing step.

Mass in harvest is a result of the mass balance system of differential equations that is solved analytically by means of matrix algebra according to Eq. 2.3. A full description of the steps involved in solving the mass balance is given in Section 3.2 with rate constants describing considered inter- and intramedia fate processes for all six crop types formulated in Table 2.3 and further described in Appendix A, and with all underling input data given in Appendix B.

2.5.3. Human intake fractions from multiple crops

Human intake fractions and characterization factors are calculated as measures normalized to one unit mass of applied pesticide for 726 potential substance-crop combinations, that is, 121 substances applied to six different crops. Intake fractions of a pesticide can vary between 4 and 14 orders of magnitude for fenoxaprop-p and flufenacet, respectively, when applied to different crops at recommended doses and harvested at typical times after applications. In contrast, iF between all pesticides applied to the same crop can vary between three (potato) and sixteen (wheat) orders of magnitude, thereby indicating that substance properties are almost as influential on iF as crop properties. The lowest intake fraction is found for metam sodium applied to apple with $\text{iF} = 1.7 \times 10^{-20}$ $\text{kg}_{\text{intake}}\,\text{kg}^{-1}_{\text{applied}}$, whereas the highest intake fraction is found for epoxiconazole applied to lettuce with $\text{iF} = 1.9 \times 10^{-1}$ $\text{kg}_{\text{intake}}\,\text{kg}^{-1}_{\text{applied}}$.

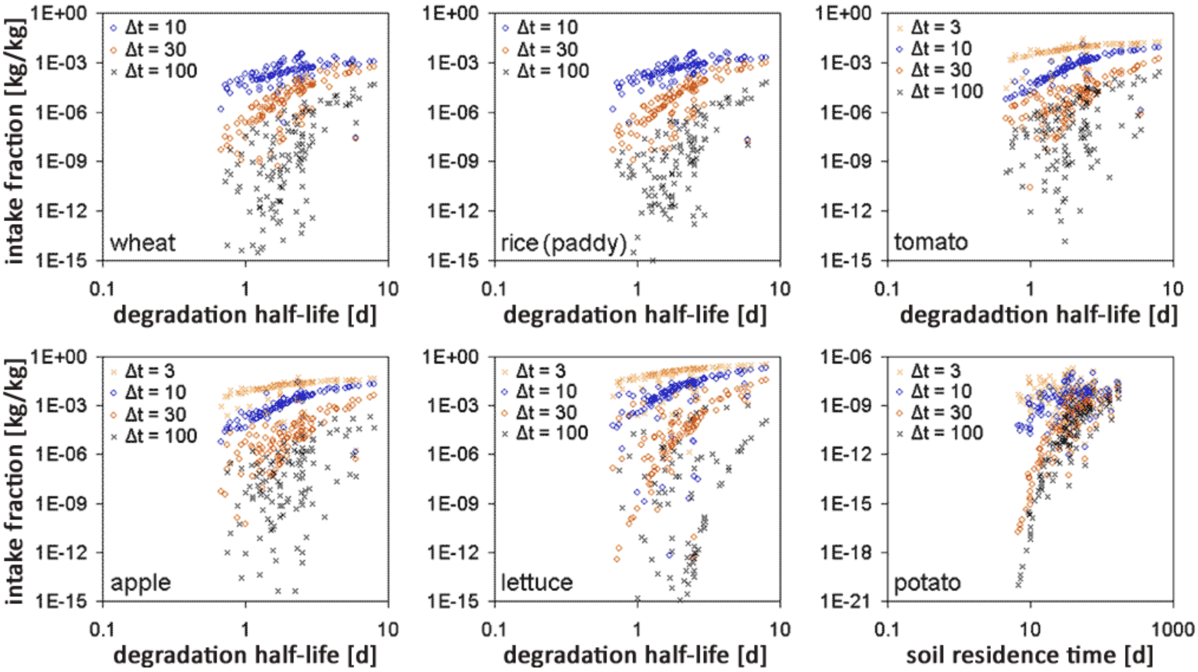


Figure 2.7.: Intake fractions as a function of degradation half-lives of pesticides ($n = 121$) in plants for different time periods between substance application and crop harvest (Δt) for each of the six studied crops.

Substance degradation in plants and the *time between pesticide application and crop harvest* are known to predominantly determine model sensitivity (Fantke et al., 2011a; Juraske et al., 2009a). In Figure 2.7, human intake fractions are presented as a function of the substance degradation half-life in plants – typically varying between 1 and 10 days – for different times to harvest. For all crops but potato, intake fractions are typically in the range of 10^{-2} and 10^{-8} $\mathrm{kg_{intake}\,kg_{applied}^{-1}}$ for typical times between application and harvest. Decreasing the half-life in plants results in continuously decreasing iF, with the magnitude of decrease being amplified up to 10 orders of magnitude with higher time lag between application and harvest. In this case, the difference in degradation of pesticides within crops has more time to establish a significant influence. When looking at potato, there is little influence of the degradation half-life in plant. Instead, the residence time in soil is a main factor of influence affecting iF variation in Figure 2.7. Residence times in soil are more adequate than half-lives to examine iF variation for potato, since they encompass the various removal processes in soil and since the pesticide always has to pass the heterogeneous soil layer, before entering the tuber. In this case, soil characteristics become predominant (Paraíba and Kataguiri, 2008; Juraske et al., 2011).

How crop and substance characteristics as well as time to harvest are influencing the variation of intake fractions is contrasted in Figure 2.8. For the same generic time between application and harvest of 20 days (dark boxes), potato shows the lowest range of intake fractions with a median of 2.7×10^{-7} $\mathrm{kg_{intake}\,kg_{applied}^{-1}}$ and less than 3 orders of magnitude variation between 5th and 95th percentiles. Potato is followed by cereals and fruit crops, for which one basically obtains a similar behavior with median iF ranging from 2×10^{-5} to 2.5×10^{-4} $\mathrm{kg_{intake}\,kg_{applied}^{-1}}$ and typical variation ranges from 2 to 4 orders of magnitude between pesticides. In contrast, lettuce as leafy crop shows highest iF with a median of 4.3×10^{-4} $\mathrm{kg_{intake}\,kg_{applied}^{-1}}$ and 6 orders of magnitude variation.

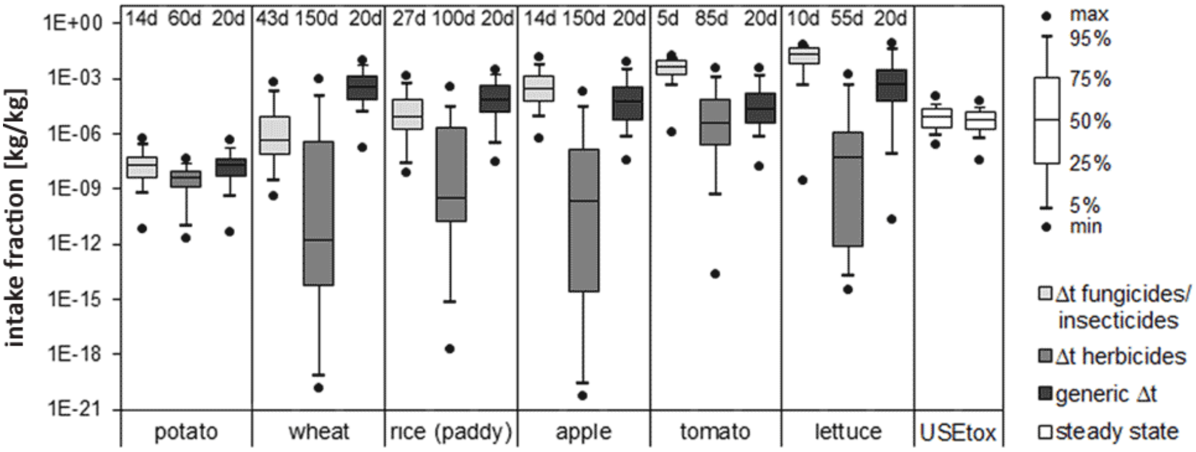


Figure 2.8.: Box and whisker plot of human intake fractions for pesticides directly applied to the six selected crops ($n = 121$, dynamic assessment for different times between application and harvest Δt) and from fractions lost from the field ($n = 97$, assessed with USEtox, steady state, left box: losses via wind drift, right box: losses via run off and leaching).

Another set of influencing factors are the intrinsic crop characteristics, mainly due to losses during application via wind drift, LAI growth over time and food processing after harvest. Drift fractions, however, are not only crop-specific, but also depend on application method, for example, foliar spray or soil injection, whereas loss fractions due to food processing also differ between substances. In practice, times between application and harvest depend on crop species, pest occurrence, weather conditions and a pesticide's mode of action. However, for providing best estimates it is required to distinguish between pesticide target classes for arriving at typical times to harvest. For fungicides and insecticides, officially reported minimum pre-harvest intervals are selected. Usually, fungicides and insecticides can be applied in late life stage depending on pest infection; hence, the official interval serves as benchmark for calculating times to harvest. Herbicides, in contrast, are usually applied pre-emergent or during early crop growth in order not to damage the cultivated species resulting in relatively long times to harvest between 55 and 150 days. However, there are two special cases. First, conditions for apple as perennial plant are generally less strict, if herbicides are applied careful enough to not wetting the leaves. Second, herbicide application on potato is also allowed during later crop stages to help withering unwanted aerial plant parts. Overall, average times to harvest range between 5 days for fungicides/insecticides applied to tomato and 150 days for herbicides applied to wheat and apple. Varying application times lead to additional iF variation between pesticides with herbicides showing lower intake fractions and higher variation due to their longer time lags between application and harvest. (Figure 2.8, gray middle boxplots). For fungicides and insecticides, the later application leads to higher intake fraction, especially for tomato and lettuce, for which application can take place only 5 to 10 days before harvest (Figure 2.8, left box plots).

In addition, the calculated crop-specific characterization factors for direct residues are compared and eventually combined with generic characterization factors as calculated with the USEtox model (Rosenbaum et al., 2008) for the set of selected test substances accounting for the pesticide fraction that is lost to beyond the field boundaries. Figure 2.8 also enables to compare direct pesticide application modeled dynamically with these fractions calculated by USEtox assuming steady-state conditions and continuous input (see two white box-plots at the right end of Figure 2.8). With the generic time to harvest of 20 days, all crops except potato show higher iF due to direct application residues compared to iF due to fractions lost from the field. For recommended times to harvest, median iF of herbicides applied to all crops and of fungicides/insecticides applied to cereals decrease below USEtox values. In contrast, for fungicide/insecticide applied shortly before harvest (tomato, lettuce), median intake fractions from the fractions lost to beyond field boundaries strongly underestimate overall intake by up to 4 orders of magnitude. Finally, in the case of potatoes, residues from direct application of all pesticides remain of minor importance, that is, with lower median iF values, than due to fractions lost from the field.

2.5.4. Characterization factors and impact scores

Characterization factors for the set of 121 pesticides applied to the six selected food crops are calculated according to Eq. 2.20 to characterize the direct impact per kg of pesticide applied. However, since not all substance-crop combinations are officially authorized, overall impacts per ha are only calculated for a subset of 181 substance-crop combinations authorized for use in at least one of the countries listed in the Codex Alimentarius (CAC Codex Alimentarius Commission, 2010) with given recommended amounts applied. The whole source to impact pathway from pesticide application to human impacts is summarized in Table 2.9 for the six different crops, except effect factors, which are not crop-dependent. Median effect factors with 5^{th} and 95^{th} confidence interval limits given in brackets are for cancer effects $\text{EF}_{\text{cancer}} = 0.17\ (0.007 - 1.6)$ $\text{DALY}\,\text{kg}_{\text{intake}}^{-1}$ and for noncancer effects $\text{EF}_{\text{noncancer}} = 0.11\ (0.009 - 2.5)$ $\text{DALY}\,\text{kg}_{\text{intake}}^{-1}$. Variability in human impacts is before all due to variation in intake fraction (15 orders of magnitude). Additional limited variability is introduced by human effect factors, more specifically by substance-specific dose-response slope factors. Information related to cancer effects is given in Rosenbaum et al. (2008) for less than 20% of the 121 pesticides, which is in line with Huijbregts et al. (2005). In addition, 77% of substances with available information related to cancer do not show any cancer potential (effect factors set to zero). This indicates that most of today's pesticides are rather leading to noncancer effects. All in all, effect factors vary by 3.5 orders of magnitude between pesticides. The combination of large variations in intake fractions with lower variations in effect factors leads to an overall variation in characterization factors of almost 17 orders of magnitude (Table 2.9). Combining this with variability in applied pesticide mass of 4 orders of magnitude tends to reduce the overall variability on the impact score to 13 orders of magnitude, suggesting that some of the pesticides applied at low dose tend to have rather high toxicity potentials.

Table 2.9.: Median values with 5th and 95th percentiles (in brackets) of crop-specific application amount m_{applied}, intake fraction iF, characterization factor CF, and impact score IS for 121 pesticides.

crop	m_{applied} [$\text{kg}_{\text{applied}}\,\text{ha}^{-1}$]	iF [$\text{kg}_{\text{intake}}\,\text{kg}^{-1}_{\text{applied}}$]	CF [$\text{DALY}\,\text{kg}^{-1}_{\text{applied}}$]	IS [$\text{DALY}\,\text{ha}^{-1}$]
wheat	0.16 (0.01 – 2.9)	1.0×10^{-4} ($10^{-16} - 3.9 \times 10^{-4}$)	1.2×10^{-7} ($10^{-18} - 5.5 \times 10^{-5}$)	3.1×10^{-5} ($10^{-15} - 3.6 \times 10^{-5}$)
paddy rice	0.75 (0.04 – 3.8)	6.9×10^{-3} ($10^{-10} - 2.3 \times 10^{-3}$)	1.3×10^{-6} ($10^{-12} - 3.3 \times 10^{-4}$)	5.7×10^{-4} ($10^{-13} - 9.7 \times 10^{-4}$)
tomato	0.27 (0.02 – 4.8)	3.9×10^{-2} ($10^{-12} - 1.7 \times 10^{-2}$)	4.1×10^{-4} ($10^{-13} - 1.7 \times 10^{-2}$)	2.4×10^{-3} ($10^{-9} - 6.3 \times 10^{-3}$)
apple	0.86 (0.04 – 3.2)	9.5×10^{-3} ($10^{-18} - 6.0 \times 10^{-3}$)	1.4×10^{-5} ($10^{-20} - 2.2 \times 10^{-3}$)	9.0×10^{-4} ($10^{-15} - 4.2 \times 10^{-4}$)
lettuce	0.2 (0.03 – 1.6)	4.3×10^{-2} ($10^{-14} - 9.5 \times 10^{-2}$)	4.8×10^{-4} ($10^{-16} - 4.1 \times 10^{-2}$)	8.5×10^{-3} ($10^{-8} - 4.9 \times 10^{-3}$)
potato	0.89 (0.03 – 101)	1.8×10^{-6} ($10^{-9} - 4.7 \times 10^{-6}$)	1.4×10^{-8} ($10^{-11} - 2.6 \times 10^{-6}$)	1.2×10^{-6} ($10^{-11} - 9.9 \times 10^{-6}$)

2.5.5. Functional assessment and pesticide substitution

When assessing the change in impacts linked to substitution of pesticides, a functional assessment is required, ensuring that the combination and quantities of pesticides applied are able to control a set of distinct pests in an equivalent way. A set of substitution scenarios of different pesticide target classes applied to wheat against a set of common pests is developed and presented in Figure 2.9 as example of how to conduct crop-specific substitution.

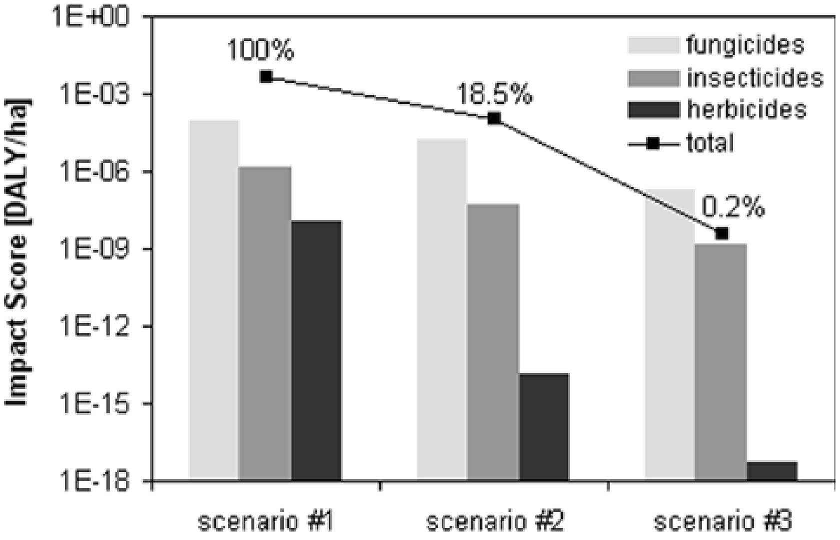


Figure 2.9.: Human toxicity impact scores of different scenarios expressed in DALY per ha of applied fungicides, insecticides, herbicides and total pesticides applied on wheat, and relative impact scores normalized to scenario #1.

Table 2.10 presents the background information for the three scenarios of substituting a mix of (a) insecticides, (b) fungicides and (c) herbicides based on the combination of applied dose and toxicity potential. Data on common wheat pests are derived from Jørgensen et al. (2008); LWK Landwirtschaftskammer Nordrhein-Westfalen (2009); Prescott et al. (1986). Pesticide target classes focus on distinct pest categories, for example, fungi, insects, weeds. Substitution, hence, must be discussed separately within each pesticide target class, for example, insecticides can only be substituted by other insecticides targeting the same insect pests.

In scenario #1, applications of β-cyfluthrin and carbaryl are exemplarily combined on wheat against a set of common wheat-damaging insects (wheat bulb fly, cereal leaf beetle, aphids, and thrips). This insecticide mix is substituted by a combination of the less human health impacting insecticides α-cypermethrin and deltamethrin in scenario #3. Individual insecticides and application rates are chosen to ensure a similar ability to control the same unwanted insects in both scenarios. Figure 2.9 demonstrates that substituting scenario #1 by scenario #3 reduces the total impact score of applied insecticides by more than 4 orders of magnitude to less than 0.1% of the impact score of scenario #1.

This approach is similarly applied to fungicides and herbicides, where substituting scenario #1 by scenario #3 results in impact scores reduced by more than 2 and 6 orders of magnitude, respectively. Scenario #2 represents an intermediary situation showing some, but not as much reduction in impact scores for all target classes as scenario #3.

Table 2.10.: Pesticide target class, scenario, selected pesticides (classified according to target class), target species, recommended application amount m_{applied} [kg ha^{-1}], substance-specific impact score $\text{IS}_{\text{substance}}$ [DALY ha^{-1}], impact score aggregated over target class IS_{class} [DALY ha^{-1}], and relative impact score θ_{IS} normalized to scenario #1 for three pesticide substitution scenarios on wheat.

	scenario	pesticide	target pests*				m_{applied}	$\text{IS}_{\text{substance}}$	IS_{class}	θ_{IS}
insecticides			A	B	C	D				
	#1	β-cyfluthrin	x	x	x		13.75	2.2E-07	1.5E-05	100%
		carbaryl		x	x	x	1.48	1.5E-05		
	#2	cyhalothrin	x	x	x	x	0.008	5.2E-08	5.3E-08	0.4%
		esfenvalerate		x	x	x	0.012	9.4E-10		
	#3	α-cypermethrin	x	x	x	x	0.015	2.2E-10	2.4E-10	<0.1%
		deltamethrin	x	x	x	x	0.009	2.5E-11		
fungicides			E	F	G	H				
	#1	cyproconazole	x	x	x	x	0.08	3.5E-04	3.6E-04	100%
		azoxystrobin	x	x	x	x	0.238	7.1E-06		
	#2	epoxiconazole	x	x	x	x	0.125	6.3E-05	6.3E-05	17.5%
		pyraclostrobin	x	x	x	x	0.175	8.7E-08		
		fenpropimorph		x	x	x	0.45	9.3E-09		
	#3	tebuconazole		x		x	0.219	2.3E-07	2.7E-06	0.8%
		chlorothalonil	x	x	x		1.5	2.4E-06		
		mancozeb	x	x	x		2.35	1.2E-07		
herbicides			J	K	L	M				
	#1	pendimethalin	x	x			1.4	2.5E-08	2.5E-08	100%
		fenoxaprop-p	x		x		0.069	4.7E-10		
		prosulfocarb	x	x		x	3.5	2.2E-16		
	#2	glyphosate	x	x	x	x	1.37	8.1E-11	8.1E-11	0.3%
	#3	iodosulfuron		x	x		0.01	4.3E-15	4.3E-15	<0.1%
		propoxycarbazone-sodium	x			x	0.05	1.7E-17		

* A: wheat bulb fly (*Delia coarctata*), B: cereal leaf beetle (*Oulema melanopa*), C: aphids (*Aphidoidea*), D: thrips (*Thysanoptera*), E: septoria leaf blotch (*Mycosphaerella graminicola*), F: wheat leaf rust (*Puccinia triticina*), G: wheat yellow rust (*Puccinia striiformis*), H: powdery mildew (*Blumeria graminis f. sp. Tritici*), J: slender meadow foxtail (*Alopecurus myosuroides*), K: annual meadow grass (*Poa annua*), L: common wild oat (*Avena fatua*), M: couch grass (*Elytrigia repens*).

2.5.6. Conclusions

Potential and limitations. The presented approach demonstrates the importance of dynamic pesticide assessment and enables the user to distinguish between various food crops. By identifying the combined influence of crop characteristics, application times and substance properties it was demonstrated that it is crucial to choose appropriate times to apply pesticides and that the fractions lost to beyond the field boundary may be significant for early application, whereas human intake for late application before harvest might be strongly underestimated when disregarding residues in directly treated crops. For practical implementation, it is therefore recommended to use crop-specific characterization factors to account for direct application residues. Thereby, it was stressed that results must always be interpreted as a function of times to harvest, that is, recalculations are required to account for changing the date of pesticide application. To account for impacts caused by the fractions lost from the field in addition to direct residues, initial loss fractions from air via wind drift and from soil via run off and leaching should be multiplied by the USEtox characterization factors for emissions to urban air and agricultural soil, respectively. For typical foliar application, crop-specific loss fractions to air range from 5 to 25% and to soil from 5 to 70%, respectively, where the latter also depends on crop development stage. All crop-specific characterization factors are global averages and based on generic values for most underlying parameters, such as human lifetime and body weight. Hence, for a spatial assessment, these parameters need to be adjusted accordingly. The present approach is so far limited to neutral organic substances, since inorganics require a different consideration of their partitioning behavior and ionizable compounds require considering electrochemical interactions for the dissociated species.

Differences between crops. Variation in crop-specific intake is mainly driven by distinct characteristics between crop archetypes, for example, with respect to harvested plant components, from which food crops can basically classified into roots and tubers, fruits and cereals, as well as leafy vegetables. Overall, leafy vegetables only contribute to 2% of the total human vegetal consumption, but may nevertheless lead to human impacts comparable or even higher than via ingestion of cereals. Cereals, on the other hand, contribute to 37% of the human vegetal consumption (including paddy cereals), but substances are usually applied earlier for these crops, leading to lower intake fractions. Highest impacts are expected via consumption of herbaceous crops and fruit trees with usually high intake fractions and consumption, while roots and tubers only contribute little due to very low intake fractions.

Pesticide Substitution. Whenever developing substitution scenarios, it is strongly recommended to consider aspects related to pesticide authorization, since a substance may be authorized for use on particular crops in some countries, but not in others, because of decreased susceptibility of target pests (resistance) to certain pesticides. Furthermore, for considering multiple applications at different application times, Eq. 2.19 can be summed up over various applications in addition to summing up over pesticides per crop. However, usually only the latest application plays a predominant role due to increasing reduction of intake fractions with time (Juraske et al., 2011).

3. Matrix-based system analysis and uncertainty assessment for model evaluation and parameterization

3.1. Summary

Dynamic plant uptake models are suitable for assessing environmental fate and behavior of toxic chemicals in food crops. However, existing tools mostly lack in-depth analysis of system dynamics. Furthermore, no existing model is available as parameterized version that is easily applicable for use in spatial or nested multimedia models applied in comparative impact assessment. Therefore, the dynamics of substance masses in a multi-compartment crop-environment system is analyzed by applying mathematical decomposition techniques (Section 3.2). The focus is on the evolution of pesticide residues in crop components harvested for human consumption by taking wheat grains as example. Results show that fruit, fruit surface and soil are the compartments predominantly influencing the mass evolution of most pesticides in the plant-environment system as a function of substance degradation in plant components and overall residence time in soil. Additional influences are associated with substance molecular weight and time span between pesticide application and crop harvest. To evaluate the findings and thereby the functioning of the dynamical system, model results were already compared against independent data, i. e. experimentally derived pesticide residues in different crops, in Sections 2.3 and 2.4. Building on these findings, an accurate and yet simple linear approximation of the dynamical system is provided to predict masses in harvested crop components relative to the total applied pesticide. This simplified model version can finally be used in existing health impact assessments of pesticide use to also account for the fraction of an applied pesticide that ends up as residues in the treated food crops.

For identifying crop-specific key aspects and quantifying their influence on model output, a matrix-based sensitivity and uncertainty assessment is performed including the consideration of correlations between input variables (Section 3.3). Overall model output uncertainty is lowest for potato and highest for lettuce.

As final step, a parametric model is designed for six major crop types as a linear combination of individual compartments to predict pesticide residues in crop harvest (Section 3.4). Parameterized predictions correspond well with results from the full dynamic model, with an overall deviation of a factor 22 for harvest fractions in the relevant range

between 1 and 10^{-10} in wheat and with deviations in the same relevant range between a factor of 4 for harvest fractions in potato and a factor of 276 for harvest fractions in tomato. The in-depth analysis of model dynamics provides additional information of the evolution of pesticides in food crops, which is important for regulators and practitioners. In addition, the parametric representation of system dynamics allows for drastically reducing input data requirements and for comparing harvest fractions of a wide range of substances without using a complex dynamic model.

3.2. Analyzing the functioning of the system and model parameterization

3.2.1. Introduction and background

Multimedia plant uptake models are widely used tools to assess the fate of toxic chemicals, such as pesticides, in the complex plant-environment system and to evaluate subsequent human exposure towards substance residues in food crops (Fryer and Collins, 2003; Fantke et al., 2011a). The dynamics of the underlying compartmental mass balances is controlled on the one hand by fate processes of chemicals and on the other hand by functions describing substance application or emission. Fate processes in field crops, i. e. uptake, translocation and elimination mechanisms, depend on substance properties and vary considerably between individual plant species (Trapp and Kulhanek, 2006; Fantke et al., 2011b). Uptake models, hence, need to assess substances individually and to account for crop-specific characteristics. Emissions usually are described as constant input, such as continuous background emissions of rather persistent chemicals yielding steady-state conditions. In contrast, direct pesticide application via e. g. foliar spray is adequately described by a pulse input function. Here, steady-state assumptions will be invalid, since the steady state might never be reached, and a dynamic assessment is required to solve the resulting system of differential equations (Charles, 2004).

In recent years, several crop-specific dynamic uptake models for assessing the mechanistic principles of substance flows in field crops cultivated for human or animal consumption have been developed. Some of the models are designed to focus on cereals (Fantke et al., 2011a; Rein et al., 2011), others on vegetables (Fujisawa et al., 2002a; Juraske et al., 2009a) or root-crops (Trapp et al., 2007; Juraske et al., 2011), and yet others on fruit trees (Paraíba, 2007). Such models are usually based on ordinary first order kinetics with constant coefficients describing substance elimination and inter-compartmental transfer processes. However, existing models require a large set of crop- and chemical-specific input parameters, while at the same time lacking a comprehensive understanding of the functioning of the underlying multi-compartment system. This is particularly critical, as many input parameters describing certain substance properties and crop characteristics are only rarely, if at all, available and come along with high uncertainties, such as crop development over time (Bechini et al., 2006) or substance degradation in plants (Thomas et al., 2011). To manage the complexity resulting from a multi-compartment system relying on numerous input parameters, some dynamic models use numerical methods for solving underlying mass balances, whereas others apply analytical solutions. Although numerical methods allow to also addressing time-varying processes and are thus able to simulate truly dynamic system behavior (Holzbecher, 2007), they only provide moderate insight into the functioning of their dynamical systems. Hence, for assessing the fate of pesticides in multi-compartment systems in a transparent and concise way, analytical solutions are clearly favored wherever possible, which is in line with Hertwich (2001b); Charles (2004) and Rein et al. (2011). When using analytical methods, the mass balance can either be solved for each compartment individually or for all compartments at the same time, of which the latter provides high transparency. Rein et al. (2011) developed a dynamic uptake model, where the mass balance differential equations for all involved compartments are solved simultaneously by means of matrix algebra. However, this approach is reported to be restricted to unidirectional transfer between compartments. A unidirectional system implies that feedbacks from backflow, reverse or bidirectional processes are omitted (Trapp and Matthies, 1998), which is a clear constraint for the flexibility of a modeled system. Flexibility, however, is a precondition when a dynamic uptake model is designed to assess various crop types within a single framework with each crop type requiring a different number of involved compartments and a specific set of fate processes (Fantke et al., 2011b). Since all existing tools build on a fixed set of environmental and plant compartments, a new approach was developed to analytically solve a flexible system of differential equations with first order kinetics as described in Chapter 2.

It is the aim of this study to present the underlying transparent and concise analytical technique to simultaneously solve a flexible set of differential equations simulating the full dynamiCROP model. The approach is based on a particular mathematical decomposition of the equations representing the dynamical system. Thereby, an in-depth analysis of the system's functioning is provided with focus on the influence of initial conditions, process rate coefficients and compartment characteristics by looking at the pesticide mass evolution in harvested plant components relevant for human or animal consumption. The following specific questions will be addressed in the present section: “To what extent do the various source compartments contribute to the pesticide residues in harvested plant components?” and “What is the influence of initial mass distribution on residues in harvest?”.

3.2.2. Decomposition of the dynamical system

The considered plant-environment system is described by a set of interconnected compartments, namely air, soil, paddy water, leaf and fruit surface, leaf, fruit, stem and roots. Fruit surface and fruit compartments are omitted for simulating root crops, such as potato, and leafy crops, such as lettuce, and paddy water is exclusively relevant for simulating paddy rice. All processes defining a chemical's fate including degradation, diffusive and advective transfers are aggregated and expressed as rate coefficients with a summary given in Table 2.3. Transfer coefficients connect the different compartments. Coefficients denoting degradation and transport beyond the model domain, e. g. leaching towards the groundwater level, constitute losses from compartments. Mathematically, this leads to a dynamical system that can be described by a set of ordinary first order linear differential equations with constant coefficients for translating the compartmental system and the chemical's behavior in that system into a typical multi-compartmental mass balance problem. The set of coupled differential equations thereby describes the conditions concerning the change of the system's state variable, namely the time-dependent substance mass, as follows:

$$\lim_{\Delta t \to 0} \left\{ \frac{\Delta \vec{m}(t)}{\Delta t} \right\} = \frac{\mathrm{d}\vec{m}(t)}{\mathrm{d}t} = \mathbf{K}\,\vec{m}(t) + \vec{s} \tag{3.1}$$

The term $\mathrm{d}\vec{m}(t)/\mathrm{d}t$ describes the change of masses over time and is proportional to $\vec{m}(t)$ with vector $\vec{m} \in \mathbb{R}^n$ containing elements to describe the masses of a chemical [kg] at time t [d]. Under inhomogeneous conditions, i. e. with continuous emissions or background concentrations as input, $\vec{s} \in \mathbb{R}^n$ represents the vector containing elements of constant input [kg d^{-1}]. Finally, $\mathbf{K} \in \mathbb{R}^{n \times n}$ is the square matrix of first order rate coefficients k_{ij} [d^{-1}]. Each main diagonal element of $\mathbf{K}$, i. e. k_{ij} with $i = j$ and $i, j \in \{1, \ldots, n\}$, contains the bulk removal rate coefficient in compartment i, $k_{i,\mathrm{loss}}$, plus the sum of transfer rate coefficients from compartment i to relevant adjacent compartments j, and off-diagonal elements of $\mathbf{K}$, i. e. k_{ij} with $i \neq j$ and $i, j \in \{1, \ldots, n\}$ contain individual transfer rate coefficients from compartment j to compartment i. $\mathbf{K}$, hence, has the following structure:

$$\mathbf{K} = \begin{pmatrix} k_{11} & \cdots & k_{1n} \\ \vdots & \ddots & \vdots \\ k_{n1} & \cdots & k_{nn} \end{pmatrix} \text{ with } k_{ij} = \begin{cases} k_{ij} & \text{for } i \neq j \\ -\left(k_{i,\mathrm{loss}} + \sum\limits_{l=1,\, l \neq i}^{n} k_{li} \right) & \text{for } i = j \end{cases} \tag{3.2}$$

with line and column indices for receiving and source compartments, respectively. For characterizing the dynamical system, the mass balance is solved by finding a vector function $\vec{m}(t)$ that verifies the differential equation in Eq. 3.1 for any value of the independent variable t in its domain.

Different analytical methods exist for solving the mass balance in Eq. 3.1, e. g. Laplace transforms or matrix decomposition. Both concepts have been successfully applied in environmental science for solving multicompartment mass balance problems (Hertwich, 2001b; Logan, 2001; Ott et al., 2003; von Waldow et al., 2008; Fantke et al., 2011a) and are based on the transformation of a system from its original into another domain to simplify the problems' manipulations. However, the frequency domain as used in the Laplace transform approach describes the behavior of a system at specific frequencies and is typically an input/output representation. In contrast, the time domain as used in matrix decomposition approaches is a state space representation typically containing information on inputs, outputs, and internal states of a system. More precisely, the vector of masses $\vec{m}(t)$ in Eq. 3.1 at any time t contains the full information of the system's evolution over all past and future times. Therefore, $\vec{m}(t)$ is referred to as the system's state with its elements representing the state variables. Since in the present approach the evolution of substance masses in the various compartments over time is of interest, a state space representation is the more convenient and direct approach. For solving the multi-compartment system, the original mass balance problem is therefore decomposed, thereby maintaining all fundamental information that helps to fully understand the functioning of the system. Before performing the decomposition, the system will be simplified (homogenized), as solving a homogeneous system and transferring the solution back to the original, inhomogeneous system avoids solving integrals for considering constant input terms. Furthermore, a pulse application of pesticides as input function is of primary interest, which is already represented by the initial conditions and no constant input term is required, i. e. $\vec{s} = 0$. For the sake of completeness, the solution for a system with constant, continuous input $\vec{s}$ is also provided, of which the condition $\vec{s} = 0$ is a particular case. To homogenize the system, a differential equation can be written for

$$\vec{m}_{\Delta}(t) \triangleq \vec{m}(t) - \vec{m}_{\mathrm{ss}} \tag{3.3}$$

where $\vec{m}_{\Delta} \in \mathbb{R}^n$ defines the difference between the actual mass vector $\vec{m}(t)$ and the steady state mass vector $\vec{m}_{\mathrm{ss}}$. The steady state mass vector is obtained by solving Eq. 3.1 in the particular case $\mathrm{d}\vec{m}(t)/\mathrm{d}t = 0 = \mathbf{K}\,\vec{m}_{\mathrm{ss}} + \vec{s} \Rightarrow \vec{m}_{\mathrm{ss}} = -\mathbf{K}^{-1}\,\vec{s}$, where $\mathbf{K}$ is non-singular, i. e. the inverse of $\mathbf{K}$ exists (Lipschutz and Lipson, 2009). With that, a set of differential equations is obtained as a function of $\vec{m}_{\Delta}(t)$ to arrive at a homogeneous system:

$$\begin{aligned}
\frac{\mathrm{d}\vec{m}_{\Delta}(t)}{\mathrm{d}t} &= \frac{\mathrm{d}\vec{m}(t)}{\mathrm{d}t} - \overbrace{\frac{\mathrm{d}\vec{m}_{\mathrm{ss}}}{\mathrm{d}t}}^{=0} \\
&= \mathbf{K}\,\vec{m}(t) + \vec{s} && \text{(substituting Eq. 3.3)} \\
&= \mathbf{K}\big(\vec{m}_{\Delta}(t) + \vec{m}_{\mathrm{ss}}\big) + \vec{s} \\
&= \mathbf{K}\,\vec{m}_{\Delta}(t) + \mathbf{K}\,\vec{m}_{\mathrm{ss}} + \vec{s} \\
&= \mathbf{K}\,\vec{m}_{\Delta}(t) - \mathbf{K}\,\mathbf{K}^{-1}\,\vec{s} + \vec{s} && \text{(substituting } \vec{m}_{\mathrm{ss}}\text{)} \\
&= \mathbf{K}\,\vec{m}_{\Delta}(t)
\end{aligned} \tag{3.4}$$

With the composition of **K** given in Eq. 3.2 it can be seen that the system is coupled by transfer rate coefficients connecting compartments. To decouple the equations, matrix decomposition techniques are applied, more specifically an *Eigendecomposition*, which allows to further analyze the system dynamics. In what follows, it is assumed that the matrix of rate coefficients **K** possesses n linearly independent Eigenvectors $\vec{v}_i, i \in \{1,\dots,n\}$ with corresponding Eigenvalues $\lambda_i, i \in \{1,\dots,n\}$, i. e. the pairs satisfy the linear Eigenvalue equation (Kamaraju and Narasimham, 2009):

$$\mathbf{K}\,\vec{v}_i = \lambda_i\,\vec{v}_i, \qquad i \in \{1,...,n\} \tag{3.5}$$

from which the matrix $\mathbf{V} \in \mathbb{R}^{n\times n}$ of Eigenvectors is defined, ordered according to the order of the diagonal elements of the diagonal matrix $\mathbf{\Lambda} \in \mathbb{R}^{n\times n}$ of corresponding Eigenvalues as follows:

$$\mathbf{V} \triangleq \begin{pmatrix} \vec{v}_1 & \cdots & \vec{v}_n \end{pmatrix}, \quad \mathbf{\Lambda} \triangleq \begin{pmatrix} \lambda_1 & & 0 \\ & \ddots & \\ 0 & & \lambda_n \end{pmatrix} \tag{3.6}$$

All Eigenvalues are strictly negative due to decreasing masses over time in each compartment, thereby ensuring that the contribution of all exponential terms containing an Eigenvalue converge against zero for masses evolving towards steady state conditions, i. e. for $t \to \infty$. Eq. 3.5 can now be re-written in vector-matrix notation and solved for $\mathbf{\Lambda}$ or **K**, respectively:

$$\mathbf{K}\,\mathbf{V} = \mathbf{V}\,\mathbf{\Lambda} \tag{3.7a}$$

$$\mathbf{\Lambda} = \mathbf{V}^{-1}\,\mathbf{K}\,\mathbf{V}, \quad \mathbf{K} = \mathbf{V}\,\mathbf{\Lambda}\,\mathbf{V}^{-1} \tag{3.7b}$$

For the next step, base change/domain change operations for matrices are recognized, i. e. **K** and $\mathbf{\Lambda}$ are the same matrix seen from two different bases or in two different domains. More precisely, **K** and **Λ** are said to be *similar* with the physical (or canonical) basis being the basis for **K** (the presented physical system of compartments) and the Eigenvectors constituting a basis for **Λ** (the transformed system). This is as with the given structure, **K** is assumed to be diagonalizable and invertible, i. e. non-singular (Kwak and Hong, 2004) and can thus be transformed into another, similar matrix by ordinary matrix multiplication. Since the transformation is based on similarity, most of the properties of **K**, such as the dynamics of masses in the system, are kept in the similar matrix **Λ**, while some specific properties have changed. The most important difference is that the mass system is uncoupled after its transformation into new coordinates, allowing to independently solving the transformed mass balance equations in Eigenbasis. Using matrix **V** of Eigenvectors from Eq. 3.6, a change of coordinates for the deviation mass vector $\vec{m}_{\Delta(\mathrm{E})}(t)$ is defined as follows:

$$\vec{m}_{\Delta(\mathrm{E})}(t) = \mathbf{V}^{-1}\,\vec{m}_{\Delta}(t), \quad \vec{m}_{\Delta}(t) = \mathbf{V}\,\vec{m}_{\Delta(\mathrm{E})}(t) \tag{3.8}$$

With that, the differential equation for the transformed deviation mass vector in Eigenbasis $\vec{m}_{\Delta(\mathrm{E})}(t)$ is obtained:

$$\begin{aligned}
\frac{\mathrm{d}\vec{m}_{\Delta(\mathrm{E})}(t)}{\mathrm{d}t} &= \frac{\mathrm{d}\big(\mathbf{V}^{-1}\,\vec{m}_{\Delta}(t)\big)}{\mathrm{d}t} && \text{(substituting } \vec{m}_{\Delta(\mathrm{E})}(t) \text{ from Eq. 3.8)}\\
&= \mathbf{V}^{-1}\,\frac{\mathrm{d}\vec{m}_{\Delta}(t)}{\mathrm{d}t} && \text{(by product rule)}\\
&= \mathbf{V}^{-1}\mathbf{K}\,\vec{m}_{\Delta}(t) && \text{(substituting Eq. 3.4)}\\
&= \mathbf{V}^{-1}\,\mathbf{K}\,\mathbf{V}\,\vec{m}_{\Delta(\mathrm{E})}(t) && \text{(substituting } \vec{m}_{\Delta}(t) \text{ from Eq. 3.8)}\\
&= \mathbf{\Lambda}\,\vec{m}_{\Delta(\mathrm{E})}(t) && \text{(substituting } \mathbf{\Lambda} \text{ from Eq. 3.7b)}
\end{aligned} \tag{3.9}$$

The solution of Eq. 3.9 can be written as linearly depending on the initial conditions $\vec{m}_{\Delta(\mathrm{E})}(0)$:

$$\vec{m}_{\Delta(\mathrm{E})}(t) = \mathrm{e}^{\mathbf{\Lambda}\,t}\;\vec{m}_{\Delta(\mathrm{E})}(0) \tag{3.10}$$

This system has the advantage to be uncoupled as **Λ** is diagonal, which translates into a simple, diagonal form for $\mathrm{e}^{\mathbf{\Lambda}\,t}$:

$$\mathrm{e}^{\mathbf{\Lambda}\,t} = \begin{pmatrix} \mathrm{e}^{\lambda_1\,t} & & 0 \\ & \ddots & \\ 0 & & \mathrm{e}^{\lambda_n\,t} \end{pmatrix} \tag{3.11}$$

This indicates that each component of $\vec{m}_{\Delta(\mathrm{E})}(t)$ has the form $m_{\Delta(\mathrm{E}),i}(t) = \mathrm{e}^{\lambda_i\,t}\;m_{\Delta(\mathrm{E}),i}(0)$, $i \in \{1,\ldots,n\}$, which describes a simple exponential decrease. In this basis, the long term dynamics are therefore dominated by the component with the smallest $|\lambda_i|$ and a non-zero initial condition $m_{\Delta(\mathrm{E}),i}(0) \neq 0$ (Stroebe et al., 2004). How to compute this solution based on the exponential of a matrix defined as the limit of the sequence $\left[\mathrm{e}^{\Lambda t}\right]_{ij}$, $i, j \in \{1, \ldots, n\}$, can be found elsewhere, e. g. in Kwak and Hong (2004, p. 232 ff.). It can now be proceeded to transform this solution back into the homogeneous physical coordinates by performing an inverse transformation, more specifically by substituting Eq. 3.10 in Eq. 3.8:

$$\vec{m}_{\Delta}(t) = \mathbf{V}\,\vec{m}_{\Delta(\mathrm{E})}(t) = \mathbf{V}\ \mathrm{e}^{\mathbf{\Lambda}\,t}\ \vec{m}_{\Delta(\mathrm{E})}(0) \tag{3.12}$$

which is the solution in homogeneous physical coordinates in dependence of the initial conditions $\vec{m}_{\Delta(\mathrm{E})}(0)$ given in homogeneous Eigencoordinates. Since as the next step one wants to express the solution in dependence of the initial conditions $\vec{m}_{\Delta}(0)$ in homogeneous physical coordinates, the inverse transformation needs to be applied also to the initial conditions in Eigenbasis, i. e. to the right-hand side of Eq. 3.12. Thus, $m_{\Delta(\mathrm{E})}(t)$ from Eq. 3.8 can be substituted in Eq. 3.12, which yields:

$$\vec{m}_{\Delta}(t) = \mathbf{V}\ \mathrm{e}^{\mathbf{\Lambda}\,t}\ \mathbf{V}^{-1}\,\vec{m}_{\Delta}(0) \tag{3.13}$$

The structure of Eq. 3.13 allows for expressing the solution of the homogeneous mass balance system as a sum of contributions from the various compartments in their original domain, i. e. coordinates that allow physical interpretation. Simplifying the notation yields:

$$\begin{aligned}\vec{m}_{\Delta}(t) &= \underbrace{\mathbf{V}\ \mathrm{e}^{\mathbf{\Lambda}\,t}\ \mathbf{V}^{-1}}_{=:\ \mathbf{\Phi}(t) = \mathrm{e}^{\mathbf{K}\,t}}\,\vec{m}_{\Delta}(0) \\ &= \mathbf{\Phi}(t)\,\vec{m}_{\Delta}(0)\end{aligned} \tag{3.14}$$

The advantage of the expression in Eq. 3.14 is that from the combination of the matrix exponential $\mathrm{e}^{\mathbf{\Lambda}\,t}$ and both the Eigenvector matrix and its inverse, the fundamental or flow matrix $\mathbf{\Phi}(t) \in \mathbb{R}^{n \times n}$ can be defined as described in Antoulas (2005). From Eq. 3.14 – the solution of the homogeneous case for the difference between the actual mass in compartments and the steady state mass – the solution of the problem stated in Eq. 3.1 in inhomogeneous physical coordinates is obtained. The solution is expressed in dependence of the initial conditions $\vec{m}(0)$ and, in addition, of the mass conditions at steady state $\vec{m}_{\mathrm{ss}}$. The steady state mass vector is re-incorporated by substituting $\vec{m}_{\Delta}(t)$ from Eq. 3.3 in Eq. 3.14:

$$\begin{aligned}\vec{m}(t) &= \vec{m}_{\Delta}(t) + \vec{m}_{\mathrm{ss}} \\ &= \mathbf{\Phi}(t)\,\vec{m}_{\Delta}(0) + \vec{m}_{\mathrm{ss}} \\ &= \mathbf{\Phi}(t)\,\big(\vec{m}(0) - \vec{m}_{\mathrm{ss}}\big) + \vec{m}_{\mathrm{ss}}\end{aligned} \tag{3.15}$$

The solution, i. e. the vector of residual substance masses in all compartments at any time, converges to a unique, constant steady state that is unequivocally determined by both the $\mathbf{K}$ matrix and the source vector $\vec{s}$.

Substance masses in some compartments increase until they reach some maximum, before they start decreasing – in case of pulse input only, i. e. for $\vec{s} = 0 \Rightarrow \vec{m}_{\mathrm{ss}} = 0$, substance masses converge towards zero, while in case of additional constant source, substance masses converge towards a non-zero steady state. The time $t_{\max,i}$, $i \in \{1, \ldots, n\}$, at which an element of $\vec{m}(t)$ reaches such a maximum $m_i(t_{\max,i})$, $i \in \{1, \ldots, n\}$, is determined by means of a numerical interior-point algorithm for the solution of a constrained nonlinear minimization problem as described in Waltz et al. (2006). This approach was chosen over the approximate ratio $t_{\max,i} = \frac{\log(k_{ij})-\log(k_{ji}+k_{\mathrm{loss},i})}{k_{ij}-(k_{ji}+k_{\mathrm{loss},i})}$, $i, j \in \{1, \ldots, n\}$, which is applied e. g. by Paraíba and Kataguiri (2008) as a basis for estimating maximum concentrations in plant compartments. The numerical algorithm takes all system interactions into account, while the approximate ratio only considers elements of rate coefficient matrix $\mathbf{K}$ that are either in line or column of compartment i of interest, thereby ignoring transfer processes between compartments j with $j \neq i$, which nevertheless indirectly affect $m_i(t_{\max,i})$.

3.2.3. Analysis of system functioning

Since direct pesticide application can typically be referred to as pulse input, the focus is on the solution given in Eq. 3.15 for the particular case $\vec{s} = 0 \Rightarrow \vec{m}_{\mathrm{ss}} = 0$:

$$\begin{aligned} \vec{m}(t) &= \mathbf{\Phi}(t) \left(\vec{m}(0) - \vec{m}_{\mathrm{ss}}\right) + \vec{m}_{\mathrm{ss}} \\ &= \mathbf{\Phi}(t)\, \vec{m}(0) \end{aligned} \tag{3.16}$$

This solution is specifically designed to cover pulse input defined by the initial conditions as appropriate functions for representing pesticide application and is similar to the structure of the homogenized problem given in Eq. 3.14. The term*source compartment* is hereafter referred to as compartment with non-zero initial condition, keeping in mind that source term is identically equal to zero at all times. The structure of Eq. 3.16 allows observing the dynamics of the decomposed system from different perspectives. In fact, due to linearity of the system underlying Eq. 3.16, relative masses completely characterize the system dynamics. Therefore, in the following observations one is not primarily interested in absolute masses in compartments, but rather in relative masses (or mass fractions) related to overall applied or total residual mass. This involves components of $\mathbf{\Phi}(t)$, whose element at the ith row and jth column is denoted $\varphi_{ij}(t)$ with $i, j \in \{1, \ldots, n\}$. This allows us to express Eq. 3.16 component-wise:

$$m_i(t) = \sum_{k=1}^{n} \varphi_{ik}(t)\, m_k(0), \qquad i \in \{1, ..., n\} \tag{3.17}$$

With the elements of $\mathbf{\Phi}(t)$ the dynamical system can be analyzed in more detail. Starting from the perspective of a single source compartment (e. g. air, soil, or leaf surface) allows to keep track of the applied pesticide mass until ending as residue in one or more receiving compartments. Mathematically, this corresponds to the following question: For a fixed $j \in \{1, \ldots, n\}$, in which receiving compartments does the chemical mass $m_j(0)$ applied to the jth source compartment at time $t = 0$ finally end up as residue? It can be assumed that at time $t = 0$ the total mass $m_{\text{total}}(0)$ is applied exclusively to the jth compartment, while all other initial conditions are kept zero, i. e. $m_j(0) = m_{\text{total}}(0)$ and $m_k(0) = 0$ for all $k \in \{1, \ldots, n\}$, $k \neq j$. Since the total initial mass is applied as an initial condition to a single compartment j, the residual mass in a receiving compartment at any time is a direct consequence of this initial condition. After normalizing the mass in the receiving compartment of interest by the total mass present in the system at time t, this perspective helps to identify compartments that dominate the system dynamics at harvest time. With that, $fr\_m_{i \leftarrow j}(t)$, $i, j \in \{1, \ldots, n\}$, the pesticide mass applied to the jth source compartment at time $t = 0$ is obtained that finally ends up as residue in the ith receiving compartment at time t, $m_i^{j,0}(t)$, $i, j \in \{1, \ldots, n\}$, relative to the overall residual mass in the system, $m_{\text{total}}(t)$, by substituting Eq. 3.17:

$$\begin{aligned} fr\_m_{i \leftarrow j}(t) &= \frac{m_i^{j,0}(t)}{m_{\text{total}}(t)} \\ &= \frac{\varphi_{ij}(t)\, m_j(0)}{\sum_{l=1}^{n} \varphi_{lj}(t)\, m_j(0)} \\ &= \frac{\varphi_{ij}(t)}{\sum_{l=1}^{n} \varphi_{lj}(t)}, \qquad i, j \in \{1, ..., n\} \end{aligned} \tag{3.18}$$

The emission perspective with focus on a single source compartment helps to understand the system dynamics with Eq. 3.18 only depending on the jth column of $\mathbf{\Phi}(t)$. However, considering conditions of realistic pesticide application, the initial mass is not exclusively applied to a single compartment, but distributes between several source compartments according to $m_k(0) = \theta_k\, m_{\text{total}}(0)$, $k \in \{1, \ldots, n\}$, where $0 \leq \theta_k \leq 1$, $k \in \{1, \ldots, n\}$, is the fraction of the total pesticide mass applied to the system that enters the kth source compartment at time $t = 0$, and $\sum_{k=1}^{n} \theta_k = 1$, denoting that all initial mass fractions must sum up to 100%. Furthermore, from a practitioner's or consumer's point of view, one is interested in the perspective of the receiving compartments by focusing on the pesticide residues in edible plant components at harvest time and the contribution of the different source compartments to the evolution of these residues. Mathematically, this corresponds to the following question: For fixed $i \in \{1,\dots,n\}$, from which source compartments does the residual mass $m_i(t)$ of a chemical present in the ith receiving compartment at time t come from? The contribution of the jth source compartment at time $t = 0$ to the residual mass fraction in the ith receiving compartment at time t, $c_{i\leftarrow j}(t)$, $i, j \in \{1,\dots,n\}$, is obtained as follows:

$$\begin{aligned} c_{i\leftarrow j}(t) &= \frac{m_i^{j,0}(t)}{m_i(t)} \\ &= \frac{\varphi_{ij}(t)\, m_j(0)}{\sum_{k=1}^{n} \varphi_{ik}(t)\, m_k(0)} \\ &= \frac{\varphi_{ij}(t)\, \theta_j}{\sum_{k=1}^{n} \varphi_{ik}(t)\, \theta_k}, \qquad i, j \in \{1,...,n\} \end{aligned} \tag{3.19}$$

The receiving perspective with focus on harvested crop components helps to analyze the influence of different source compartments over time to the residual mass at crop harvest for fixed initial mass distribution. However, since for any given $i \in \{1,\dots,n\}$, Eq. 3.19 depends on both the ith row of $\mathbf{\Phi}(t)$ and initial conditions given by θ_j, $j \in \{1,\dots,n\}$, it can be realized that there is no obvious way to distinguish these two influences and that $c_{i\leftarrow j}$ refers to a fixed initial condition only. To investigate the influence of varying initial mass distributions on pesticide residues in harvest, the two perspectives assessed above can be ultimately combined. Mathematically, this corresponds to the following question: If the distribution of the total applied mass at time $t = 0$ is changing between the different source compartments, how is the mass in the ith receiving compartment affected at time t for fixed $i \in \{1,\dots,n\}$? Again, it is assumed for the initial distribution that $m_k(0) = \theta_k\, m_{\text{total}}(0)$, $k \in \{1,\dots,n\}$, where $0 \le \theta_k \le 1$, $k \in \{1,\dots,n\}$, is the fraction of the total pesticide mass applied to the system that enters the kth source compartment, and $\sum_{k=1}^{n} \theta_k = 1$. With that, $fr\_m_i(t)$, $i \in \{1,\dots,n\}$, the fraction of total applied pesticide mass at time $t = 0$ that finally ends up as residue in the ith receiving compartment at time t is obtained:

$$\begin{aligned} fr\_m_i(t) &= \frac{m_i(t)}{m_{\text{total}}(0)} \\ &= \frac{\sum_{k=1}^{n} \varphi_{ik}(t)\, m_k(0)}{\sum_{k=1}^{n} m_k(0)} \\ &= \frac{\sum_{k=1}^{n} \varphi_{ik}(t)\, \theta_k}{\sum_{k=1}^{n} \theta_k} \\ &= \sum_{k=1}^{n} \varphi_{ik}(t)\, \theta_k, \qquad i, j \in \{1,...,n\} \end{aligned} \tag{3.20}$$

Combining both perspectives with focus on harvested crop components allows to analyze the influence of varying θ_k, $k \in \{1, \dots, n\}$, on the residual mass in harvest for a fixed point in time.

3.2.4. Evolution of pesticide masses

For analyzing the evolution of substance masses in the modeled system from a compartmental perspective, insecticide carbaryl, herbicide dicamba and insecticide cyromazine were selected, all exemplarily applied to wheat with contrasting residence times in fruit, on fruit surface and in soil compartments as summarized in Table 3.1. Compartment-specific degradation residence times $\tau_{\mathrm{deg}},i = t_{1/2,i}$ are derived from the degradation half-life $t_{1/2,i}$ of a substance in the ith compartment. Degradation half-lives on plant surface and in plant are compiled from experimental studies by Ishii (2004); Lim et al. (1990) and Roy et al. (2001) for carbaryl, cyromazine and dicamba, respectively. Degradation half-lives in soil are derived from the FOOTPRINT database (AERU Agriculture and Environment Research Unit, 2011) with a value based on field studies for cyromazine and with values averaged over field and laboratory studies for carbaryl and dicamba. However, persistence is not exclusively related to degradation. Instead, the system dynamics is rather related to the overall residence time in a compartment, considering both degradation and transfer processes with the latter often being dominant especially in soil. From the selected pesticides, cyromazine shows highest persistence in fruit, dicamba on fruit surface and carbaryl in soil (bold values in Table 3.1). In addition to persistence, also the typical time from substance application to crop harvest Δt varies between herbicide dicamba applied at an early crop stage, that is around 120 days before harvest, and the two insecticides cyromazine and carbaryl typically applied 10 and 20 days before harvest, respectively.

Table 3.1.: Time between substance application and harvest Δt, degradation residence times τ_{deg} [d] and overall residence times τ [d] in fruit, fruit surface and soil compartments for three pesticides applied to wheat. Bold values indicate compartment with longest overall residence time per substance.

substance	Δt	$\tau_{\mathrm{deg,fruit}}$	$\tau_{\mathrm{deg,fruit\,surface}}$	$\tau_{\mathrm{deg,soil}}$	τ_{fruit}	$\tau_{\mathrm{fruit\,surface}}$	τ_{soil}
cyromazine	10	6.2	10.1	14.0	**4.2**	3.2	3.5
dicampa	120	4.0	6.1	11.5	0.9	**2.1**	0.8
carbaryl	20	2.7	17.3	23.1	0.6	2.0	**10.7**

To study the mass evolution of these three pesticides in the wheat crop, air, soil, leaf surface, fruit surface, leaf and fruit interior, stem and root are considered as receiving compartments, of which the first four are also available as source compartments potentially receiving a fraction of initially applied pesticide mass.

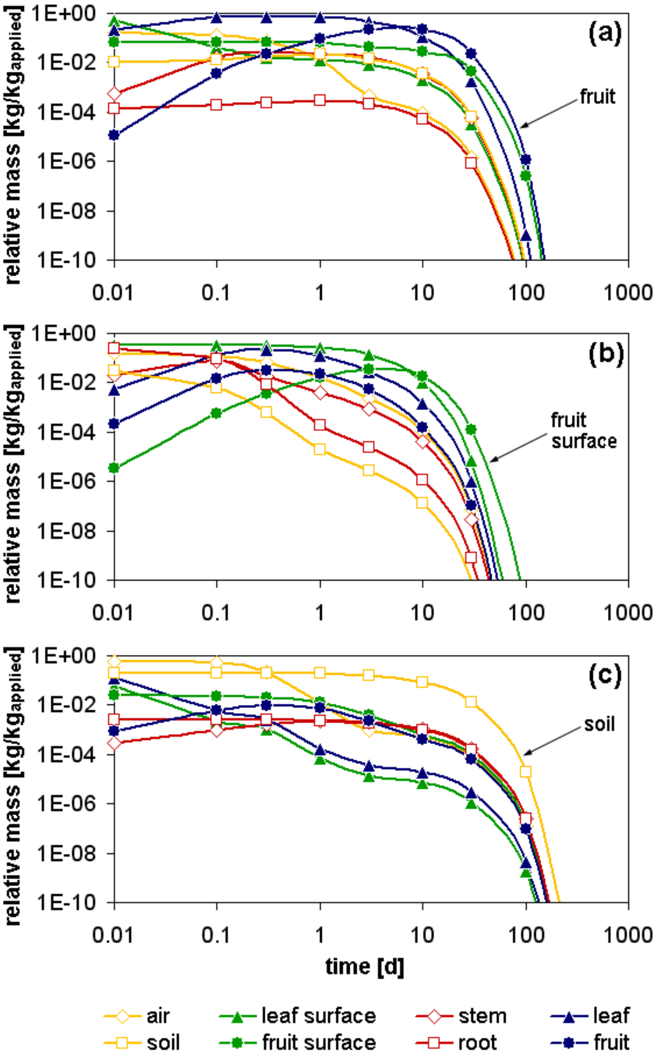


Figure 3.1.: Evolution of masses of three pesticides with mainly driving compartments 'fruit' for cyromazine (a), 'fruit surface' for dicamba (b) and 'soil' for carbaryl (c) after application to wheat.

Figure 3.1 contrasts pesticide mass evolutions for the three selected pesticides, for which the system dynamics at harvest time is mainly driven by one particular compartment. The initial mass distribution varies with plant characteristics at the time of application, such as intercepting surface area, that depend on a crop's life stage. After initial distribution, the pesticide masses instantaneously start to decrease in all compartments that receive a fraction of the applied substance. In contrast, masses in receiving compartments – in case of wheat most notably the fruit compartment that corresponds to the harvested wheat grains – usually increase from initial conditions until a certain point in time for each compartment separately, where a maximum mass is reached. Maximum relative masses per kg applied pesticide range from 0.74 $\mathrm{kg\,kg_{applied}^{-1}}$ in leaf after time $t_{\mathrm{max,leaf}} = 0.6$ days to 2.9×10^{-4} $\mathrm{kg\,kg_{applied}^{-1}}$ in root after $t_{\mathrm{max,root}} = 1.2$ days, both for cyromazine (Figure 3.1a). From the maximum, pesticide masses start decreasing more or less exponentially until harvest, since mainly degradation processes dominate the middle-term system dynamics. When finally looking at the long-term system behaviors in Figure 3.1, it can be seen that after a certain point in time the overall system dynamics is driven by a single compartment with the highest residual mass, namely fruit for cyromazine, fruit surface for dicamba and soil for carbaryl, which corresponds to the longest overall residence time in Table 3.1.

Evolution of substance masses in multi-compartment systems can be predicted by several dynamic models. However, only the mathematical decomposition of such systems allows to further analyze the contribution of individual source compartments to the overall mass evolution from the perspective of both source and receiving compartments. One starts by following the pesticide mass evolution in the system under the assumption that the substance is exclusively applied to a single source compartment. Figure 3.2 (left side) enables us to analyze how the distribution of masses evolves in the system after application to the leaf surface compartment as an example source compartment.

Figure 3.2 (left side) shows that after application of cyromazine (a) to leaf surface only, the major fraction of the pesticide quickly diffuses into the inner leaf, before it is further transported into the fruit compartment, which dominates in the long-term. In contrast, when applying dicamba (b) to leaf surface only, this source compartment remains predominant for at least 30 days, before the fruit surface takes over in the long-term. Finally, after application of carbaryl (c) to leaf surface only, the pesticide immediately distributes almost evenly between air and both crop surface compartments, before soil dominates the overall distribution starting at 3 days after application.

3.2.5. Influence of source compartments and initial distribution

To reflect realistic conditions of pesticide application, each source compartment receives a certain fraction of the initial mass as a function of crop characteristics and development stage, meteorological conditions at application time as well as a function of pesticide formulation and type of application. Ultimately, the interest is on the compartments finally harvested for human or animal consumption, such as for wheat the fruit compartment representing the actual wheat grain, as only the harvested parts are exclusively important for impact assessment (Fryer and Collins, 2003). In case of harvested crop components, the residual mass in harvest relative to the mass of applied substance equals the harvest

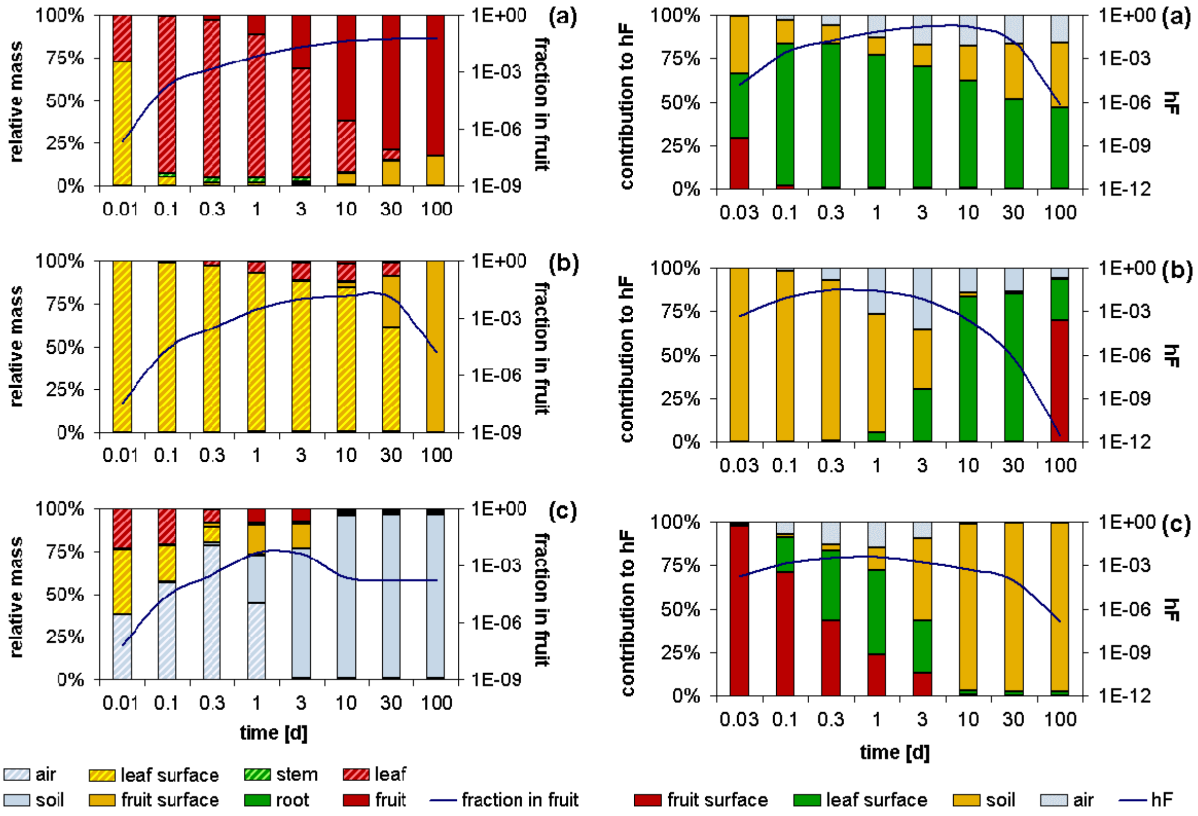


Figure 3.2.: Left: Bars indicating distribution of masses in compartments relative to total residual mass at different times and line describing evolution of mass in harvested fruit compartment relative to total residual mass for cyromazine (a), dicamba (b), and carbaryl (c) applied to wheat with total initial mass exclusively applied to leaf surface. Right: Bars indicating relative contributions of initial pesticide masses in air, soil, leaf surface and fruit surface to the harvest fraction in fruit at different times and line denoting evolution of harvest fractions for cyromazine (a), dicamba (b), and carbaryl (c) applied to wheat at 10, 120 and 20 days before harvest, respectively.

fraction. In this context, Figure 3.2 (right side) presents harvest fractions differentiated according to contributions from the different source compartments.

Figure 3.2 (right side) demonstrates that for herbicide dicamba (b) the soil contributes almost exclusively to early mass in fruit compartment, which is mainly attributable to substance application at early crop stage with a large substance fraction depositing onto soil due to a small initial plant surface area. In contrast, for cyromazine (a) and carbaryl (c) with application times of only 10 and 20 days before harvest, the plant surface compartments receive a higher fraction of the applied pesticides and drive the early residual masses in fruit. Unsurprisingly, the source compartment identified to be dominating the system long-term evolution has proportionally the highest contribution to the mass in fruit. For dicamba, this means that fruit surface becomes driving at harvest times after 100 days of application and for carbaryl, soil already starts to be dominant when harvesting 10 days after application. In case of cyromazine, where fruit itself was identified as the main driving compartment, none of the sources exclusively dominates in the long-term. This approach can be extended to look at how residual mass conditions in receiving compartments vary continuously with different initial mass distributions between source compartments. Hence, with respect to the harvested crop components, the question is now addressed, how varying initial mass conditions affect harvest fractions at harvest time.

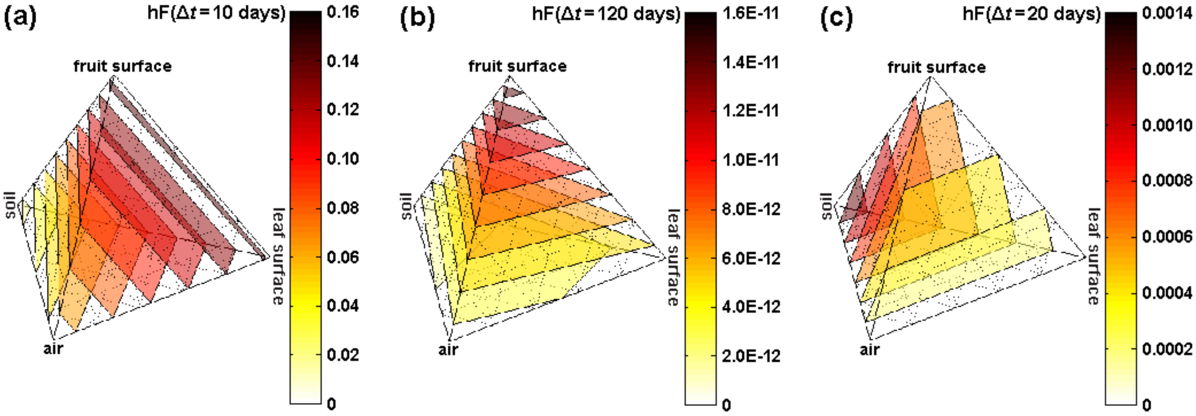


Figure 3.3.: Regular tetrahedra characterizing the influence of air, soil, leaf surface and fruit surface to the harvest fraction with iso-hF-surfaces denoting areas of equal harvest fractions for cyromazine (a), dicamba (b), and carbaryl (c) applied to wheat at 10, 120 and 20 days before harvest, respectively.

Figure 3.3 presents all possible initial mass conditions for the three example pesticides. Each vertex, i.e. tetrahedron corner point, represents the condition, where a single source compartment exclusively receives the total applied mass, which corresponds to conditions in Figure 3.2. Any other point in the tetrahedron space refers to a particular initial condition with contribution from all four source compartments. Generally, for shorter time to harvest, the residual mass in harvested crop components is higher due to less time for degradation processes to establish an influence. In terms of the initial mass distribution it is furthermore important to look at the fraction that reaches a specific source compartment. For dicamba, fruit surface was identified as driving the system dynamics at harvest time. This is consistent with Figure 3.3, showing high sensitivity of the harvest fraction to higher mass fractions initially reaching fruit surface for dicamba. Furthermore, it is consistent with the very short overall residence time of dicamba in leaf surface compartment of 5.5 hours compared to the residence time in fruit surface of 2.1 days. For carbaryl, the fraction reaching soil is dominant with some additional, but minor influence of fruit surface. In contrast, for cyromazine, the fruit not being a source compartment was identified as driving the system dynamics starting at 10 days after application. While air and soil have only little influence, the contribution to the residual mass evolution is driven by a combination of fruit surface and leaf surface, thereby explaining that no source compartment is exclusively dominating the harvest fraction.

3.2.6. Conclusions

In the present section, it was successfully demonstrated how to extensively analyze the substance dynamics in a complex multimedia plant-uptake model. One understands that the harvest fraction of most pesticides applied to wheat is linearly dependent on the influence of different compartments, namely fruit, fruit surface and soil. This approach can relatively easily be applied to also assess crop components harvested for animal consumption and to analyze similar crop-environment systems like fruit trees or herbaceous fruits and vegetables, based on findings from Fantke et al. (2011b).

Further study, however, is required for understanding the relative sensitivities of input variables and the propagation of uncertainties in the full dynamic model. A systematic sensitivity and uncertainty analysis based on matrix algebra is, hence, presented in Section 3.3. Both, the assessment of sensitivities and the functioning of the underlying dynamical system form the basis for finally parameterizing the the complex system for use in spatial modeling frameworks as applied in impact assessment, thereby potentially reducing uncertainties.

3.3. Sensitivity assessment and uncertainty propagation

3.3.1. Introduction and background

A prerequisite for the evaluation of model results as well as for model parameterization is an extensive sensitivity and uncertainty analysis, since the role of different factors in controlling chemical partitioning, fate and behavior processes of pesticides in the plant-environment system is still not fully understood (Barber et al., 2004). This indicates that distinct aspects may contribute differently to uncertainty in model predictions (Schenker et al., 2009; Hertwich et al., 1999; MacLeod et al., 2002). As a first step, it has already been identified in Sections 2.4 and 3.2 that the time to harvest along with degradation half-lives in plants play a crucial role for some crops (Fantke et al., 2011b, 2012), but additional aspects may be important for other crop types. For finally parameterizing dynamiCROP as a function of key input variables, the variability and uncertainty of input data including their covariances will be assessed in the present section. This helps focusing attention on accurately quantifying model input and related uncertainties (MacLeod et al., 2002).

As a result, three objectives will be addressed in the present section: (1) Relevant model input variables are selected and their uncertainty ranges defined as a function of each variable's variability and uncertainty. (2) Based on that, key input variables are identified for each studied crop type and across pesticides from the variables' contribution to overall model sensitivity including the consideration of correlations between variables. (4) Finally, the uncertainty propagation is studied, i. e. the contribution of input variables to overall model output uncertainty for the full dynamic model.

3.3.2. Input variables and their uncertainty

Categorization of model input data. For studying the uncertainty of input data across pesticides for each crop type individually, model input is categorized into (a) pesticide physicochemical properties, (b) crop-specific characteristics, (c) generic or average system boundaries, and (d) time from substance application to crop harvest and reduction of residues due to food processing.

Table 3.2.: Full range of physicochemical properties of 385 pesticides represented by median values, upper and lower 95% confidence interval limits as well as minimum and maximum.

input variable	unit	median	2.5%-ile	95%-ile	minimum	maximum
MW	[$\mathrm{g\,mol^{-1}}$]	299	136	505	32	1053
log(Kaw)	[–]	-6.7	-14.2	-2.4	-20.6	2.4
log(Kow)	[–]	3	-3.5	6.8	-4.6	8.2
log(Koc)	[$\mathrm{L\,kg^{-1}}$]	2.8	1	5.2	-3.3	7
$t_{1/2,\mathrm{air}}$	[d]	0.3	0.04	9.2	0.01	4167
$t_{1/2,\mathrm{soil}}$	[d]	28	1	365	0.2	5000
$t_{1/2,\mathrm{water}}$	[d]	16.9	0.2	180	0.1	344
$t_{1/2,\mathrm{plant\,surface}}$	[d]	6.8	1.3	26.1	0.5	100
$t_{1/2,\mathrm{plant}}$	[d]	1.9	0.3	6.5	0.1	24.8

Table 3.2 summarizes the full range of substance properties for 385 pesticides. Pesticide data for molecular weight, partition coefficients Kaw, Kow and Koc, as well as half-lives

in soil and water are derived from FOOTPRINT (AERU Agriculture and Environment Research Unit, 2011) or the Pesticide Manual (Tomlin, 2009). Half-lives in air are mostly taken from U.S. EPAs EPI-SUITE (US-EPA United States - Environmental Protection Agency, 2011a) or EFSA Pesticide Peer Review (`www.efsa.europa.eu/efsajournal`). Half-lives in plants and on plant surfaces are only rarely available and are, hence, extrapolated from soil half-lives according to Juraske et al. (2008) and Thomas et al. (2011), wherever no experimental data could be found.

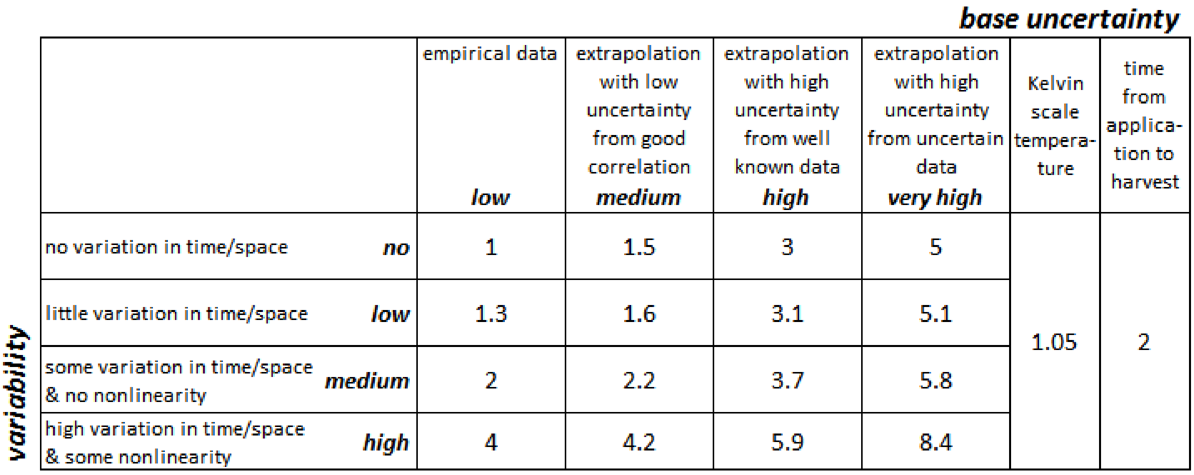
To account for differences in crop characteristics, six characteristic food crops were selected according to Section 2.4 representing the most relevant archetypes with respect to human vegetal consumption and contrasted for crop-specific input data as given in Table 2.7. All generic or average input data mostly referring to environmental conditions are provided in Appendix B.

Uncertainty of input variables. Each input variable is varied in its 95% confidence interval. Since all variables are strictly non-negative physical entities, model input is assumed to be approximately log-normally distributed and that the 2.5th and 97.5th percentiles can be obtained from the geometric mean $x^* \in \mathbb{R}$ and the squared geometric standard deviation $\mathrm{GSD}^2 \triangleq \mathrm{e}^{2\sigma}$ with $\sigma \in \mathbb{R}$, $\sigma > 0$ as standard deviation of the natural logarithm of input variable x and the probability $\{x^* / \mathrm{GSD}^2 < x < x^* \, \mathrm{GSD}^2\} = 0.95$. The choice of 2 in the exponent reflects the rounded critical value from the Student's t-distribution.

For crop characteristics and environmental properties, GSD^2 are often not well defined. Hence, a semi-quantitative method is proposed to derive GSD^2 based on qualitatively assessing the variables' spatial and temporal variability in the environment (variability) and their intrinsic data uncertainty or the quality of extrapolation used to describe the variables (base uncertainty). A classification is introduced for both variability and base uncertainty of model input and combined into a GSD^2 pedigree matrix as commonly applied for life cycle inventories according to Funtowicz and Ravetz (1990) (Table 3.3). GSD^2 in first line and column are based on reported empirical data variability. All other GSD^2 are obtained as sum of the squares of $\ln(\mathrm{GSD}^2)$ for variability and base uncertainty as two log-normally distributed multiplicative input terms referring to the same variable with uncertainties assumed mutually independent:

$$\left(\ln\left(\mathrm{GSD}^2\right)\right)^2 = \left(\ln\left(\mathrm{GSD}^2_{\text{variability}}\right)\right)^2 + \left(\ln\left(\mathrm{GSD}^2_{\text{base uncertainty}}\right)\right)^2 \qquad (3.21)$$

Table 3.3.: Pedigree matrix of geometric standard deviations for input variables based on spatial and temporal variability as well as on base uncertainty.



base uncertainty

variability		empirical data ***low***	extrapolation with low uncertainty from good correlation ***medium***	extrapolation with high uncertainty from well known data ***high***	extrapolation with high uncertainty from uncertain data ***very high***	Kelvin scale temperature	time from application to harvest
no variation in time/space	***no***	1	1.5	3	5	1.05	2
little variation in time/space	***low***	1.3	1.6	3.1	5.1		
some variation in time/space & no nonlinearity	***medium***	2	2.2	3.7	5.8		
high variation in time/space & some nonlinearity	***high***	4	4.2	5.9	8.4		

3.3.3. Assessing relative sensitivities and parameter correlation

Input Parameter Correlation. The influence of model input to model output needs to be assessed for parameterizing the system dynamics as a function of input variables with significant influence only. However, some variables are not mutually independent, i. e. all input variables directly influence model output, whereas some also influence model output indirectly via other variables. An example is the solute mobility k^* $[\mathrm{d}^{-1}]$ extrapolated from molecular weight MW $[\mathrm{g\,mol}^{-1}]$ by $\log(k^*) = -1.58 - 0.011 \times \mathrm{MW}$ (Schönherr and Schreiber, 2004). Both direct and indirect influences on model output must be finally accounted for by normalizing the influence of all input variables on model output. Hence, explicit models are provided in dynamiCROP for describing functional dependencies between input variables to express their correlations. In fact, there are two distinct sets of input variables: the first set, $x_1, \ldots, x_{P_0}$, contains input variables not considered to depend on other variables, while the second set, $x_1, \ldots, x_P$, contains input variables extrapolated from others (from the first as well as the second set) based on reported correlations. We express input variables from the second set as

$$x_k = f_k(\vec{x})\,\Delta_k, \qquad k \in \{1, ..., P\} \tag{3.22}$$

with function $f_k(\vec{x})$ as extrapolation formula, i. e. a regression model for the k^{th} dependent variable, and factor Δ_k as multiplicative regression error. With Eq. 3.22, a different set of input variables can be considered, namely

$$z_k = x_k, \qquad k \in \{1, ..., P_0\} \tag{3.23a}$$

$$z_k = \Delta_k, \qquad k \in \{P_0 + 1, ..., P\} \tag{3.23b}$$

and a function vector $\vec{v}(\cdot)$ relating the original input variables $\vec{x} = \begin{pmatrix} x_1 & \cdots & x_P \end{pmatrix}^T$ to the new input variables $\vec{z} = \begin{pmatrix} z_1 & \cdots & z_P \end{pmatrix}^T$ as $\vec{x} = \vec{v}(\vec{z})$. Consequently, GSD^2 is estimated for mutually independent input variables as well as for extrapolated model input, where for the latter it is exclusively accounted for the error Δ_k introduced by the formulation of the functional dependency. The direct influences of input variables on model output and the indirect influence on model output via extrapolated variables are then summed up. The primary interest in accounting for model input correlations is to identify the most important variables used as predictors in the crop-specific regression models. Therefore, it is required to choose a system of mutually independent variables, which is given by accounting for their correlations. Finally, model output in dynamiCROP characterized by the human intake fraction iF [$\mathrm{kg_{intake}\,kg_{applied}^{-1}}$] is given as a function

$$\mathrm{iF} = g(\vec{z}) \triangleq f\big(\vec{v}(\vec{z})\big) \tag{3.24}$$

of P input variables, $\vec{z} \in \mathbb{R}^P$, which are now assumed uncorrelated.

Relative Sensitivities. The relative sensitivity $s_{z_k}(\vec{z}^*)$ of iF with respect to input variable z_k at a specific point of interest $\vec{z}^*$ is introduced as

$$s_{z_k}(\vec{z}^*) \triangleq \left. \frac{\frac{\partial g(\vec{z})}{g(\vec{z})}}{\frac{\partial z_k}{z_k}} \right|_{\vec{z}=\vec{z}^*} = \left. \frac{\frac{\partial\,\mathrm{iF}}{\mathrm{iF}}}{\frac{\partial z_k}{z_k}} \right|_{\vec{z}=\vec{z}^*} \tag{3.25}$$

as the relative change of output variable iF per relative change of input variable z_k evaluated at $\vec{z} = \vec{z}^*$ (MacLeod et al., 2002). By moving to a logarithmic scale for model input and output, $s_{z_k}(\vec{z}^*)$ in Eq. 3.25 can be expressed equivalently as

$$s_{z_k}(\vec{z}^*) = \left. \frac{\partial \ln\big(g(\vec{z})\big)}{\partial \ln(z_k)} \right|_{\vec{z}=\vec{z}^*} = \left. \frac{\partial \ln(\mathrm{iF})}{\partial \ln(z_k)} \right|_{\vec{z}=\vec{z}^*} \tag{3.26}$$

with $\vec{z} > 0$ element-wise and $\mathrm{iF} = g(\vec{z}) > 0$, i. e. all model input and output variables are positive and their logarithms well defined. All relative sensitivities are now summarized into a row vector

$$\vec{s}_{\vec{z}} = \begin{pmatrix} s_{z_1}(\vec{z}^*) & \cdots & s_{z_Q}(\vec{z}^*) \end{pmatrix} \tag{3.27}$$

which corresponds to the $1 \times n$ Jacobian matrix, i. e. the matrix of first order partial derivatives of ln(iF) with respect to $\ln(\vec{z})$ and evaluated at $\vec{z} = \vec{z}^*$. For calculating relative sensitivities towards input referring to substance properties the full range of each property's variability is accounted for. Consequently and in order to minimize the possible effect of non-linearity, local derivatives in Eqs. 3.25 to 3.27 are replaced for substance properties by mean slopes between their 95% confidence interval limits. As a result, the final $1 \times n$ sensitivity matrix is a composite of elements taken from the Jacobian matrix (for crop characteristics and environmental properties) and of relative sensitivities obtained from extreme values (for substance properties). The square root of the ratio of model output iF_k at the confidence interval limits $z_k^* / \mathrm{GSD}_{z_k}^2$ and $z_k^* \times \mathrm{GSD}_{z_k}^2$ is denoted coefficient of variation. The coefficient of variation finally serves as measure for model output uncertainty with respect to individual input variables z_k and is used for building the regression models exclusively from input variables that most significantly influence pesticide dynamics.

3.3.4. Relative sensitivities

The sensitivity analysis indicates that harvest fractions are most sensitive to degradation half-life in plant, octanol-water partition coefficient and molecular weight, with relative sensitivities of 1.08, -0.92 and -0.90, respectively in the example of wheat. Relative sensitivities are summarized for the 35 most influential input variables in Table 3.4. Sensitivities were calculated accordingly for other crops, indicating that for potato soil characteristics are mainly influential, whereas for lettuce specific influences are related to leaf-air exchange processes.

Correlations of input variables are highest for pesticide half-lives in soil (1.17) and for air-water partition coefficient (-0.92) for extrapolations of plant surface/plant interior half-lives and leaf-air partition coefficient, respectively. These correlations indicate that despite the importance of plant degradation additional influence is given by uncertain extrapolation models. Consequently, if the model output is very sensitive to rather uncertain input variables, these variables need to be estimated more accurately in order to keep overall uncertainty at a reasonable level. More specifically, more accurate prediction models for estimating degradation half-lives in plants are required for the present approach and other plant uptake models.

3.3.5. Crop-specific uncertainty

Main sources of uncertainty in the model are related to (a) estimated physicochemical properties of pesticides, (b) crop characteristics and development, and (c) the mathematical description of the fate processes by means of rate coefficients, which is due to the limitation of using first-order kinetics (Barber et al., 2004).

Since harvest fractions are normalized for the total applied substance mass, the behavior of pesticides can be compared independently of the applied amounts. Considering

Table 3.4.: Sensitivity towards 35 most influential model input variables and rate coefficients for wheat.

input variable	s_k
degradation half-life in plant	1.08
octanol-water partition coefficient	−0.92
molecular weight	−0.90
transfer rate coefficient from thick root to root-zone soil layer	−0.78
transfer rate coefficient from leaf surface deposit to leaf	0.73
transfer rate coefficient from leaf to atmospheric boundary layer (through stomata)	−0.66
bulk soil matrix (particles)-water partition coefficient	−0.63
fruit-cuticle partition coefficient	0.43
cuticle wax-formulation deposit partition coefficient (wax/water)	−0.42
soil organic carbon-water partition coefficient	−0.28
growth rate of fruit area index	0.28
fruit-water partition coefficient	0.25
transfer rate coefficient from thick root to stem	0.21
transfer rate coefficient from atmospheric boundary layer to root-zone soil layer	−0.20
transfer rate coefficient from fruit surface deposit to fruit	0.15
leaf-cuticle partition coefficient	0.12
mean fruit area index	0.11
growth rate of leaf area index	0.11
mean leaf area index	0.09
transfer rate coefficient from atmospheric boundary layer to leaf (through stomata)	0.09
degradation half-life in bulk soil	0.09
transfer rate coefficient from root-zone soil layer to thick root	0.08
leaf-water partition coefficient	−0.08
bulk soil-water partition coefficient	−0.08
cuticle-water partition coefficient	0.08
substance capture coefficient	0.07
transfer rate coefficient from atmospheric boundary layer to fruit surface deposit	0.07
transfer rate coefficient from stem to fruit	0.07
leaf-air partition coefficient	0.05
transfer rate coefficient from atmospheric boundary layer to leaf surface deposit	0.02
air-water partition coefficient	−0.01
bulk soil-air partition coefficient	0.01
solute mobility of formulation deposit in cuticular membrane	0.01
application efficacy factor	0.005
transfer rate coefficient from leaf to stem	0.0004

the observed variation between harvest fractions and applied pesticide masses, the uncertainty on applied quantities is a factor of secondary significance. For all crops, the contribution of input variables to the model output uncertainty, i. e. the uncertainty of the human intake fraction, is presented in Figure 3.4 with aggregating all input variables that contribute less than 3% to overall model output uncertainty.

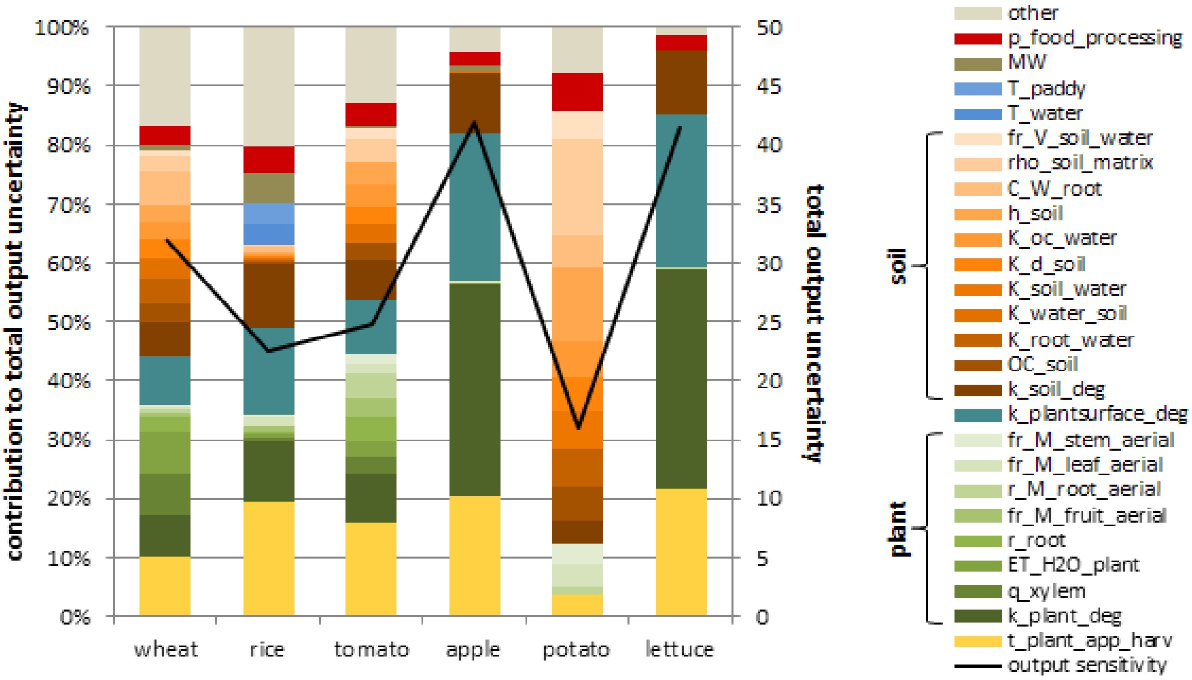


Figure 3.4.: Contribution of most important input variables to total model output uncertainty for all crops across pesticides.

Highest model output uncertainty is related to lettuce, for which a reduced compartmental system was applied with no fruit and fruit surface compartments. However, this reduced system is more sensitive to leaf-air exchange processes than all other considered crops for different reasons, such as a relatively high adsorption rate due to rough leaf surfaces and leaf growth mechanisms. Model output uncertainty is also high for apple, since the tree structure implies additional mechanisms for e. g. accounting for vertical transport in the trunk and for being a perennial crop. Overall, the time from pesticide application to crop harvest is a major contributor to model output uncertainty with a contribution between 3.7% in potato to 21.6% in lettuce, along with degradation half-lives in plant and on plant surface across all crops contributing between 7.1% in wheat to 37.5% in lettuce. For potato, contributing input variables are mainly restricted to soil characteristics, most importantly soil organic carbon-water partition coefficient contributing with 12.5% and soil matrix density contributing with 16.3% to overall model output uncertainty.

3.3.6. Conclusions

Degradation half-lives in plant and on plant surface, Koc for potato and a combination of Kaw and Kow for lettuce were identified as relevant physicochemical parameters and the time from application to harvest as a key aspect driving the system dynamics based on the influence of degradation processes. These findings will serve as input for the parameterization of the full dynamic model in the following section. Considering correlations between input variables lead to the identification of important gaps for estimating certain input variables from others, most importantly the extrapolation of plant and plant surface degradation half-lives extrapolated from soil degradation half-lives. In line with Thomas et al. (2011), these variables require a more sophisticated understanding of the underlying mechanisms based on e. g. QSAR or similar prediction methods finally leading to a more accurate prediction for pesticides. This, however, is beyond the scope of the present study, but remains an unsolved challenge for future research.

3.4. Model parameterization for use in spatial multimedia models

3.4.1. Introduction and background

As discussed before, most models assessing health impacts of pesticides either disregard plant residues at all or have one generic plant compartment, for which steady-state conditions are generally assumed. This is a considerable drawback in current pesticide exposure assessments for the following reasons: Uptake and translocation mechanisms vary between plant species and components, thereby indicating that some crop types show higher contribution to overall human pesticide intake than others (Trapp and Kulhanek, 2006; Trapp and Legind, 2011; Fantke et al., 2011b). Furthermore, pesticides are used as pulse applications to be assessed dynamically, whenever steady-state is not reached (Rein et al., 2011). In addition, models with generic plant compartments show significant uncertainties concerning the validity of exchange processes with plants and subsequent exposure calculations (Hertwich et al., 2000). Most importantly, overall pesticide exposure in current assessments will be underestimated, where unconsidered residues in food crops exceed inhalation and ingestion exposure from the pesticide fractions lost to beyond field boundaries via wind drift, run off and leaching processes as discussed in Chapter 2.

It is the aim of the present section to develop an approach for incorporating the complex model presented in Chapter 2 into impact assessment tools currently disregarding exposure to residues in crops grown for human and animal consumption. To achieve this aim, the focus is on different challenges: In its present form, dynamiCROP cannot be implemented in complex spatial or nested frameworks. A potential solution is to only use fixed characterization factors combining pesticide exposure and toxicity potentials for ingestion of food crops. However, since the time between substance application and crop harvest varies as a function of environmental conditions and occurrence time and pressure of pests (Matthews, 2000), characterization factors would have to be re-calculated, leading to different results for different times to harvest (Fantke et al., 2011b). To avoid re-running the full model with high input data requirements, the complex plant-environment system needs to be parameterized into a simplified regression with reduced data input. Such a regression model can much easier be introduced into current assessment tools.

Based on the findings from Sections 3.2 and 3.3, a transparent parametric representation for different crops will be provided, thereby drastically reducing input data requirements for easy implementation into other modeling frameworks. The influence of the most important compartments and key parameters are systematically summarized into crop-specific linear regression equations representing a parameterized version of the full dynamical multi-compartment system for all implemented crops. Finally, the parameterized models are compared with the full dynamic model using an example set of 385 pesticides applied to the six crops with what the accuracy of the theory underlying the regression is demonstrated.

3.4.2. Regression model design

Time to harvest, food processing, degradation in crops and on crop surfaces as well as residence times in environmental media are all considered key aspects driving the dynamics of pesticides in the crop-environment system along with some substance properties, which might have additional influence (Trapp and Legind, 2011; Fantke et al., 2011b, 2012). The influence of substance properties and crop characteristics on pesticide dissipation is linked to certain compartments of the crop-environment system. Hence, a three-step approach is followed: First, the log of the harvest fraction hF $[\mathrm{kg_{in\,harvest}}\,\mathrm{kg_{applied}^{-1}}]$ is designed, i. e. the pesticide mass found in harvest per kg applied, for each influential compartment separately as a function of input variables. From that, a generic model for each compartment is developed:

$$\log(\mathrm{hF}_i^x) = f^x\left(\Delta t \times \sum_{d=1}^{m} k_{i,d}^x\right) + \sum_{p=1}^{n} g_p(S_{i,p}) \tag{3.28}$$

where hF_i^x is the harvest fraction of pesticide i in a specific compartment x expressed as an initially unspecified function f of the product of the time to harvest Δt [d] and compartment-related rate coefficients $k_{i,d}^x$ [d^{-1}] for relevant dissipation and/or transfer processes d, and a set of initially unspecified functions g_p of substance properties $S_{i,p}$ accounting for different physicochemical aspects p. Based on that, a linear combination of all compartment-specific hF_i^x is performed to obtain the overall hF_i per pesticide, thereby entirely covering pre-harvest dynamics:

$$\mathrm{hF}_i = \mathrm{hF}_i^{x_1} + \cdots + \mathrm{hF}_i^{x_n} \tag{3.29}$$

Finally, one derives the human intake fraction iF_i [$\mathrm{kg_{intake}\,kg_{applied}^{-1}}$], the mass of pesticide i taken in via consumption of food crops per kg applied, from hF and an additional processing factor $\mathrm{PF}_{\mathrm{food},i}$ [$\mathrm{kg_{intake}\,kg_{in\,harvest}^{-1}}$] accounting for pesticide-specific reduction of residues due to food processing based on Eq. 2.22:

$$\mathrm{iF}_i = \mathrm{hF}_i \times \mathrm{PF}_{\mathrm{food},i} \tag{3.30}$$

The food processing factor is usually pesticide-specific. However, for most pesticides, such factors are only available for very few substances (Kaushik et al., 2009; Keikotlhaile et al., 2010). As a result, food processing factors are given per crop (related to corresponding crop-specific processing steps) and generic for all pesticides as summarized in Table 2.8.

3.4.3. Aspects influencing model regression

So far, fruit, fruit surface and soil were identified as the main compartments able to drive the system dynamics for selected pesticides as a function of residence times in these compartments in Section 3.2. Moreover, the time from substance application to crop harvest is a key aspect influencing the residual mass distribution and harvest fraction with longer time after application leading to lower harvest fractions. Most pesticides can be categorized according to these three mainly driving compartments by using a parsimonious regression-based parametric model as shown in the following. Hence, it is proposed to assess the variation in harvest fractions between 385 different pesticides, each of them applied at four different times before harvest to wheat as an example crop.

Influence of degradation in fruit and time to harvest. Variation is first plotted in Figure 3.5 as a function of the degradation rate coefficient in the harvested compartment, grouped according to different times between application and harvest. The degradation rate coefficient in fruit is thereby calculated as $k_{\mathrm{deg,fruit}} = \ln(2)/t_{1/2,\mathrm{fruit}}$ with $t_{1/2,\mathrm{fruit}}$ as degradation half-life in fruit.

For a given time to harvest, Figure 3.5 shows an approximately exponential decrease in harvest fractions with increasing substance degradation rate coefficients in fruit. At three days between application and harvest, harvest fractions are high, predominantly ranging from 10^{-1} to 10^{-4}. With increasing time to harvest, harvest fractions are significantly

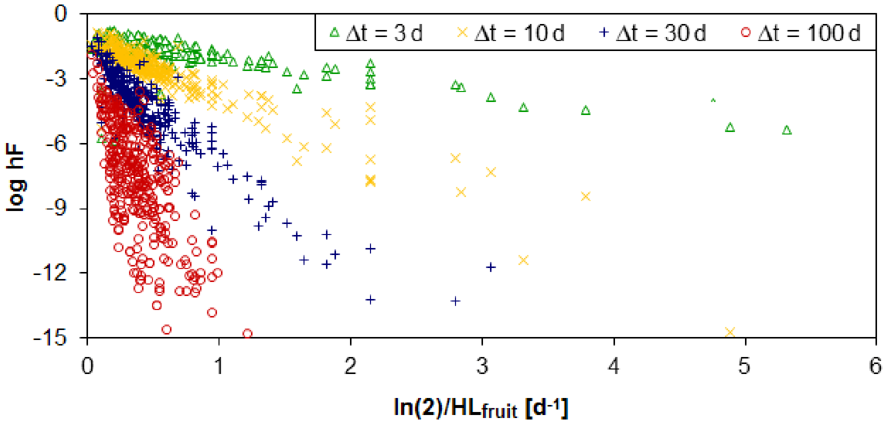


Figure 3.5.: Harvest fraction of 385 pesticides applied to wheat at four different times ($n = 1540$), plotted as a function of the degradation rate coefficient in fruit, grouped according to times between application and harvest.

reduced, whereas variation between substances is increased. The earlier pesticides are applied before harvest, the more time is available for removal processes and underlying substance and plant characteristics to act leading to higher variation between harvest fractions.

Additional influence of fruit surface and soil compartments. Figure 3.5 shows that degradation rate coefficient in fruit and time between substance application and crop harvest are predominantly driving parameters. Hence, in a second step it is tested how harvest fractions vary with the time to harvest divided by the degradation residence time in fruit to detect additional influences that can be used in the parameterization process (Figure 3.6). The residence time in fruit is calculated from the degradation rate coefficient according to $\tau_{\text{deg,fruit}} = 1/k_{\text{deg,fruit}}$. It is expected that the log of the harvest fraction of a pesticide i is linearly dependent on that ratio according to

$$\log(\text{hF}_i) = \alpha + \beta \times \frac{\Delta t}{t_{1/2,\text{fruit},i}/\ln(2)} = \alpha + \beta \times \frac{\Delta t}{\tau_{\text{deg,fruit},i}} \tag{3.31}$$

For low ratios between time to harvest and degradation residence time in fruit, Figure 3.6 shows that harvest fractions are clearly driven by the fruit compartment with degradation in fruit dominating the evolution of the harvest fraction as described by the linear Eq. 3.31. However, at higher ratios, additional influences occur and harvest fractions are not any more driven by fruit, but maintained by other compartments in which degradation residence times are higher than in fruit. The influences of fruit surface and soil on the harvest fraction are therefore also considered. For fruit surface, it is assumed that the log of harvest fractions can be linearly linked to degradation in that compartment. For soil, based on findings from Fantke et al. (2011b), harvest fractions

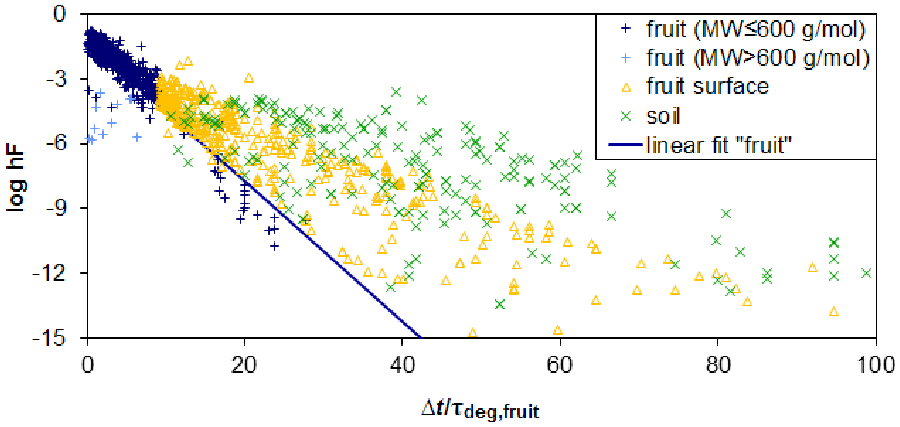


Figure 3.6.: Harvest fraction of 385 pesticides applied to wheat at four different times ($n = 1540$), plotted as a function of the ratio of time from application to harvest and degradation residence time in fruit, grouped according to mainly driving compartments at harvest time, and – in case of fruit as main driver – distinguishing between substances with molecular weight lower and higher than 600 $\mathrm{g\,mol^{-1}}$.

are assumed to be linearly dependent on the overall residence times in soil rather than on the degradation residence times. This is due to the fact that in this environmental compartment, removal processes like advective transfer to groundwater and exchange with air may also significantly influence the residence time in addition to degradation. Furthermore, Figure 3.6 shows that a pesticide's molecular weight of MW $> 600\ \mathrm{g\,mol^{-1}}$ (light crosses) may influence the harvest fraction. There is a general trend of decreasing harvest fractions with increasing molecular weight, thereby leading to lower than average data points in Figure 3.6 for substances with MW $> 600\ \mathrm{g\,mol^{-1}}$.

3.4.4. Crop-specific combined regression results

Based on the parameterization process, the final format is proposed for the overall parametric model representation with different compartment-related terms for different crops based on the overall residence time in soil and degradation residence times in plant and on plant surface. Terms correcting for the influence of molecular weights and partition coefficients between air, n-octanol, soil organic carbon and water are added, wherever leading to significant improvement in prediction accuracy was identified. This leads to the following parametric regression equations for predicting the harvest fraction of pesticide i in six crops as a linear combination of harvest fractions in compartments plant (p), plant surface (ps) and soil (s):

$$\mathrm{hF}_i = \mathrm{hF}_i^{\mathrm{p}} + \mathrm{hF}_i^{\mathrm{ps}} + \mathrm{hF}_i^{\mathrm{s}} \tag{3.32a}$$

$$\mathrm{hF}_i = \mathrm{hF}_i^{\mathrm{s}} \tag{3.32b}$$

where Eq. 3.32a is designed for wheat, rice, apple, tomato and lettuce, and Eq. 3.32b for potato. In these equations, the log of each compartment-specific harvest fraction is calculated as follows:

$$\log(\mathrm{hF}_i^{\mathrm{p}}) = \alpha_{\mathrm{p}} + \beta_{\mathrm{p}} \frac{\Delta t}{t_{1/2,\mathrm{p},i}/\ln(2)} + \beta_{\mathrm{MW}}(\mathrm{MW}_i - \mathrm{MW}_0) \tag{3.33a}$$

$$\log(\mathrm{hF}_i^{\mathrm{ps}}) = \alpha_{\mathrm{ps}} + \beta_{\mathrm{ps}} \frac{\Delta t}{t_{1/2,\mathrm{ps},i}/\ln(2)} + \beta_{\mathrm{MW}}(\mathrm{MW}_i - \mathrm{MW}_0) \tag{3.33b}$$

$$\log(\mathrm{hF}_i^{\mathrm{s}}) = \alpha_{\mathrm{s}} + \beta_{\mathrm{s}} \frac{\Delta t}{\tau_{\mathrm{s},i}} + \beta_{\mathrm{MW}}(\mathrm{MW}_i - \mathrm{MW}_0) \tag{3.33c}$$

for wheat, rice, apple and tomato, whereas for potato, the log of the soil compartment-specific harvest fraction is calculated as:

$$\log(\mathrm{hF}_i^{\mathrm{s}}) = \alpha_{\mathrm{s}} + \beta_{\mathrm{s}} \frac{\Delta t}{\tau_{\mathrm{s},i}} + \beta_{\mathrm{Koc}}\Big(\max\left[\log(\mathrm{Koc}_i); 0.75\right] - \log(\mathrm{Koc}_0)\Big) \tag{3.34}$$

and the log of compartment-specific harvest fractions for lettuce are finally calculated as:

$$\log(\mathrm{hF}_i^{\mathrm{p}}) = \alpha_{\mathrm{p}} + \beta_{\mathrm{p}}\, \Delta t \left(\frac{\ln(2)}{t_{1/2,\mathrm{p},i}} + 10^{\left(\alpha_{\mathrm{Koa}} + \beta_{\mathrm{Kaw}} \log(\mathrm{Kaw}_i) + \beta_{\mathrm{Kow}} \log(\mathrm{Kow}_i)\right)} \right) \tag{3.35a}$$

$$\log(\mathrm{hF}_i^{\mathrm{ps}}) = \alpha_{\mathrm{ps}} + \beta_{\mathrm{ps}} \frac{\Delta t \, \ln(2)}{t_{1/2,\mathrm{ps},i}} - \log\left(1 + \frac{t_{1/2,\mathrm{p},i}}{\ln(2)}\, 10^{\left(\alpha_{\mathrm{Koa}} + \beta_{\mathrm{Kaw}} \log(\mathrm{Kaw}_i) + \beta_{\mathrm{Kow}} \log(\mathrm{Kow}_i)\right)}\right) \tag{3.35b}$$

$$\log(\mathrm{hF}_i^{\mathrm{s}}) = \alpha_{\mathrm{s}} + \beta_{\mathrm{s}} \frac{\Delta t}{\tau_{\mathrm{s},i}} - \log\left(1 + \frac{t_{1/2,\mathrm{p},i}}{\ln(2)}\, 10^{\left(\alpha_{\mathrm{Koa}} + \beta_{\mathrm{Kaw}} \log(\mathrm{Kaw}_i) + \beta_{\mathrm{Kow}} \log(\mathrm{Kow}_i)\right)}\right) \tag{3.35c}$$

where α and β are dimensionless compartment-specific regression coefficients, Δt [d] denotes the time from pesticide application to crop harvest, $t_{1/2}$ [d] is the half-life in plant or on plant surface, τ_{s} [d] represents overall residence time in soil, MW [$\mathrm{g\,mol^{-1}}$] refers to molecular weight, $\mathrm{MW}_0 = 350\ \mathrm{g\,mol^{-1}}$ is a constant reference molecular weight, Kaw [–], Kow [–] and Koc [$\mathrm{L\,kg^{-1}}$] are air/water, n-octanol/water and soil organic carbon/water partition coefficients, respectively, and $\log(\mathrm{Koc}_0) = 3.5\ \mathrm{L\,kg^{-1}}$ is a constant reference

Koc. Coefficients in Eqs. 3.33, 3.34 and 3.35 are fitted on a set of 1540 pesticide-application time combinations for each crop. For fitting the regression coefficients, a weighting factor $\omega = -1/(\log(\mathrm{hF}) - 1)$ is introduced, which weights the square error for each data point by its corresponding harvest fraction over the full range of $\mathrm{hF} > 10^{-50}$ covered by the set of selected substances. This is to account for two factors: As a measure of the quality of predicted values, the residual error is increasing with decreasing harvest fractions due to the additional time for degradation to act. In addition, one is interested in being more accurate in the high harvest fraction range, more specifically in the range of $\mathrm{hF} > 10^{-10}$, for which residues in food crops after direct pesticide application may dominate human exposure, compared to exposure towards the pesticide fractions lost from the field (see Chapter 2). Mean values and standard deviations for crop-specific regression coefficients are presented in Table 3.5. From the standard deviations and related 95% confidence interval limits it can be seen that all considered regression coefficients are significantly different from zero.

Table 3.5.: Mean values $\overline{x}$ and 95% standard deviations STD for all regression coefficients of the parameterized models based on simulation runs ($n = 1540$) of 385 pesticides applied to six crops at four times before harvest.

	wheat		paddy rice		tomato		apple		potato		lettuce	
	$\overline{x}$	STD	$\overline{x}$	STD	$\overline{x}$	STD	$\overline{x}$	STD	$\overline{x}$	STD	$\overline{x}$	STD
α_{s}	-4.38	0.42	-6.02	1.08	-84.56	15.11	-6.48	0.62	-6.75	0.20	-3.28	0.39
α_{ps}	-2.98	0.34	-2.78	0.49	-37.80	6.62	-1.43	0.16	–	–	-1.16	0.92
α_{p}	-1.29	0.13	-1.06	0.23	-1.88	0.40	-1.94	0.20	–	–	-0.33	0.23
β_{s}	-0.39	0.04	-0.38	0.10	-0.01	0.002	-0.26	0.03	-0.45	0.04	-0.41	0.05
β_{ps}	-0.56	0.04	-0.53	0.06	-0.30	0.04	-1.37	0.10	–	–	-1.17	0.19
β_{p}	-0.32	0.03	-0.35	0.07	-0.16	0.03	-0.31	0.03	–	–	-0.43	0.02
β_{MW}	-0.003	0.001	-0.002	0.001	-0.001	0.001	-0.001	0.001	–	–	–	–
β_{Koc}	–	–	–	–	–	–	–	–	-0.79	0.15	–	–
α_{Koa}	–	–	–	–	–	–	–	–	–	–	5.66	0.66
β_{Kaw}	–	–	–	–	–	–	–	–	–	–	1.03	0.17
β_{Kow}	–	–	–	–	–	–	–	–	–	–	-0.52	0.03

3.4.5. Evaluation of crop-specific regression models

In Figure 3.7, harvest fractions predicted with the parameterized regression models are evaluated against harvest fractions compiled by the full dynamic model for the 1540 pesticide-application time combinations for the six crops.

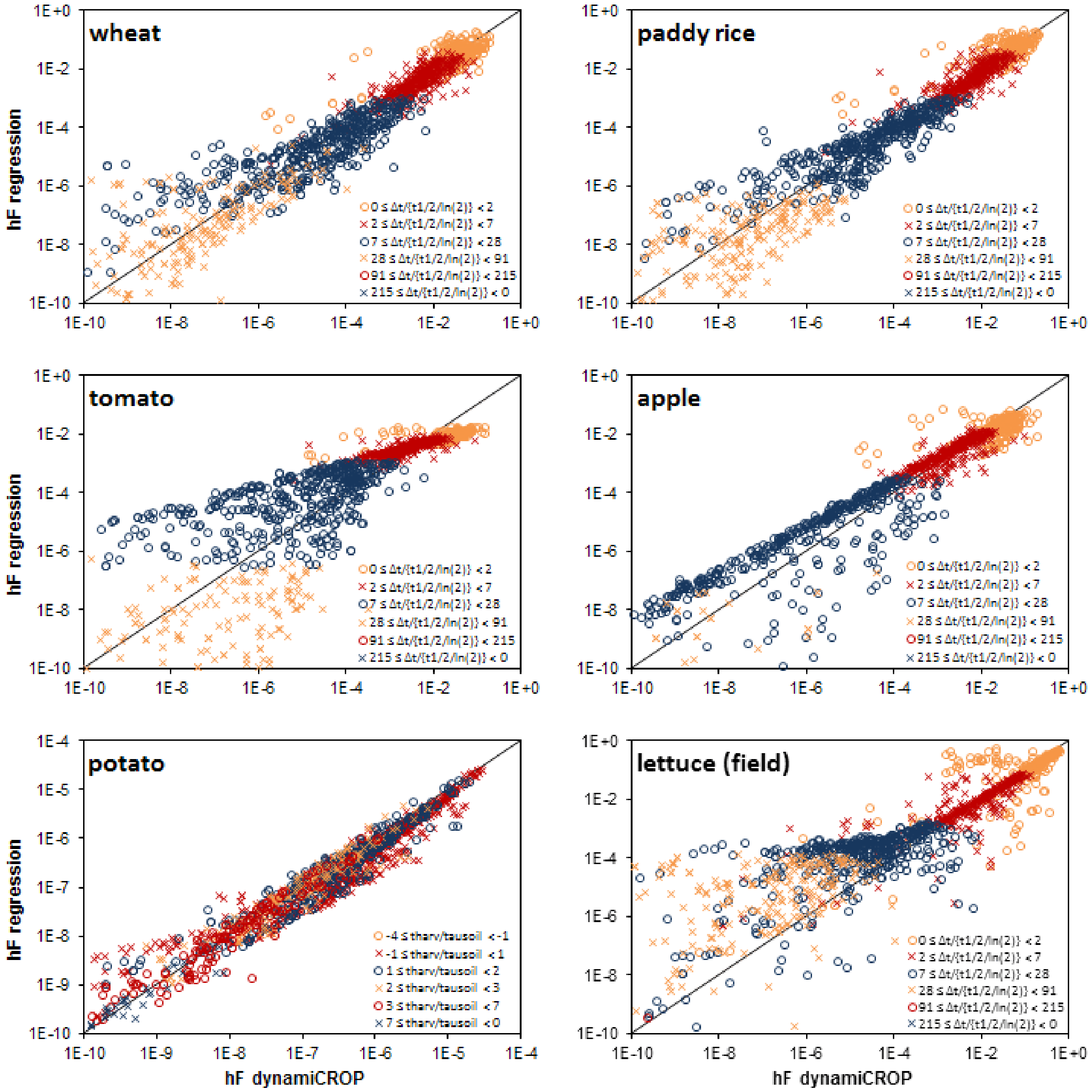


Figure 3.7.: Comparison of parameterized and full dynamic model for harvest fractions of 385 pesticides applied to six crops at four different times ($n = 1540$), grouped according to the ratio of time from application to harvest and degradation residence time in plant (for potato: residence time in soil).

Harvest fractions are presented and evaluated in the main range of interest, i. e. for hF $> 10^{-10}$. Predicted harvest fractions from the parameterized regression models and harvest fractions from the full dynamic model correspond well in the in the considered range and over the whole range of $\Delta t/\tau_{\mathrm{deg,p}}$ with the regression models explaining 91% (wheat), 92% (rice and potato), 66% (tomato), 75% (apple), and 80% (lettuce) of the variability of the full model in that range. Coefficients of variation vary from a factor of 21 (wheat), 17 (rice), 276 (tomato), 180 (apple), 4 (potato), and 137 (lettuce). Figure 3.7 also shows that the accuracy of predicted values increases with increasing harvest fractions. Values in Figure 3.7 are for all crops but potato grouped according to the ratio of time to harvest and degradation residence time in fruit, i. e. the required characteristic time until around 63% of the residual pesticide mass fraction in fruit is degraded. Increasing ratios lead to a decrease in harvest fractions. However, the good fit across crops would not be possible without accounting for plant surface and soil as important influences to the harvest fraction, of which the latter is exclusively driving the system dynamics for potato. In general, the longest residence time representing the predominantly driving compartment in the long-term must be taken into consideration in the regressions.

3.4.6. Conclusions

It was successfully demonstrated how to parameterize the full dynamic model into an accurate and yet parsimonious linear regression equation for each of the studied crops. By simplifying a complex model that builds upon 24 process rate coefficients based on about 80 underlying input variables, the input data requirements in the parameterization were reduced to finally a handful of variables. For adapting this approach to assess impacts of pesticides from ingestion of other food crops, systematic statistics will be required for the date of substance application and data on pesticide half-lives in plants and on plant surfaces.

If the substance-specific time from application to harvest is available, the additional uncertainty of less than one order of magnitude in the high hF range linked to the use of the parameterized model is much lower than the uncertainty of up to ten orders of magnitude resulting from a generic time to harvest, which is different from the actual time to harvest, applied in the full dynamic model. Further analysis is, however, required when applying the parameterized model to substances with very different properties than used in the present study.

Finally, spatial differences in assessing the environmental fate of pesticides as well as human exposure pathways that are not directly linked to uptake into food crops and subsequent intake via consumption may play a considerable role in human exposure assessments. From this perspective, it is an important advantage that the parameterized regression models are ultimately designed for integration into existing spatial multimedia models used in impact assessment. Such models are usually restricted to assess impacts from environmental emissions, which in case of pesticides refer to the mass fractions lost from the target field via wind drift, run off and leaching, thereby ignoring intake of pesticides from the mass directly reaching the target crops grown for human consumption.

Integrating the presented regression models will allow to account for both impacts caused by intake of pesticides directly applied to food crops, and impacts from the initial pesticide fractions that are lost from the target crop field. Accounting for both pathways finally ensures a fully integrated assessment of pesticide impacts on humans.

4. Assessment of human health impacts and damage costs related to pesticide use in Europe in 2003: A case study

4.1. Summary

Constantly growing environmental pollution from the intentional and unintentional release of chemicals including pesticides has been identified as the single mayor source of various negative effects on humans, animals, crops and ecosystems (Fiedler, 2003; Ebel and Davitashvili, 2005; Lerche and Glaesser, 2006). With respect to human health effects of pesticides, Margni et al. (2002); Hamilton and Crossley (2004); Humbert et al. (2007) and Juraske et al. (2009b) state that consumption of directly treated food crops is by far the most important exposure pathway. However, all these studies lack a comprehensive dynamic assessment of residues in various crop types contrasted against the pesticide fractions lost to beyond the field boundaries during and after application.

The present case study aims at filling this gap by providing a transparent and consistent approach of accounting for exposure towards pesticide residues in directly treated food crops as well as inhalation and ingestion exposure caused by the pesticide fractions lost from the field, all contributing to human health impacts from the same application amount. By contrasting impacts from direct crop consumption and from exposure towards fractions lost from the field, it will be evaluated to what extent each exposure pathway contributes to overall human health impacts. Thereby, it will be demonstrated that consumption of food crops directly treated with pesticides is the major contributor to overall human health impacts from pesticide application and that the contribution largely depends on the crop type and its intrinsic characteristics, such as crop-specific application time before harvest and harvested crop components.

Environmental problems have become of economic concern due to a constantly growing population and related scarcity of natural resources like land area for cultivating food crops. Since many environmental problems can negatively influence the welfare of a society as a whole or at least the welfare of some member groups of a society (Bowles and Webster, 1995; Markandya and Tamborra, 2005), negative effects on welfare have an economically measurable value. However, many of these negative effects arising from decisions within the economic market affect members of a society not directly involved in the decision. Hence, negative externalities occur leading to social costs that are not

accounted for on the related market products. More precisely, when consuming a food product leads to a negative effect from pesticide ingestion in a person that was not involved in the decision of applying pesticides on the corresponding food crop, such a negative externality occurs that can be expressed in terms of external or damage costs and that must be accounted for in the price of the marketed food product.

So far, available studies on damage costs related to pesticide use disregarded exposure from directly treated crops, e. g. Pimentel et al. (1992); Davison et al. (1996); Waibel and Fleischer (1998); Bailey et al. (1999); Pretty et al. (2000, 2001); Tegtmeier and Duffy (2004); Pimentel (2005); Rabl (2007) and finally Leach and Mumford (2008). By ignoring the exposure towards pesticide residues in food crops it is likely that these studies underestimate human health damages caused by pesticide use. However, many of these studies include costs from hospitalization or incapacitation for work to be used in cost-benefit analysis (CBA) or cost-effectivness analysis, which is beyond the scope of the present approach, where the focus is exclusively on the human health damage costs and not on identifying trade-offs between economic benefits of pesticide use in terms of e. g. avoided crop losses and the costs of pesticide use in terms of a specific environmental or social parameter. In addition, costs other than direct health damage costs are independent of the exposure pathway and can, hence, be added to the damage costs for conducting a comprehensive CBA or CEA, if desired. In Section 4.2, the overall approach for assessing human health damage costs from pesticide application is introduced, whereas in Section 4.3, a case study on quantifying health impacts and related damage costs for pesticides applied in Europe in the year 2003 is performed, of which the results are finally discussed in Section 4.4.

4.2. Followed approach to quantify external costs from pesticide application

4.2.1. Externalities from the use of pesticides

An externality or external effect, which can either be positive or negative, refers to the influence of a decision on the well-being of a third party and occurs outside the marked mechanism (Friedrich and Bickel, 2001; Bowles and Webster, 1995). As a consequence, an externality associated with e. g. the use of pesticides in agricultural food crop production is generally not taken into account in the decision making at the farmer level. However, since ignoring externalities in market prices can result in distortions in making decisions and in welfare reduction of parties not involved in the decision process (NRC Committee on Health, Environmental, and Other External Costs and Benefits of Energy Production and Consumption; National Research Council, 2010), it is important to account for externalities in regulatory actions.

It is stated by the EEA European Environment Agency (2005, p. 8) that "[m]any environmental problems stem from incorrect pricing of what we consume at the time we consume it. The challenge for European policy-makers is to ensure that the real costs of pollution and resource inefficiency are internalized into the prices of products and services, as opposed to later on at the end of the chain in the form of a pollution clean-up bill, damaged health or diminished ecosystems." In order to internalize negative effects into market prices, these effects must be (a) identified, (b) quantified and (c) translated into monetary terms (Bowles and Webster, 1995). With respect to the use of pesticides in current agricultural practice, human health impacts as well as damages on the environment are identified as negative external effects (Hamilton and Crossley, 2004; Pretty, 2005; Hanson and Ritter, 2010). Despite the benefits of using pesticides, such as constantly increasing crop yield along with maintaining a high food quality Cooper and Dobson (2007); EC European Commission (2007a), especially effects on human health are of continuous concern of the general public (EFSA European Food Safety Authority, 2006; Chalak et al., 2008; Karabelas et al., 2009).

Many studies exist addressing one or the other aspect of positive or negative external effects of pesticide use, e. g. Pimentel et al. (1992); Bowles and Webster (1995); Scott Frey (1995); Davison et al. (1996); Barnard et al. (1997); Waibel and Fleischer (1998); Bailey et al. (1999); Fleischer and Waibel (1999); Gray and Hammitt (2000); Pretty et al. (2000, 2001); Wilson and Tisdell (2001); Tegtmeier and Duffy (2004); Pimentel (2005); Cooper and Dobson (2007); Rabl (2007); Leach and Mumford (2008) and finally Koleva et al. (2011). However, with respect to the methodology to quantify external effects of pesticide application there exist large inconsistencies and gaps in existing assessments (Bowles and Webster, 1995; van der Bijl and Bleumink, 1997; Vorley and Keeney, 1998; Pretty et al., 2000). As an example, Bowles and Webster (1995) and Vorley and Keeney (1998) comment on studies by Pimentel and co-authors, e. g. (Pimentel et al., 1992), that it was not distinguished between different food commodities and that generic parameters were developed from individual measurements and applied without discussion to the entire agricultural sector. Another example is that van der Bijl and Bleumink (1997) and Pretty et al. (2000) criticize the overestimation of damage costs due to misleading questioning methods in studies by Davison et al. (1996). In addition, most of the pesticide external cost studies focus on aggregated commodity and pesticide levels, although different food crops and pesticide contribute significantly different to overall negative effects on humans. The problem of extrapolation between different pesticides is e. g. stated by Barnard et al. (1997). Pretty (2005, p. 42) finally summarizes the situation as follows: "Despite the fact that it has been common knowledge [...] that many pesticides cause harm to the environment and to human health, it is remarkable that there is an almost complete absence of a full costing of a single product." The authors further state that we don not know the marginal cost but, at best, only the total costs for the current situation. In the study by Leach and Mumford (2008), the authors therefore assess individual pesticides. However, 6 out of the 11 selected substances are not authorized for use in the considered countries. In order to overcome some of the drawbacks in existing studies on external costs of pesticide use, the following sections are devoted to a substance- and crop-specific assessment of human health impacts and related damage costs caused by pesticide application.

4.2.2. Impact Pathway Approach for pesticides

The present case study follows a structure, which is in line with the methodology of a general full chain assessment recommended by the EC European Commission (2008b) as a best practice methodology for assessing damage costs caused by environmental releases of chemicals. This bottom-up assessment methodology is referred to as Impact Pathway Approach (IPA) as described in Friedrich et al. (2001); EC European Commission (2005a) and integrates the input of different scientific disciplines within a consistent calculation framework as developed in the frame of ExternE, a project series funded by the European Commission (Ebel and Davitashvili, 2005). Starting with the activity of interest, i. e. in the present assessment the application of pesticides in agricultural practice, the IPA follows a pesticide's environmental fate predominantly starting with plant uptake from the atmosphere via equilibrium partitioning between vegetation and the gas phase, kinetically limited gaseous deposition as well as wet and dry particle-bound deposition (McLachlan, 1999; Böhme et al., 1999). As a next step, the IPA assesses the exposure towards pesticide concentrations either in relevant environmental media, such as air and (fresh) water, or directly in food crops harvested for human consumption. From the exposure, impacts on human health are estimated based on relationships between exposure levels and corresponding physical effects, such as cancer, commonly referred to as exposure- or dose-response relationships (ERF, DRF). However, in case of pesticides, information about ERF or DRF is only rarely available from other than pure occupational exposure studies (Alavanja et al., 2004; Sanborn et al., 2004). Hence, in the present assessment, effect factors from LCIA will be applied instead to arrive at the level of physical impacts in humans. The final step of an IPA is the translation of physical impacts into monetary terms expressed as damage costs, which might be used e. g. in CBA for evaluating environmental policies. All steps of an IPA applied for estimating damage costs caused by releases of pesticides into the environment are briefly described in the following.

Pesticide application and emission data

Only for very few pesticides – mostly classical persistent pesticides, such as DDT and γ-HCH – emissions have been officially estimated on the basis of emission factors by e. g. the EEA European Environment Agency (2009). As the fraction lost into air largely depends on the vapor pressure of a pesticide, emission factors can be classified on the basis of vapor pressure and, thus, usually be estimated for a wide range of pesticides (US-EPA United States - Environmental Protection Agency, 1995; EEA European Environment Agency, 2009). However, even with pesticide-specific emission factors at hand, required application data are rarely, if at all, available at both, the European and the national scale, since in many countries such data are subject to confidentiality clauses or only available to selected authorities. Without these data, emissions of pesticides cannot be calculated adequately according to Scholtz et al. (1999). In order to overcome these constraints, data on actual pesticide application are required as input for the subsequent case study and preferred over pure statistics on market sales or import/export of pesticides. In addition, statistics must not be aggregated over e. g. pesticide target classes, such as herbicides, fungicides and insecticides, but need to be pesticide-specific due to the substance-intrinsic differences with respect to the environmental fate and toxicity of pesticides as discussed further below.

Environmental fate assessment

The main outcome of the environmental fate assessment of pesticides is on the one hand a pesticide's residue in a particular food crop after direct treatment and on the other hand the fraction lost to beyond the crop field boundaries during and after the application process (see Figure 1.1). Pesticide residues in crops serve as input for obtaining the harvest fraction $\mathrm{hF}_{i,x}$ $[\mathrm{kg}_{\text{in harvest}}\,\mathrm{kg}^{-1}_{\text{applied}}]$, which relates the residual mass $m_{\text{residue},i,x}(t)$ of pesticide i in crop x at harvest time $t = t_{\text{harvest}}$ to 1 kg applied pesticide mass $m_{\text{applied},i,x}$ as defined in Eq. 2.16. Since only the latest application is taken into account in the present study according to Juraske et al. (2011), i. e. no background mass from previous applications is accounted for, the harvest fraction as applied in the subsequent case study calculates as follows:

$$\mathrm{hF}_{i,x} = \frac{m_{\text{residue},i,x}(t)}{m_{\text{applied},i,x}} \tag{4.1}$$

In contrast, the fraction of a pesticide lost from the crop field serves as input for calculating the concentrations in the environment subsequently required for assessing inhalation and ingestion exposure towards pesticide fractions lost via wind drift, run off and leaching.

Human exposure assessment

Human exposure is distinguished in the following case study into exposure caused by consumption of treated food crops containing pesticide residues and exposure from inhalation and ingestion of pesticide fractions lost from the crop field. As measure to express pesticide exposure to residues in food crops the human intake fraction $\mathrm{iF}_{i,x}$

$[\mathrm{kg}_{\mathrm{intake}}\,\mathrm{kg}^{-1}_{\mathrm{applied}}]$ is used as the product of $\mathrm{hF}_{i,x}$ and a loss factor accounting for food processing $\mathrm{PF}_{i,x}$ $[\mathrm{kg}_{\mathrm{intake}}\,\mathrm{kg}^{-1}_{\mathrm{in\,harvest}}]$ according to the definition in Eq. 2.22. However, since food processing factors are only available crop-specifically, but not for individual pesticides, a generic factor over all pesticides is applied per crop, i. e. PF_x:

$$\mathrm{iF}_{i,x} = \mathrm{hF}_{i,x} \times \mathrm{PF}_x \tag{4.2}$$

Human health impact assessment

Building on the results of the human exposure assessment, health impacts are calculated from exposure to pesticide residues in food crops and from exposure towards fractions lost from the target field. To express both by an equivalent measure, the human characterization factor $\mathrm{CF}_{i,x}$ is used as defined in Eq. 2.20 for residues in food crops and as defined in Rosenbaum et al. (2008) for the fractions lost from the field via wind drift to air, via run off to fresh water and via leaching to groundwater. Since for residues in crops, dynamiCROP is used to calculate $\mathrm{CF}_{\mathrm{residue},i,x}$ and since fractions lost into specific compartments c beyond the field boundaries, $\mathrm{CF}_{\mathrm{field-loss},i,x,c}$ are available from the USEtox model, both types of factors will finally be used to characterize human health impacts.

At this point it is necessary to discuss, why characterization factors originally developed for use in LCA are used instead of ERF or DRF information from epidemiological studies directly. There are many epidemiological studies regarding pesticides and human health available. However, findings from different studies are still highly controversial. For ethical reasons, randomized controlled trials are not performed with potentially harmful chemicals like pesticides (Sanborn et al., 2007). Consequently, we rely on different study designs with marked limitations as stated by Sanborn et al. (2004): (a) Most of the available studies are of occupational nature, i. e. they examine farmers, pesticide applicators, gardeners, and other occupational groups with higher exposures to pesticides than those of the general population. (b) Examined individuals are mostly adult males, which were subject to multiple exposures to various pesticides and other toxins and carcinogens such as diesel fumes, animal viruses, and cadmium. (c) If evaluated at all, the exposure history is often indirect and may be determined by a surrogate measure such as type of crop grown, annual expenditure on pesticides, or job description, rather than by direct evaluation of the exposed persons. (d) Confounding factors and covariates are often incompletely assessed, and information, such as cause of death from death certificates, may be inaccurate or incomplete. (e) The harmful health effects of the so-called inert substances used in pesticide products to potentiate the active ingredients can be difficult to separate from those of the active pesticide ingredients. (f) Finally, because all humans have some degree of background environmental pesticide exposure, there is never a true control group for any study design. As a consequence, ERF or DRF information from such studies is generally limited with respect to high exposure levels as observed from occupational exposure and is therefore not considered feasible for extrapolation to the general public. Instead, information on effects derived from pesticide dose-response slope factors is obtained according to the procedure for calculating effects as described in Section 2.5, finally applied to characterize the toxicity of individual pesticides. Detailed information on dose-response slope factors for generic cancer and non-cancer effects is given in the Appendix (Table C.3) based on ED50 or NOEL information collected from US-EPA United States - Environmental Protection Agency (2011b); AERU Agriculture and Environment Research Unit (2011); OCSEH Office of Chemical Safety and Environmental Health (2010); Huijbregts et al. (2005); FAO Food and Agriculture Organization of the United Nations (2005); Tomlin (2009) and Krieger and Krieger (2001).

To arrive at actual health impacts per country $\mathrm{IS}_{i,x}$ [DALY country^{-1}], characterization factors are combined with the respective mass in $\mathrm{kg}_{\mathrm{applied}}$ per country in crops (residues) or the environment (fractions lost from field) according to:

$$\mathrm{IS}_{\mathrm{residue},i,x} = \mathrm{CF}_{\mathrm{residue},i,x} \times m_{\mathrm{applied},i,x} \tag{4.3a}$$

$$\mathrm{IS}_{\mathrm{field-loss},i,x} = \sum_{c=1}^{n} \left(\mathrm{CF}_{\mathrm{field-loss},i,x,c} \times \mathit{fr\_m}_{\mathrm{applied},i,x,c} \right) \times m_{\mathrm{applied},i,x} \tag{4.3b}$$

where $\mathit{fr\_m}_{\mathrm{applied},i,x,c}$ [$\mathrm{kg}_{\mathrm{in\,compartment}}\ \mathrm{kg}^{-1}_{\mathrm{applied}}$] refers to the fraction of applied pesticide mass lost to environmental compartment c. Disability-adjusted life years, DALY, as applied by the WHO are used as composite metric for combining years of life lost (YOLL) due to premature mortality and years lived with a disability (YLD) due to the time lived in health states less than ideal health into an aggregated, time-based measure to assess the burden of disease (BoD) (Murray and Lopez, 1996a,b). Human health impacts are so far crop- and pesticide-specific, because substance-specific properties may significantly influence the mode of action of a chemical of concern (Lydy et al., 2004; Sanborn et al., 2004, 2007; Bassil et al., 2007). Hence, an assessment at substance basis is required, i. e. it is not adequate to assess and monetize related damages of pesticides aggregated according to their target or chemical classes, which is consistent with approaches followed by Hertwich and McKone (2001); Margni (2003) and Rosenbaum et al. (2008). However, according to Lydy et al. (2004) and Adam et al. (2008) it is possible to finally sum up health effects and, hence, related damage estimations, assuming additive toxicity as long as there is no other approach available for properly considering mixing effects of multiple substances. Human health impacts will, hence, be aggregated over all pesticides and finally also over all consumed crops:

$$\mathrm{IS}_{\mathrm{residue}} = \sum_{i=1}^{m} \sum_{x=1}^{n} \mathrm{IS}_{\mathrm{residue},i,x} \tag{4.4a}$$

$$\mathrm{IS}_{\mathrm{field-loss}} = \sum_{i=1}^{m} \sum_{x=1}^{n} \mathrm{IS}_{\mathrm{field-loss},i,x} \tag{4.4b}$$

Finally, both health impacts caused by pesticide residues in food crops and from fractions lost to beyond field boundaries can be integrated to arrive at overall impacts per country $\mathrm{IS}_{\mathrm{total}}$ [DALY country^{-1}] due to pesticide use in this country:

$$\mathrm{IS}_{\mathrm{total}} = \mathrm{IS}_{\mathrm{residue}} + \mathrm{IS}_{\mathrm{field-loss}} \tag{4.5}$$

Monetary valuation

Physical effects, i. e. in the present assessment human health impacts due to pesticide use in agriculture, can finally be translated into damages expressed in monetary terms, namely external costs EC [Euro country^{-1}]. These damages are in their simplest form calculated by multiplying the quantity of human health impacts $\mathrm{IS}_{\mathrm{total}}$ [DALY country^{-1}] from Eq. 4.5 by a corresponding monetary value, i. e. the damage factor DF [Euro DALY^{-1}] according to:

$$\mathrm{EC} = \mathrm{IS}_{\mathrm{total}} \times \mathrm{DF} \tag{4.6}$$

The damage factor represents, ideally, the "population average of the maximum willingness to pay for a unit improvement in this physical metric" (NRC Committee on Health, Environmental, and Other External Costs and Benefits of Energy Production and Consumption; National Research Council, 2010, p. 30). More precisely, the damage factor reflects the preferences of people for reducing the health impact given their income and wealth. Analogously, this damage factor refers to the price that people are willing to pay for a marketed product, such as commodities produced from food crops. Considering the scope of the present case study, namely Europe or more precisely EU25 (see Section 4.3.1), a damage factor of DF = 40,000 [Euro DALY^{-1}] is applied as recommended by Desaigues et al. (2011) based on a contingent valuation survey conducted in 9 European countries.

4.3. Case study on pesticide use in Europe in 2003

4.3.1. Substance-specific pesticide application

the scope of the present study is not on pesticide emissions (fractions lost from the target field via wind drift, run off and leaching), but on the total amount of applied pesticides (in contrast to pure market sales or trade statistics). Hence, none of the European-wide statistics databases, such as FAO (`http://faostat.fao.org`), EUROSTAT (`http://epp.eurostat.ec.europa.eu`) or the OECD Environmental Data Compendium (`http://www.oecd.org/dataoecd/56/45/41255417.pdf`), nor any national database is used. Instead, a review study from the EC European Commission (2007b) has been selected providing an overview report with detailed tables on the use of the most extensively used pesticides applied on the main crops in the EU25 (excluding Malta and with aggregated data for Belgium and Luxembourg) for all years between 1992 and 2003.

Table 4.1.: Share of 5 most extensively applied pesticides per country on overall pesticide amount applied per country for different crop classes and averaged over all crops.

country	cereals	maize	oil seeds	potato	sugar beets	grapes/vines	fruit trees	vegetables	total
AT	55%	35%	88%	93%	85%	77%	7%	61%	73%
BE	51%	35%	92%	81%	25%	n/a	n/a	55%	59%
CY	n/a	n/a	n/a	n/a	n/a	95%	n/a	100%	98%
CZ	19%	84%	54%	77%	72%	49%	n/a	63%	59%
DE	34%	30%	53%	70%	68%	85%	6%	73%	61%
DK	78%	n/a	84%	95%	81%	n/a	4%	51%	80%
EE	10%	n/a	88%	83%	n/a	n/a	n/a	n/a	60%
ES	24%	83%	n/a	66%	79%	91%	1%	81%	64%
FI	24%	n/a	93%	77%	96%	n/a	5%	40%	60%
FR	29%	34%	53%	85%	50%	78%	6%	46%	56%
GB	41%	n/a	63%	80%	52%	n/a	6%	48%	56%

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Table 4.1 (continued)

country	cereals	maize	oil seeds	potato	sugar beets	grapes/vines	fruit trees	vegetables	total
GR	34%	88%	n/a	57%	73%	87%	4%	38%	61%
HU	30%	62%	23%	37%	30%	74%	n/a	21%	43%
IE	36%	n/a	62%	90%	25%	n/a	0%	26%	48%
IT	18%	49%	48%	52%	45%	79%	3%	76%	55%
LT	8%	n/a	59%	95%	10%	n/a	n/a	4%	44%
LV	20%	n/a	19%	92%	10%	n/a	n/a	22%	44%
NL	60%	47%	14%	66%	79%	n/a	n/a	36%	51%
PL	43%	69%	68%	77%	58%	n/a	4%	65%	60%
PT	31%	73%	n/a	59%	75%	87%	3%	74%	63%
SE	42%	n/a	100%	43%	74%	n/a	5%	64%	59%
SI	81%	29%	50%	64%	29%	84%	10%	50%	52%
SK	37%	86%	47%	82%	69%	79%	10%	23%	62%

As the data situation differs between the years with 2003 being the year with the most complete dataset for pesticide usage, the year 2003 is selected as assessment year for the present case study. However, the report by EC European Commission (2007b) only covers the 5 most extensively used pesticide per country with respect to overall quantity applied, thereby amounting to 133 different pesticides used in EU25 in 2003. In addition, the total amount of applied pesticides per country has been reported, from which the share of the 5 listed pesticides per country to the total amount can be calculated. Table 4.1 gives an overview of the share of reported pesticide application amounts to the overall amount of applied pesticides per country. Considered countries along with their ISO 3166-1 alpha-2 codes according to ISO International Organization for Standardization (2011) are given in the Appendix (Table C.1).

In none of the listed countries the provided pesticides cover 100% of the overall applied amount in 2003. The range of the share on the total amounts applied varies from 43% for Hungary to almost 98% for Cyprus averaged over all considered crops. On average, the reported 5 most extensively used pesticides per crop type contribute to the overall applied amount per crop type with 5% for fruit trees, 36% for cereals, 51% for vegetables, 57% for maize and sugar beets, 61% for oil seeds, 74% for potato and finally 80% for grapes/vines. In total, only around 59% of the total amount of pesticides applied in EU25 in 2003 are provided. However, being the single exclusive source reporting pesticide-specific application data for EU25, this reference is nevertheless used as basis for the present case study. Figure 4.1 gives an overview of the actual mass applied per country considering the 5 most extensively used pesticides per country.

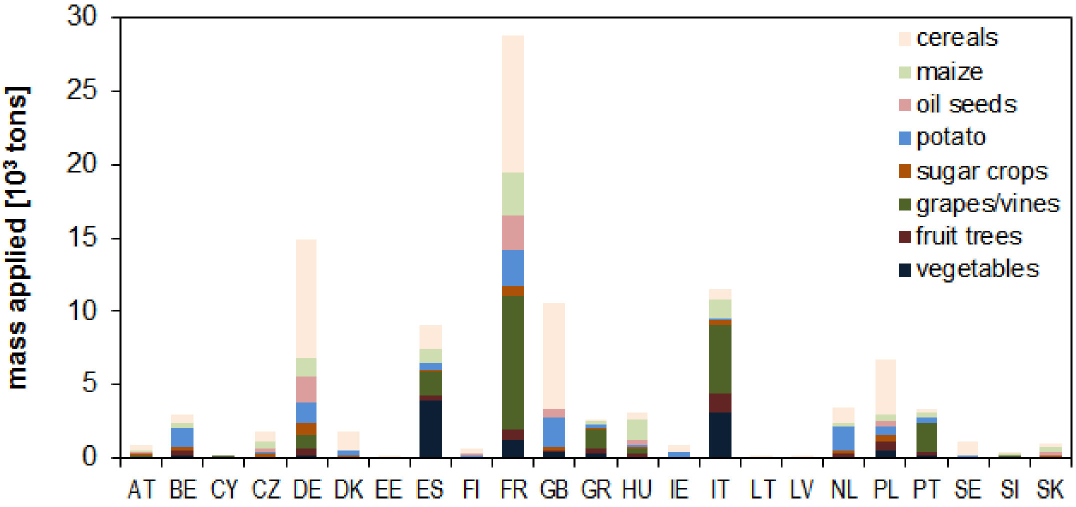

Figure 4.1.: Mass of 5 most extensively used pesticides per crop applied in EU25 in 2003 compiled from data provided by EC European Commission (2007b).

Considering only the reported individual pesticides, the highest amount is applied on cereals and the lowest amount is applied on sugar beets with a sum over all countries of about 30,000 tons and 3,900 tons, respectively, in 2003. France applies by far the highest amount of pesticides with more than 20,000 tons reported only for the 5 most extensively used pesticides in 2003, thereby contributing to the overall reported amount in Europe with almost 25%. France is followed by Germany, Italy, United Kingdom and Spain, all with reported amounts of around 10,000 tons in 2003 and accounting together with France for more than 70% of the overall pesticide use reported in Europe.

4.3.2. Human health characterization factors

Before using the reported pesticide amount applied in 2003 as input for calculating the related impacts on human health, the applied pesticides must be characterized. As measure to characterize a pesticide independently from the actually applied amount is the characterization factor, i. e. this measure is calculated normalized to 1 kg mass applied. Characterization factors with respect to human health effects from ingestion of pesticides via food crop consumption are calculated by means of the dynamiCROP model as presented in Chapter 2. Since the categorization of crops in the report from EC European Commission (2007b) does not match the crops implemented in the dynamiCROP model (see Section 2.4), which are distinguished on the basis of worldwide consumption pattern according to FAO Food and Agriculture Organization of the United Nations (2011), both crop classifications were merged as a function of crop characteristics. As a result, wheat in dynamiCROP is applied for calculations of pesticides sprayed on cereals, maize and oil seeds, potato is applied to potato and sugar beet, tomato is applied to grapes/vines and vegetables as well as apple is finally applied to represent fruit trees. In contrast, characterization factors obtained from Rosenbaum et al. (2008) for the pesticide fractions lost from the crop field are independent of any crop, hence, the crop classification as explained above was applied to also account for human health effects from inhalation and ingestion caused by the fraction lost from the field during and after application.

Characterization factors for residues in food crops vary for cancer effects between 8.7×10^{-12} DALY per $\mathrm{kg}_{\mathrm{applied}}$ for fosetyl applied to potato to 1.7×10^{-03} DALY per $\mathrm{kg}_{\mathrm{applied}}$ for prochloraz applied to lettuce and for non-cancer effects between 5.8×10^{-31} DALY per $\mathrm{kg}_{\mathrm{applied}}$ for trinexapac-ethyl applied to wheat to 6.1×10^{-02} DALY per $\mathrm{kg}_{\mathrm{applied}}$ for diquat applied to lettuce. On average over all considered pesticides ($n = 133$), characterization factors for non-cancer effects are in the same range as factors for cancer effects, despite the fact that for 17 out of 29 reported effect factors for cancer effects a zero value was used, indicating that these 17 pesticides do not cause any cancer effect at all (in contrast to missing information indicated by 'n/a'). When disregarding the zero values for cancer effects, the average characterization factors (median or 50%-ile) over all considered pesticides are 1.7×10^{-07}, 2.9×10^{-05}, 5×10^{-05}, 1.5×10^{-06}, 1.2×10^{-08} and 5.4×10^{-05} DALY per $\mathrm{kg}_{\mathrm{applied}}$ for wheat, paddy rice, tomato, apple, potato and lettuce, respectively. Average characterization factors for non-cancer effects over all considered pesticides are 1.6×10^{-08}, 7.3×10^{-06}, 1.6×10^{-05}, 7.3×10^{-07}, 5.8×10^{-09} and 2.8×10^{-05} DALY per $\mathrm{kg}_{\mathrm{applied}}$ for wheat, paddy rice, tomato, apple, potato and lettuce, respectively. In contrast to cancer-related characterization factors, information on non-cancer effects is available for all 133 considered pesticides, which is why finally the non-cancer effects will contribute more to the overall human health impacts caused by pesticide application in EU25 in 2003 than the cancer effects. All characterization factors for resides in food crops are given in the Appendix (cancer effects: Table C.4, non-cancer effects: Table C.5).

In contrast to characterization factors for residues in food crops, factors obtained from Rosenbaum et al. (2008) for pesticide fractions lost from the field via air and soil were only available for 27 substances with respect to cancer effects, of which 17 have zero value assigned, and for 73 substances with respect to non-cancer effects out of the full list of 133 considered pesticides. Lowest characterization factors were reported for non-cancer effects of metiram with 1.2×10^{-11} DALY per $\mathrm{kg}_{\mathrm{field\text{-}loss}}$ and fosetyl with 2.4×10^{-11} DALY per $\mathrm{kg}_{\mathrm{field\text{-}loss}}$, both due to the fraction lost via soil and highest factors were reported for non-cancer effects of chlorfenvinphos with 3.4×10^{-05} DALY per $\mathrm{kg}_{\mathrm{field\text{-}loss}}$ due to the fraction lost via soil and oxyfluorfen with 2.6×10^{-05} DALY per $\mathrm{kg}_{\mathrm{field\text{-}loss}}$ due to the fraction lost via air. When disregarding the zero values for cancer effects, the median characterization factors for the fraction lost via air are 5.1×10^{-08} for cancer effects and 5.2×10^{-07} for non-cancer effects as well as for the fraction lost via soil 3.1×10^{-08} for cancer effects and 1×10^{-07} for non-cancer effects. All characterization factors for fractions lost from the field via air and soil are given in the Appendix (Table C.6). In

Figure 4.2, characterization factors for residues in food crops are contrasted to factors for fractions lost from the field via air and soil.

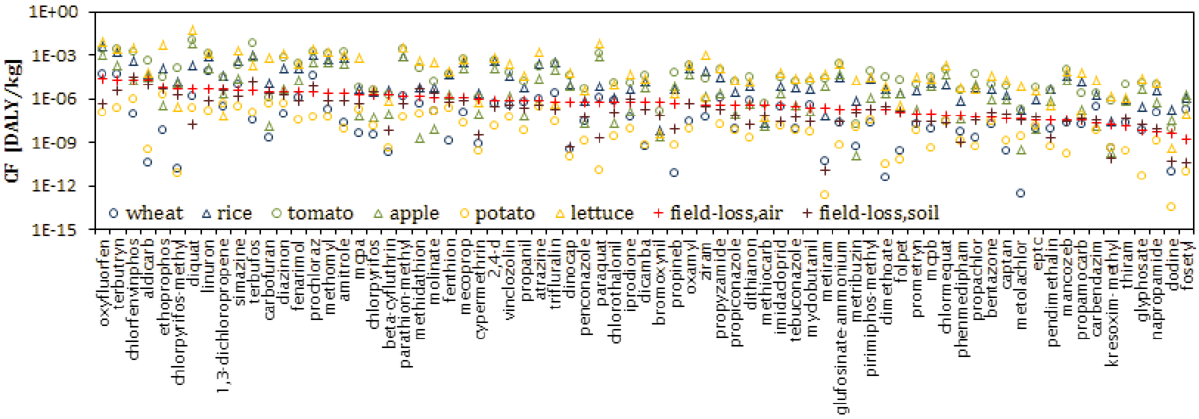

Figure 4.2.: Comparison of crop-specific human toxicity characterization factors from residues with human toxicity characterization factors due to fractions lost from the field via air and soil for the 73 pesticides with available toxicity data from Rosenbaum et al. (2008), all aggregated over cancer and non-cancer effects.

In Figure 4.2, it can be seen that for all considered pesticides ($n = 73$) for which effect information was available from both dynamiCROP and Rosenbaum et al. (2008), characterization factors related to residues in food crops are always the highest values for any pesticide, thereby indicating that disregarding residues in food crops after direct application of pesticides onto these crops will strongly underestimate the overall effects on human health. However, Figure 4.2 also indicates that the contribution to human health effects also depends on the considered food crop with potato showing values usually lower than values related to field loss via air and soil, while lettuce, tomato and rice exceed values related to field loss for almost all pesticides. For wheat and apple the relative contribution to overall effects depends on the pesticide, since for some substances, values are higher than values from field loss and for other substances, values are lower than values from field loss via air and soil. When summing up all considered crops, however, it is clear that residues in food crops always strongly dominate the overall human health effects of pesticides used in the EU25 in 2003.

The importance of the characterization factors provided in the present section is that they can be applied to obtain human health impacts for other scenarios just by multiplying the pesticide- and exposure pathway-specific factors with the corresponding mass applied to a food crop or mass lost from the field via the corresponding environmental medium according to Eqs. 4.3a and 4.3b. Since characterization factors are calculated from the environmental fate of individual pesticides, they largely depend on the substances physicochemical properties (see Sections 2.3 and 2.4). An overview of the target class (e. g. fungicide, herbicide, insecticide), molecular weight, partition coefficients and degradation half-lives for the 133 pesticides considered in the present case study is given in the Appendix (Table C.2).

4.3.3. Human health impacts from pesticide use

Human health impacts caused by pesticide application are expressed in DALY per country and summarized in Figure 4.3 for EU25 countries in 2003. Overall, highest impacts on human health are found in Spain, Italy and France with 485, 442 and 370 DALY, respectively. Health impacts in these 3 countries alone sum up to 78% of the overall health impacts in the EU25 in 2003. On the lower end, Estonia, Lithuania and Sweden only face health impacts of 0.05, 0.17 and 0.42 DALY, respectively. The average health impacts due to all exposure pathways over all considered countries and grown crops would be around 73 DALY in 2003. Detailed information on health impacts per country are given in the Appendix (Table C.7), distinguished according to exposure pathway (residues in food crops and field loss via air and soil) and health effect (cancer and non-cancer).

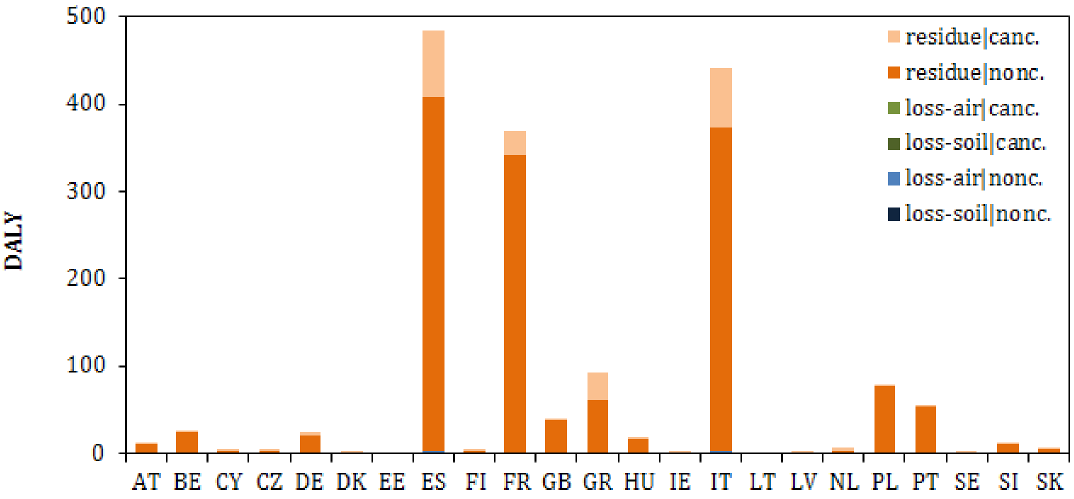

Figure 4.3.: Overall human health impacts expressed in DALY per country due to both ingestion of pesticide residues via food crop consumption and pesticide intake due to fractions lost from the field via air and soil for EU25 in 2003, distinguished according to cancer (canc) and non-cancer (nonc) effects.

Overall, health impacts caused by the fractions lost from the field via air and soil sum up to only 9.5 DALY in EU25 in 2003 (Figure 4.4), again showing highest values for Spain, Italy and France with 3.4, 2.3 and 0.9 DALY per country. Highest contribution to overall health impacts caused by field loss fractions is due to loss via air leading to non-cancer effects followed by loss via soil, also leading to non-cancer effects. Fractions

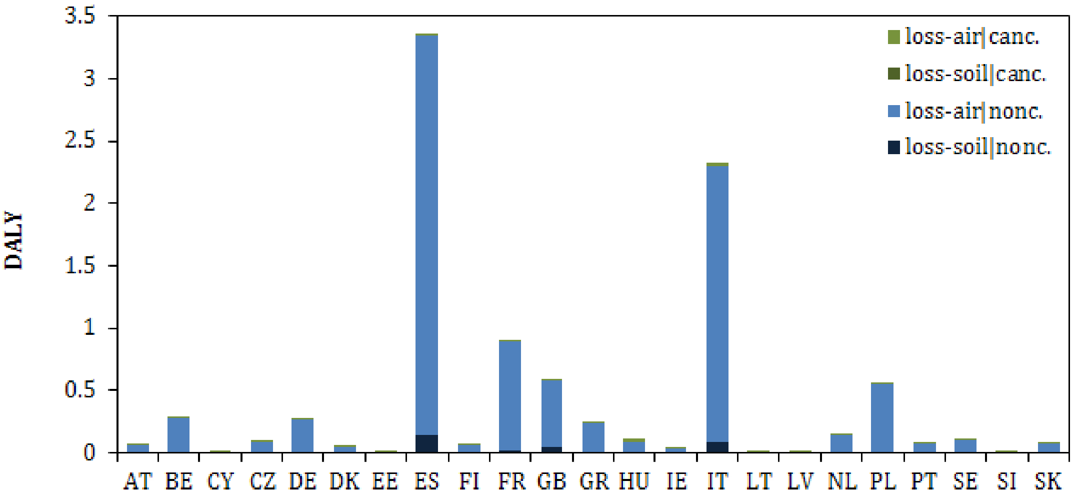

Figure 4.4.: Human health impacts expressed in DALY per country caused by pesticide intake due to fractions lost from the field via air and soil for EU25 in 2003, distinguished according to cancer (canc) and non-cancer (nonc) effects.

lost via air all in all contribute to health impacts due to field loss with a variation between 93% in the United Kingdom and 99.9% in Latvia. In contrast, losses via soil all in all only contribute to health impacts due to field loss with an average of 1.5% over all countries.

Summarizing the results on health impacts from pesticide application in EU25 in 2003, residues in food crops contribute most to the overall health impacts in all considered countries with a variation between 75.5% in Sweden and 99.9% in Slovenia as shown in Figure 4.5.

In countries with the highest overall health impacts, residues in food crops contribute with 99.3% (Spain), 99.5% (Italy) and 99.7% (France) to impacts per country. In contrast, fractions lost via air and soil only contribute with an average of 2.6% (0.4 DALY) to the overall health impacts per country. Among residues in food crops, the contribution of cancer effects to health impacts varies between 0.3% in Poland and 61% in the Netherlands with an average of around 10% over all countries. Compared to that, the contribution of non-cancer effects to health impacts due to residues in food crops varies between 36.7% in the Netherlands and 99.3% in Slovenia with an average of 87% over all countries. Consequently, the contribution of fractions lost from the field via air and soil on average only amounts to 2.6% over all countries with the minimum and maximum contribution to overall health impacts per country of 0.04% in Slovenia and 24.5% in Sweden, respectively. Detailed information on the contribution of different exposure pathways to overall health impacts per country are given in the Appendix (Table C.8).

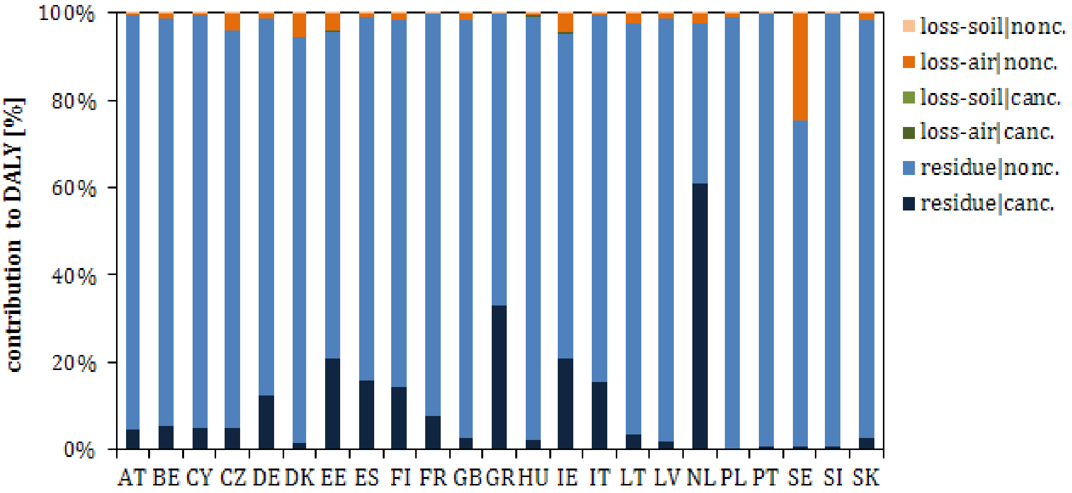

Figure 4.5.: Contribution of ingestion of pesticide residues via food crop consumption and pesticide intake due to fractions lost from the field via air and soil to overall human health impacts per country for EU25 in 2003, distinguished according to cancer (canc) and non-cancer (nonc) effects.

4.3.4. Human health damage costs from pesticide use

Table 4.2.: Overall health damage costs expressed in million Euro per country, health damage costs due to residues in food crops and fractions lost from the field expressed in million Euro per country as well as contribution θ of residues in food crops and fractions lost from the field to overall health damage costs in EU25 in 2003.

country	EC_{total}	$EC_{residue}$	$EC_{field\text{-}loss}$	$\theta_{EC,residue}$	$\theta_{EC,field\text{-}loss}$
AT	0.48	0.48	2.37×10^{-03}	99.51%	0.49%
BE	1.03	1.02	1.17×10^{-02}	98.87%	1.13%
CY	0.11	0.11	5.11×10^{-04}	99.55%	0.45%
CZ	0.10	0.09	3.96×10^{-03}	95.86%	4.14%
DE	0.96	0.95	1.08×10^{-02}	98.88%	1.12%
DK	0.04	0.04	2.19×10^{-03}	94.61%	5.39%
EE	0.002	0.002	8.34×10^{-05}	95.77%	4.23%
ES	19.39	19.25	1.35×10^{-01}	99.31%	0.69%
FI	0.16	0.16	2.43×10^{-03}	98.47%	1.53%
FR	14.80	14.76	3.65×10^{-02}	99.75%	0.25%
GB	1.57	1.55	2.40×10^{-02}	98.48%	1.52%
GR	3.68	3.67	9.80×10^{-03}	99.73%	0.27%

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Table 4.2 (continued)

country	EC_{total}	$EC_{residue}$	$EC_{field\text{-}loss}$	$\theta_{EC,residue}$	$\theta_{EC,field\text{-}loss}$
HU	0.67	0.66	4.72×10^{-03}	99.29%	0.71%
IE	0.03	0.03	1.24×10^{-03}	95.38%	4.62%
IT	17.68	17.59	9.28×10^{-02}	99.48%	0.52%
LT	0.01	0.01	1.60×10^{-04}	97.68%	2.32%
LV	0.02	0.02	2.77×10^{-04}	98.78%	1.22%
NL	0.25	0.25	5.97×10^{-03}	97.63%	2.37%
PL	3.08	3.06	2.24×10^{-02}	99.27%	0.73%
PT	2.20	2.20	3.63×10^{-03}	99.84%	0.16%
SE	0.02	0.01	4.26×10^{-03}	75.47%	24.53%
SI	0.41	0.41	1.83×10^{-04}	99.96%	0.04%
SK	0.20	0.20	3.30×10^{-03}	98.39%	1.61%

Human health effects expressed in DALY per country translated into monetary values yield human health damages in terms of damage costs or external costs expressed in Euro per country. Overall human health damage costs are summarized in Figure 4.6 and in Table 4.2 for EU25 countries in 2003. In line with the human health impacts as discussed in the previous section, highest damage costs are found in Spain, Italy and France with 19.4×10^{06}, 17.7×10^{06} and 14.8×10^{06} Euro per country, respectively, in 2003, accounting for about 78% of the overall health damage costs in EU25 in 2003. Countries with least health damage costs in 2003 are Estonia, Lithuania and Sweden with only 1.97×10^{03}, 6.88×10^{03} and 17.38×10^{03} Euro per country, respectively. The average health damage costs due to all exposure pathways over all considered countries and grown crops sum up to around 67 million Euro in 2003. Detailed information on human health damage costs per country is given in in the Appendix (Table C.9) with substance-specific damage costs per country also being available in the Appendix (cancer effects due to intake of residues in food crops: Table C.10; non-cancer effects due to intake of residues in food crops: Table C.11).

Human health damage costs due to fractions lost from the field via air and soil are summarized in Figure 4.7 highest for Spain, Italy and France with 1.3×10^5, 8.9×10^4 and 3.6×10^4 Euro, respectively, per country. Lowest damage costs are expected in Slovenia, Lithuania and Estonia with 183.1, 159.8 and 83.4 Euro, respectively, per country. On average over all considered countries, damage costs due to fractions lost from the field are 3.8×10^5 Euro per country with average damage costs of 3.6×10^5 Euro per country for fractions lost via air and 1.3×10^4 Euro per country for fractions lost via soil for EU25 in 2003.

Human exposure towards pesticide residues in treated food crops predominantly contributes to overall human health damage costs in EU25 in 2003 (Table 4.2) with a

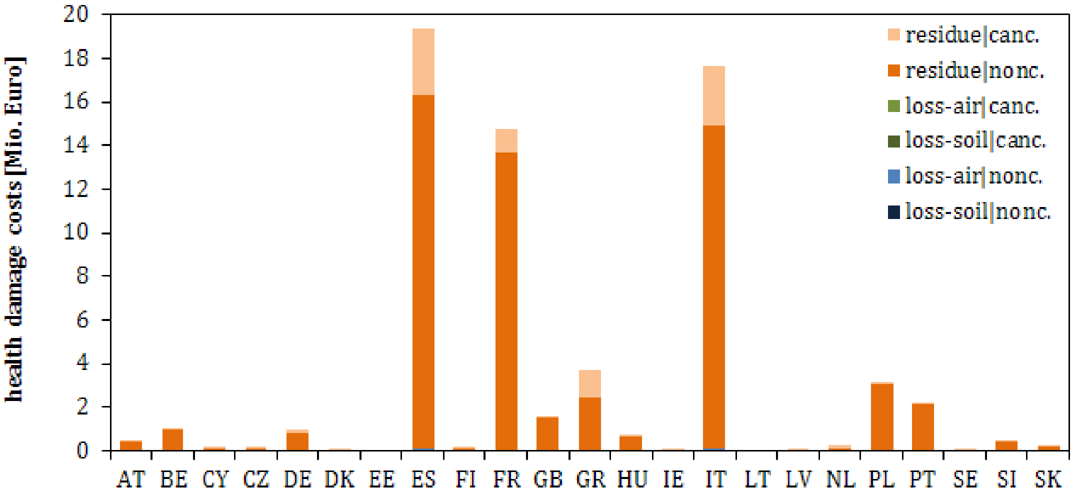

Figure 4.6.: Overall health damage costs expressed in 10^6 Euro per country due to both ingestion of pesticide residues via food crop consumption and pesticide intake due to fractions lost from the field via air and soil for EU25 in 2003, distinguished according to cancer (canc) and non-cancer (nonc) effects.

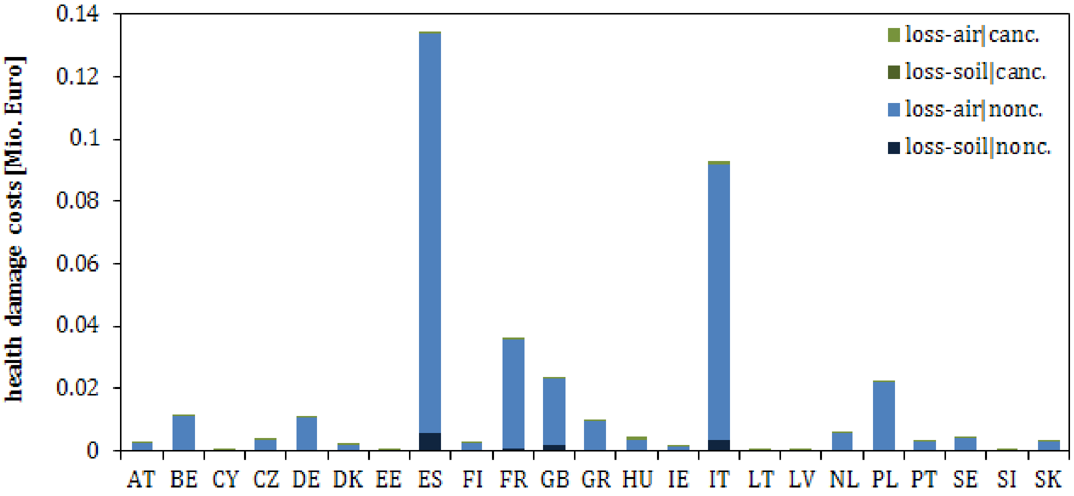

Figure 4.7.: Health damage costs expressed in 10^6 Euro per country due to ingestion of pesticide residuess via food crop consumption for EU25 in 2003, distinguished according to cancer (canc) and non-cancer (nonc) effects.

contribution between 75.5% in Sweden and 99.9% in Slovenia. With respect to damages exclusively caused by residues in food crops (Figure 4.8), cancer effects contribute only between 0.3% in Poland and 62% in the Netherlands, i. e. on average, cancer effects contribute with about 11% to damage costs per country caused by food residues.

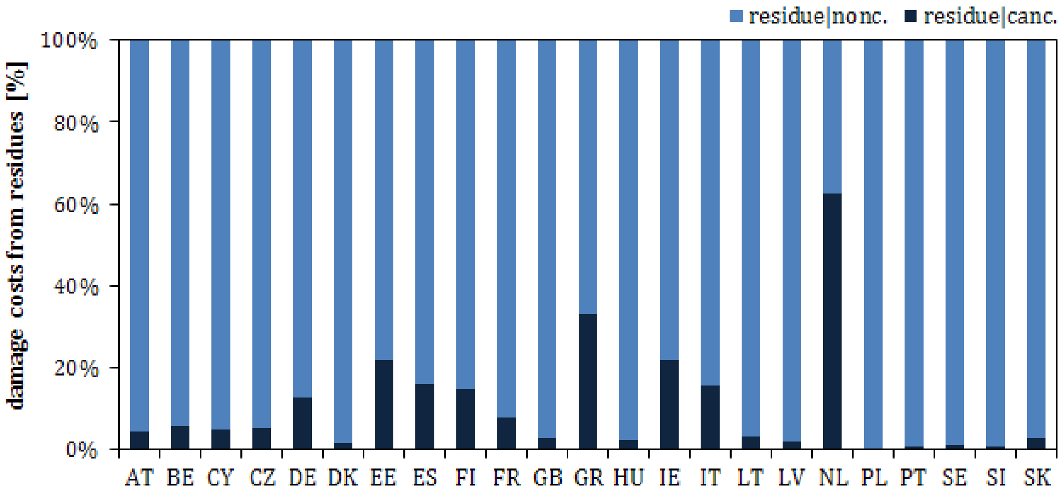

Figure 4.8.: Contribution of cancer and non-cancer effects to health damage costs due to ingestion of pesticide residues via food crop consumption per country for EU25 in 2003.

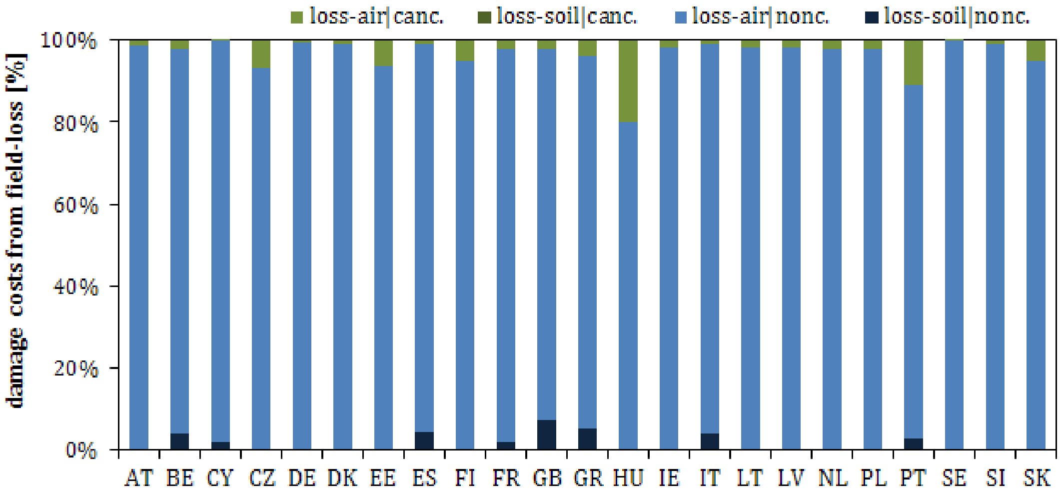

Figure 4.9.: Contribution of cancer and non-cancer effects as well as of fractions lost from the field via air and soil to health damage costs per country for EU25 in 2003.

In contrast, non-cancer effects on average amount to about 89% contribution to damages caused by food residues with highest contributions in Poland, Slovenia, Portugal and Sweden with 99.7%, 99.3%, 99.2% and 99%, respectively. With respect to damages exclusively caused by fractions lost from the field via air and soil (Figure 4.9), losses via air are predominant with a contribution between 92.9% in the United Kingdom and 99.9% in Estonia. On average, fractions lost from the field via air and soil contribute with 98.5% and 1.5%, respectively, to damage costs due to field losses. Again, non-cancer effects are predominating damage costs caused by field losses with a contribution between 79.8% in Hungary and 99.7% in Sweden. On average, cancer and non-cancer effects contribute with 3.5% and 96.5%, respectively, to health damage costs per country caused by field losses via air and soil. Overall, non-cancer effects caused by field losses via air are predominating damage costs due to field losses with an average contribution of 95.1% over all countries.

For getting an impression of the damage costs per kg of an applied pesticide per country, Table 4.3 summarizes for all countries the minimum and maximum damage costs per kg applied pesticide expressed in Euro per kg. The high variation between pesticides implies a high variation of pesticide-intrinsic toxicity potentials of several orders of magnitude. Variation between countries for the same pesticide is due to the application to different food crops, i. e. in case that a pesticide is authorized for use on more than one crop, applying the pesticide to another crop yields different costs per kg applied as a function of the crop-specific substance fate and corresponding residues. Lowest damage costs per kg applied pesticide are found in Slovenia and Italy with damage costs of 2.3×10^{-26} and 7×10^{-20} Euro per kg applied, respectively. In contrast, highest damage costs per kg applied pesticide are obtained for Greece with 58.8 Euro per kg applied and for Finland and Poland with each 54.6 Euro per kg applied.

Table 4.3.: Overall health damage costs per kg applied pesticide expressed in Euro/kg per country in EU25 in 2003.

country	min Euro/kg	substance	max Euro/kg	substance
AT	6.5×10^{-19}	PYRIDATE	36.12	DAZOMET
BE	5.5×10^{-05}	FLUAZINAM	36.12	DAZOMET
CY	1.5×10^{-01}	CHLORPYRIFOS	3.91	MANCOZEB
CZ	1.3×10^{-11}	ACETOCHLOR	3.91	MANCOZEB
DE	7.3×10^{-08}	QUINMERAC	3.91	MANCOZEB
DK	2.2×10^{-05}	FENPROPIMORPH	0.81	MANCOZEB
EE	4.8×10^{-05}	GLYPHOSATE	0.37	PROMETRYN
ES	1.3×10^{-11}	ACETOCHLOR	49.83	METHOMYL
FI	1.8×10^{-13}	FLUAZIFOP-P-BUTYL	54.61	LINURON
FR	1.3×10^{-11}	ACETOCHLOR	36.12	DAZOMET
GB	4.8×10^{-05}	GLYPHOSATE	8.92	SIMAZINE
GR	6.2×10^{-05}	METAMITRON	58.82	AMITROLE
HU	1.3×10^{-11}	ACETOCHLOR	3.91	MANCOZEB
IE	2.2×10^{-05}	FENPROPIMORPH	10.74	TRIFLURALIN
IT	7.0×10^{-20}	CYCLOXYDIM	10.74	TRIFLURALIN

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Table 4.3 (continued)

country	min Euro/kg	substance	max Euro/kg	substance
LT	4.8×10^{-05}	GLYPHOSATE	4.31	CLOPYRALID
LV	4.8×10^{-05}	GLYPHOSATE	4.31	CLOPYRALID
NL	6.5×10^{-19}	PYRIDATE	9.99	AMITROLE
PL	1.3×10^{-11}	ACETOCHLOR	54.61	LINURON
PT	1.4×10^{-05}	S-METOLACHLOR	3.91	MANCOZEB
SE	1.6×10^{-06}	DICHLORPROP-P	4.31	CLOPYRALID
SI	2.3×10^{-26}	TRINEXAPAC-ETHYL	24.39	DIAZINON
SK	1.3×10^{-11}	ACETOCHLOR	24.39	DIAZINON

An important aspect in the assessment of health damages due to pesticide use is the assessment year and the corresponding registration status for each considered substance. With respect to European legislation in 2011, only 94 out of 133 substances considered in the present case study are still authorized for use in plant protection products according to current pesticide legislation (see Annex I of Council Directive 91/414/EEC, EC European Commission (1991)).

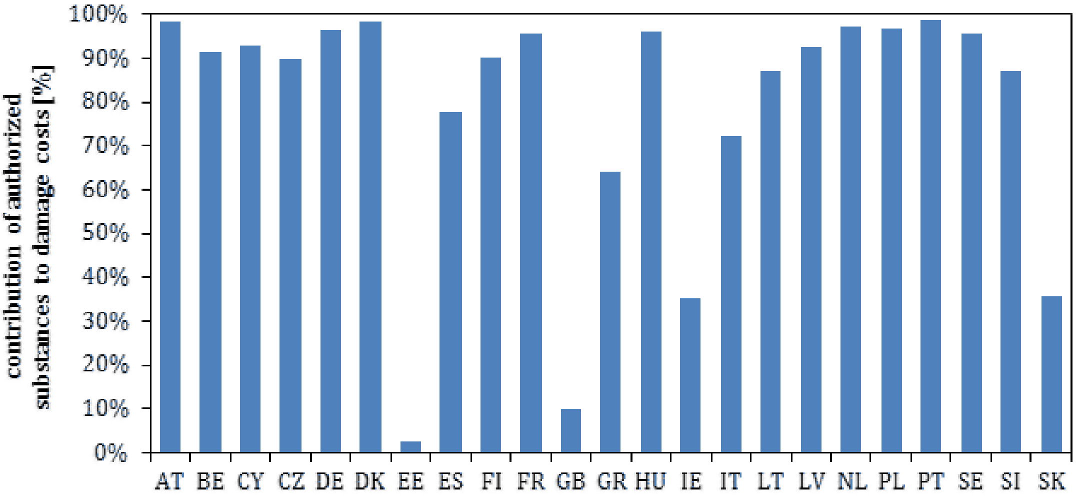

Figure 4.10.: Contribution of pesticides authorized for use in plant protection products in the EU in 2011 (see Annex I of Council Directive 91/414/EEC, EC European Commission (1991)) to the overall health damage costs per country due to pesticide use in 2003.

If only pesticides had been applied in the case study for the assessment year 2003, which are still authorized to be marketed in 2011, the overall health damage costs in EU25 countries would have been reduced to only 54 million Euro. More specifically, pesticides authorized in 2011 would contribute to overall damage costs in 2003 with an average of

78.3% per country. Highest contributions are obtained in Portugal, Austria and Denmark with a contributin of still authorized pesticides to overall damage costs in 2003 of 98.8%, 98.3% and 98.2%, respectively, whereas lowest contributions are obtained in Estonia and United Kingdom with a contribution of still authorized pesticides to overall damage costs in 2003 of only 2.4% and 9.8%, respectively (see Figure 4.10).

4.4. Discussion of case study results

In the present chapter, the Impact Pathway Approach was successfully applied for estimating human health damage costs caused by application from pesticides in EU25 in 2003 considering two important exposure pathways, namely ingestion of pesticide residues via consumption of food crops as well as pesticide intake caused by fractions lost from the field via air and soil. It was demonstrated that human health damage costs due to pesticide residues in treated food crops are exceeding damage costs due to field losses via air and soil between a factor of 3 in Sweden and more than 3.5 orders of magnitude in Slovenia with an average exceedance over all considered countries of more than 2 orders of magnitude per country. Overall health damage costs amount to 67 million Euro in EU25 in 2003, of which damages from residues in food crops contribute with 99.4% in contast to damages from field losses only contributing with 0.56%.

As basis for quantifying human health effects and related damage costs two input components are required: (a) data on actual pesticide application amounts on a substance-specific basis and (b) human toxicity characterization factors normalized to a unit pesticide application mass based on cancer and non-cancer effect information. Both components are currently restricted with respect to data availability, thereby leading to additional assumptions in the frame of a consistent impact assessment.

Application data. Country-specific application data are restricted in terms of availability for the full set of applied substances in any considered country within EU25 for confidentiality and other reasons. However, pesticides can significantly differ in their toxicity, persistence and mobility (Barnard et al., 1997). This is especially problematic, because there is no possibility to compare toxicities of reported pesticides with toxicities of pesticides that are in addition applied in a country. More specifically, pesticides that are not reported in the considered application data source, i. e. EC European Commission (2007b), might very well show much higher toxicity than pesticides that are applied in reported high amounts. This is, because it is likely that farmers apply higher amounts of pesticides that are less toxic – first and foremost to themselves as practitioners applying pesticides (Wilson and Tisdell, 2001). Hence, linearly extrapolating from existing pesticide application data to the overall amount of applied pesticides will most probably underestimate overall human health impacts and related damage costs in EU25 in 2003.

Effect data. Substance-specific cancer and non-cancer effect information on human health are restricted in terms of availability for the full set of applied substances and probably in terms of all potential health effects. In particular, information of cancer effects is lacking for many of the considered substances, i. e. no cancer effect information is available for 104 of 133 considered pesticides (78%). This does not indicate that a substance leads to higher health impactts in humans via non-cancer effects than via cancer effects, but simply reflects the availability on corresponding effect data. However, due to the fact that effect information is strongly pesticide-specific, extrapolation between different substances e. g. simply based on similar chemical class or target class is not possible (Barnard et al., 1997). In addition, cancer as well as non-cancer effects, of which the latter are usually extrapolated from information on NOEL, are aggregated into a single generic factor for each effect category, i. e. generic cancer and generic non-cancer effect factors. These generic factors are mostly extrapolated from animals as studied receptors, such as rats or dogs and furthermore extrapolated from subacute or subchronic to chronic effects (see Tabl C.3 in the Appendix), thereby leading to additional uncertainties in the current approach.

Overall uncertainties sum up from every single step in the applied approach, i. e. from the quantification of pesticide application amounts up to the translation of human health impacts into monetary values. Highest uncertainties, however, are related to missing or extrapolated effect information (Huijbregts et al., 2005; Sanborn et al., 2004, 2007), followed by inconsistent understanding of pesticide degradation kinetics in the environment, in particular in food crops (Dubus et al., 2003; Juraske et al., 2008; Thomas et al., 2011), of which the latter has been discussed in the frame of an extensive sensitivity and uncertainty analysis of the dynamiCROP model applied to estimate human toxicity characterization factors as described in Chapter 3.

Finally, apart from damage costs related to impacts on human health there are costs arising from damages on the environment that most probably predominate overall damage costs (Brock et al., 2009; Pretty, 2005), and costs arising from crop losses due to proliferation of pests and effects on agricultural soils from pesticide pollution. Wilson and Tisdell (2001) state that in such a situation, not only the total revenue from agriculture is affected, but also the production costs are increased.

However, despite all considered uncertainties and assumptions involved in the presented approach to estimate human damage costs caused by pesticide application in Europe, the presented damage cost estimates for EU25 in 2003 represent damages on human health that (a) are within an acceptable accuracy range and that (b) otherwise could not or only qualitatively be assessed. Consequently, the present approach is a suitable tool to support both practitioners in human health impact assessment of pesticides – especially by implementing the parameterized version of the dynamic multicrop model for assessing pesticide residues in food crops as introduced in Section 3.4 – and decision makers in the context of evaluating current and developing future environmental policies with respect to pesticide regulation at the national and European level.

5. Conclusions and outlook

5.1. Conclusions

Technology assessments in Europe have mainly focused on air quality management with respect to energy conversion and road transport. However, other environmental media must also be considered to arrive at an integrated perspective for developing strategies towards more sustainability and an improved human welfare. Consequently, bioaccumulation of pollutants in the environment, in food crops and in animal food products leads to human ingestion exposure that must be accounted for. Since only little is known about how the health of the general population is affected by current agriculture in Europe, especially with respect to the use of pesticides, the presented work aimed at improving existing health impact assessments of pesticide use by contrasting pathways of human exposure to pesticides. In this context, key priorities of the Sixth Environment Action Programme of the European Community 2002-2012 are amongst others human health and quality of life (EC European Commission, 2002). Within these priorities, European policy calls for the development of thematic strategies including a coherent and integrated strategy on the sustainable use of pesticides to minimize the impacts to human health and the environment stemming from the use of pesticides and to reduce the levels of harmful pesticides used, in particular by substituting the most dangerous substances with safer alternatives (EC European Commission, 2007a).

Human health impact assessments help to identify the most harmful substances in Europe by integrating over pesticides, effects on human health and human exposure pathways towards pesticides. However, despite the success of applying existing methods in the frame of assessing health impacts and related damage costs caused by pesticide use, the focus has mostly been restricted to occupational exposure and on an aggregated level of substances, thereby disregarding the identification of pesticides of highest concern and pesticide exposure of the general public towards important exposure pathways, such as residues in directly sprayed food crops. This is mostly due to the inherent complexity of assessing pesticide residues in different food crops on a substance-specific basis requiring a dynamic approach.

It was the first objective of the present study to develop a new operational modeling approach for quantifying human health impacts and related damage costs from exposure to pesticide residues in food crops, resolved according to account for different food crop types and for intrinsic differences of pesticide physicochemical properties and toxicity.

It was the second objective to then compare the outcome of this new modeling approach with health impacts due to the fractions lost from the field via air and soil as calculated by means of existing modeling tools.

A major challenge was to design a framework that consistently accounts for the complexity of plant uptake and translocation processes of pesticides in a dynamic way in line with pesticide pulse application. To address this challenge, the newly developed framework is based on a transparent matrix algebra approach representing a flexible set of all relevant environmental and plant compartments interconnected via an aggregated set of transfer processes. Due to the complexity of the model design with high input data demand, the framework has been finally parameterized in a way that it can be easily used to extend existing frameworks and by only building on a handful of required input parameters, thereby keeping the disaggregation of crops and substances.

The present framework was applied for assessing human health impacts of the 133 most extensively used pesticides applied in EU25 in 2003. Results indicate that there exist large differences of health impacts between countries mainly due to the country-specific application amounts of individual pesticides on crops and because these pesticides have distinct human cancer and non-cancer toxicity potentials. This strongly emphasizes that European pesticide regulation authorities should consider crop- and substance-specific assessments in contrast to current practice in estimating health impacts related to pesticide use on aggregated levels.

However, introducing a detailed assessment level is accompanied by additional uncertainty. Predominantly, this uncertainty is driven by missing or extrapolated substance-specific effect information as well as by lacking knowledge regarding pesticide degradation kinetics in the environment, underlining the fact that any mathematical model, regardless of its physical level of detail, is by definition only a simplification of reality (Oberkampf et al., 2002). Uncertainty in the present approach was assessed by evaluating model results against independent data, i. e. modeled pesticide residues in different crops were compared with measured concentrations from independent studies. In addition, a systematic matrix-based sensitivity and uncertainty assessment was conducted for identifying the most important aspects driving pesticide dynamics in the different considered crop-environment systems and for propagating and reducing uncertainties of most important input variables. Results of the uncertainty assessment provide evidence of the suitability of the presented approach to be applied for health impact assessment of pesticides with reasonable accuracy.

It was shown in a case study of estimating health damages caused by pesticide use in EU25 that total damages amount to 67 million Euro in 2003. Results of the case study demonstrate a strong correlation between human health damages and a combination of both pesticide application amount and substance-intrinsic toxicity. Damages per kg applied pesticide range from 2.3×10^{-26} Euro per kg for an application of the plant growth regulator trinexapac-ethyl to oil seeds in Slovenia to 58.8 Euro per kg for an application of the herbicide amitrole to grapes and vines in Greece. Residues in food crops are considered the single most important exposure pathway with respect to human health impacts contributing with 97.4% to overall impacts in EU25 in 2003. With respect to the 5 most extensively applied pesticides, Spain, Italy and France show highest human health impacts of 485, 442 and 370 DALY per country, respectively, leading to damage costs of 19.4×10^6, 17.7×10^6 and 14.8×10^6 Euro per country, respectively. Consequently, disregarding residues in food crops as exposure pathway will lead to strongly underestimating overall human health impacts from pesticide use in Europe. Generally, non-cancer effects dominate calculated impacts, which is partly due to missing cancer effect information.

Compared to damages of classical air pollutants, such as sulfur dioxide and nitrogen oxides, the contribution of the 5 most extensively used pesticides applied in EU25 is rather marginal. More specifically, the total quantifiable damage costs due to pesticide application as provided by EC European Commission (2007b) for the year 2003 constitute about 0.029% of those of classical air pollutants amounting to 230 billion Euro with a 3% discount rate and about 0.028%, when damage costs from classical air pollutants are discounted at a rate of 0% and summing up to about 240 billion Euro, both for the year 1990 (Droste-Franke, 2005). Compared to damage costs of trace elements, such as arsenic and lead, damages from pesticide application EU25 in 2003 constitute about 6.3% of those of trace elements amounting to 1.05 billion Euro with a 3% discount rate and about 0.1%, when damage costs from trace elements are discounted at a rate of 0% and summing up to about 63 billion Euro, both for the year 1990 (Bachmann, 2006).

It should be taken into account that overall pesticide application may lead to significantly higher damage costs due to human health impacts considering the lack of available data for about 50% of the pesticide amount applied in EU25 in 2003 and the variation in pesticide-specific toxicity effect factors of up to 5 orders of manitude. However, extrapolation from available data to estimate overall health damages from pesticide application is not considered feasible due to lack of information of pesticide usage and differences between pesticides with respect to environmental fate and exposure behavior as well as with respect to differences in toxicities.

All in all, results of the present study emphasize the need of considering pesticide residues in food crops as human exposure pathway along with the ability and strength of the developed approach to dynamically account for these residues in a substance- and crop-specific way for use in pesticide health impact assessments. The presented approach is moreover applicable to consider changing initial conditions and provides an easy-to-apply parameterized model version for extending existing impact assessment frameworks.

Finally, a method of how to account for pesticide substitution was presented, helping practitioners and decision makers to compare impacts of individual pesticides by taking application amount, toxicity and pest control capacity into account. Hence, the presented approach is helpful for future assessments and easy to use within other frameworks to estimate exposure towards pesticides with the limitation to assess neutral organic compounds.

5.2. Outlook

With respect to assessing negative impacts caused by the use of pesticides in European agricultural practice, it is important not only to focus on human health, but to also consider the environment, since many pesticides may in fact lead to higher impacts on ecosystems than harming human health (Coats and Yamamoto, 2003; Pretty, 2005; Brock et al., 2009). However, assessment approaches to fully quantify pesticide impacts on ecosystems are still lacking. Furthermore, benefits and impacts of alternative agricultural practices like organic crop production will have to be compared with benefits and impacts of conventional agricultural practice. From an integrated assessment perspective, it is essential for such a comparison not only to include effects of the use of pesticides, but to also include other aspects, such as the additional production area demand for keeping equal overall yield levels or alternative pest control strategies. As a potential result, health impacts due to pesticide use might very well be reduced when changing from conventional to organic agriculture (Juraske and Sanjuán, 2011), while at the same time other impacts might increase, such as impacts related to increased oil and gasoline use (Hokazono and Hayashi, 2012), thereby possibly outweighing or even exceeding pesticide-related impacts.

The presented approach can be further improved by accounting for the fact that inorganics require a different consideration of their partitioning behavior and ionizable compounds require considering electrochemical interactions for the dissociated species. With that, the presented method can be extended for also assessing other pollutants of concern like persistent organic pollutants (POPs), e. g. PCDD/Fs, PAHs, and PCBs, or substances relevant under the REACH regulation, e. g. HBCDD or PFOS. In addition to substance- and crop-specific characteristics and accounting for the system dynamics as a function of time, also spatial variation may influence results relevant for a health impact assessment of pesticide use. This is due to the fact that e. g. soil properties like organic carbon content or pesticide degradation half-lives in soil vary significantly as a function of the location (Dubus et al., 2003; Ghafoor et al., 2011). Hence, considering site-specific conditions will further improve results of pesticide-related impact assessments. Finally, results of the present work indicate that it is essential for future research with respect to improving pesticide health impact assessments to focus on the availability of substance-specific pesticide application data across all European countries, a better understanding of pesticide degradation kinetics as well as the availability of substance- and disease-specific effect information.

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Appendices

A. Formulation of dynamiCROP environmental fate processes

A.1. Partitioning between compartments/phases

The partition coefficient between n–octanol and water, $K_{\mathrm{o/w}}$ [kg·m^{-3} per kg·m^{-3}] (Table B.2), is based on the concentration ratio of a substance in n–octanol and water (Baum, 1998, p. 135; Trapp and Matthies, 1998, p. 40; Mackay, 2001, p. 85):

$$K_{\mathrm{o/w}} = \frac{C_{\mathrm{o}}}{C_{\mathrm{w}}} \tag{A.1}$$

where
C_{o} : Concentration of substance in n–octanol [kg m^{-3}]
C_{w} : Concentration of substance in water [kg·m^{-3}]

The partition coefficient between air (or the atmospheric ground layer) and water, $K_{\mathrm{a/w}}$ [kg·m^{-3} per kg·m^{-3}] (Table B.2), is calculated as a function of Henry's law constant, the universal gas constant and the temperature and is also known as the 'dimensionless Henry's law constant' (Mackay, 2001, p. 85):

$$K_{\mathrm{a/w}} = \frac{C_{\mathrm{a}}}{C_{\mathrm{w}}} = \frac{H}{R \cdot T} \tag{A.2}$$

where
C_{a} : Concentration of substance in air [kg·m^{-3}]
C_{w} : Concentration of substance in water [kg·m^{-3}]
H : Henry's law constant [Pa·m^{3}·mol^{-1}] with $H = P_{\mathrm{sat}}/S_{\mathrm{w}}$ (Baum, 1998, p. 124-26), where P_{sat} is the saturation vapor pressure [Pa] and S_{w} is the water solubility [mol·m^{-3}] at 25 °C temperature according to Lyman et al. (1990); Sander (1999); see Table B.2
R : Universal gas constant [J·mol^{-1}·K^{-1}]; see Table B.1
T : Temperature [K]

The ratio between $K_{\mathrm{o/w}}$ and $K_{\mathrm{a/w}}$ yields the partition coefficient between n–octanol and air, $K_{\mathrm{o/a}}$ [kg·m^{-3} per kg·m^{-3}] (Mackay, 2001, p. 40; 85):

$$K_{\mathrm{o/a}} = \frac{C_{\mathrm{o}}}{C_{\mathrm{a}}} = \frac{K_{\mathrm{o/w}}}{K_{\mathrm{a/w}}} \tag{A.3}$$

where
C_{o} : Concentration of substance in n–octanol [kg·m^{-3}]
C_{a} : Concentration of substance in air [kg·m^{-3}]
$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.1
$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

The partition coefficient between soil organic carbon and water, $K_{\mathrm{oc/w}}$ [L·kg^{-1}][3], is also known as 'organic carbon soil sorption coefficient', a measure of how well a substance adsorbs (sticks) to soil (Capri and Karpouzas, 2008; Baum, 1998). Wherever no substance specific value is given, $K_{\mathrm{oc/w}}$ can be derived as a function of $K_{\mathrm{o/w}}$ by means of a linear regression, valid for 'predominantly hydrophobics' according to EC European Commission (2003, Part III, p. 26):

$$\log K_{\mathrm{oc/w}} = a_{\mathrm{oc/w-o/w}} \cdot \log K_{\mathrm{o/w}} + b_{\mathrm{oc/w-o/w}} \tag{A.4}$$

where
$a_{\mathrm{oc/w-o/w}}$: regression coefficient (slope) in linear relation between $K_{\mathrm{oc/w}}$ and $K_{\mathrm{o/w}}$ [L·kg^{-1}]; see Table B.1
$b_{\mathrm{oc/w-o/w}}$: regression coefficient (y-intercept) in linear relation between $K_{\mathrm{oc/w}}$ and $K_{\mathrm{o/w}}$ [L·kg^{-1}]; see Table B.1
$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.1

However, for many pesticides, $K_{\mathrm{oc/w}}$ does not need to be estimated, but is given as measured value (Table B.2).

A.2. Degradation

In the present work, degradation refers to the various processes leading to a reduction of a chemical by biological, chemical and photochemical decomposition in all considered compartments, all assumed to follow first order kinetics in line with e. g. Boesten et al. (2006). The rate of pesticide degradation increases with temperature, organic matter

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[3] Unit is derived as follows: [kg$_{\text{in organic fraction}}$·kg^{-1}$_{\text{organic carbon}}$ per kg$_{\text{in solution}}$·L^{-1}$_{\text{water}}$].

content, and soil pH as higher temperature might favor both microbial and chemical decomposition (Pingali and Roger, 1995, p. 10, 121).

Whenever an overall degradation half life for a specific substance in a particular compartment is available from literature, online databases or other models, it is possible to just link the overall degradation rate coefficient in that compartment to the given overall degradation half life (Mackay, 2001, p. 126):

$$k_{\mathrm{comp}_i,\mathrm{deg}} = \frac{\ln(2)}{t_{\frac{1}{2},\mathrm{comp}_i}} \tag{A.5}$$

where

$k_{\mathrm{comp}_i,\mathrm{deg}}$: overall (bulk) degradation rate coefficient in compartment i [$\mathrm{d_{in\ compartment}}^{-1}$]

$t_{\frac{1}{2},\mathrm{comp}_i}$: overall degradation half life in compartment i [$\mathrm{d_{in\ compartment}}$]

Degradation in atmospheric ground layer

Under the different European regulations on the one hand for pesticides and on the other hand for POPs, degradation in air plays different roles. In the frame of the European pesticide regulation framework, all Member States must submit specific substance information (see also Section 1.2) for the inclusion of an active ingredient according to Annex II of Council Directive 91/414/EEC (EC European Commission, 1991) and Annex II of Regulation 1107/2009/EC (EC European Commission, 2009b). While Member States must submit e. g. information on the degradation half lives in water, soil and sediment as basis for the underlying persistence criterion for approval of an active substance (EC European Commission, 2009b, Annex II, 3.7.2.1), no such information is required for air. In contrast to pesticide regulation, when it comes to the evaluation of POPs, not only persistence, but also the potential to undergo long-range transport is an important criterion (Klecka et al., 2000; Klasmeier et al., 2005; Scheringer et al., 2009), for which the degradation half life in air plays a significant role according to the UNECE POPs Protocol (UNECE United Nations Economic Commission for Europe, 1998) and the Stockholm Convention (UNEP United Nations Environment Programme, 2004).

However, if the degradation half life in air is not available, the degradation rate coefficient can be calculated based on the combination of the individual processes that contribute to the overall degradation rate coefficient. In the compartment *atmospheric ground layer*, three processes contribute to the overall degradation rate coefficient, i. e. photochemical oxidation, photolysis and, in specific cases, hydrolysis, all calculated as a function of the intermittend character of rainfall rather than on assuming a constant value for annual rain, which goes in line with Hertwich (2001a) and Jolliet and Hauschild (2005). As a first approximation, it is assumed that all these contributing processes mostly apply to the gas phase in the atmospheric ground layer as the degradation of OH radicals is shielded by the binding to atmospheric particles. The contribution of each process to the overall degradation in the atmospheric ground layer can be thus calculated as sum of the contributing processes for the dry and wet periods, i. e. between and during rain events (Jolliet and Hauschild, 2005, p. 4514), which gives the overall gas phase degradation rate coefficient in the atmospheric ground layer (without considering particle degradation), $k_{\mathrm{a,deg}}$ [d^{-1}]:

$$k_{\mathrm{a,deg}} = k_{\mathrm{a,deg,dry}} + k_{\mathrm{a,deg,wet}} \tag{A.6}$$

where

$k_{\mathrm{a,deg,dry}}$: overall gas phase degradation rate coefficient in the atmospheric ground layer during dry periods [d^{-1}]; see Equation A.7

$k_{\mathrm{a,deg,wet}}$: overall gas phase degradation rate coefficient in the atmospheric ground layer during wet periods [d^{-1}]; see Equation A.7

Both overall gas phase degradation rate coefficients in the atmospheric ground layer during dry and wet periods, $k_{\mathrm{a,deg,dry}}$ [d^{-1}] and $k_{\mathrm{a,deg,wet}}$ [d^{-1}] are calculated based on similar principles, i. e. considering the sum of contributing processes as mentioned above (Jolliet and Hauschild, 2005, p. 4514). In this equation, the term $\left(k_{\mathrm{a,deg,H_2O}} \cdot C_{\mathrm{a,HO^-/H^+}}\right)$ represents the hydrolysis rate coefficient in the atmospheric ground layer during the dry and wet periods (US-EPA United States - Environmental Protection Agency, 2008):

$$\begin{aligned} k_{\mathrm{a,deg,dry}} &= \left(1 - \mathit{fr\_V}_{\mathrm{a,sus}}\right) \cdot k_{\mathrm{a,dry,OH}} + k_{\mathrm{a},h\nu} + k_{\mathrm{a,deg,H_2O}} \cdot C_{\mathrm{a,HO^-/H^+}} \\ k_{\mathrm{a,deg,wet}} &= \left(1 - \mathit{fr\_V}_{\mathrm{a,sus}}\right) \cdot k_{\mathrm{a,wet,OH}} + k_{\mathrm{a},h\nu} + k_{\mathrm{a,deg,H_2O}} \cdot C_{\mathrm{a,HO^-/H^+}} \end{aligned} \tag{A.7}$$

where

$\mathit{fr\_V}_{\mathrm{a,sus}}$: average fraction of substance in the atmospheric ground layer that is sorbed to suspended particles [L·L^{-1}]; see Equation A.8

$k_{\mathrm{a,dry,OH}}$, $k_{\mathrm{a,wet,OH}}$: photochemical oxidation rate coefficient in the atmospheric ground layer during daytime dry and wet period, respectively [d^{-1}]; see Equations A.10 and A.11, respectively

$k_{\mathrm{a},h\nu}$: photolysis rate coefficient in air during dry and wet period [d^{-1}]; see Table B.1

$k_{\mathrm{a,deg,H_2O}}$: degradation rate coefficient in the atmospheric ground layer due to hydrolysis [L·mol^{-1}·d^{-1}]; see Table B.1

$C_{\mathrm{a,HO^-/H^+}}$: average concentration of HO$^-$ or H$^+$ ions in the atmospheric ground layer (at pH = 7) [mol·L^{-1}]; see Table B.1

For gas phase degradation, only the average fraction of substance in the atmospheric ground layer that is not sorbed to suspended particles, $(1 - \mathit{fr\_V}_{\mathrm{a,sus}})$, is taken into account, where $fr\_V_{\text{a,sus}}$ [L·L-1] is derived as follows (Boethling and Mackay 2000, p. 239; Boethling et al. 2004, p. 2304; Jolliet and Hauschild 2005, p. 4514):

$$fr\_V_{\text{a,sus}} = \frac{K_{\text{sus/pg}} \cdot C_{\text{a,sus}}}{1 + K_{\text{sus/pg}} \cdot C_{\text{a,sus}}} \tag{A.8}$$

where

$K_{\text{sus/pg}}$: suspended particles/gas phase partition coefficient [kg·kg-1 per kg·m-3]; see Equation A.9

$C_{\text{a,sus}}$: average concentration of suspended particles in the atmospheric ground layer [kg·m-3]; see Table B.1

To calculate the fraction of substance in the atmospheric ground layer that is not sorbed to suspended particles, it is necessary to account for partitioning between suspended particles and the pure gas phase in the atmospheric ground layer. Thus, the suspended particles/gas phase partition coefficient, $K_{\text{sus/pg}}$ [kg·kg-1 per kg·m-3], is used, which is a function of the organic fraction of tropospheric aerosol and is derived as follows (Harner and Bidleman 1998, p. 1501; Jolliet and Hauschild 2005, p. 4514):

$$\log K_{\text{sus/pg}} = \log \frac{K_{\text{o/w}}}{K_{\text{a/w}}} + \log fr\_C_{\text{a,om}} + a_{\text{sus/pg-o/a}} \tag{A.9}$$

where

$K_{\text{o/w}}$: n-octanol/water partition coefficient [kg·m-3 per kg·m-3]; see Equation A.1

$K_{\text{a/w}}$: air/water partition coefficient (dimensionless Henry's law constant) [kg·m-3 per kg·m-3]; see Equation A.2

$fr\_C_{\text{a,om}}$: organic fraction of tropospheric aerosol [kg·m-3 per kg·m-3]; see Table B.1

$a_{\text{sus/pg-o/a}}$: coefficient in linear relation between $K_{\text{sus/pg}}$ and $\frac{K_{\text{o/w}}}{K_{\text{a/w}}}$ [kg·kg-1 per kg·m-3]; see Table B.1

Back to Equation A.7, the photochemical oxidation rate coefficient in the atmospheric ground layer during daytime dry period, $k_{\text{a,dry,OH}}$ [d-1], needs to be calculated, accounting for the different periods of and between rain events (Jolliet and Hauschild, 2005, Supporting Information, p. 2):

$$k_{\text{a,dry,OH}} = \frac{k^*{}_{\text{a,OH}} \cdot \overline{C}_{\text{a,OH}}}{1 - RE_{\text{a,wet,OH}} \cdot t_{\text{rain,wet}} \cdot \left(t_{\text{rain,dry}} + t_{\text{rain,wet}}\right)^{-1}} \tag{A.10}$$

where

${k^*}_{\mathrm{a,OH}}$	:	overall photochemical oxidation rate coefficient in the atmospheric ground layer [m³·mol⁻¹·d⁻¹]; see Table B.1
$\overline{C}_{\mathrm{a,OH}}$	:	average concentration of OH radicals in the atmospheric ground layer during daytime of 12 hours [mol·m⁻³]; see Table B.1
$RE_{\mathrm{a,wet,OH}}$	:	reduction coefficient of OH radicals in the atmospheric ground layer during wet period [kg·m⁻³ per kg·m⁻³]; see Table B.1
$t_{\mathrm{rain,wet}}$	:	average duration of wet period in the atmospheric ground layer, i. e. from start to end of rain event [d]; see Equation A.12
$t_{\mathrm{rain,dry}}$	:	average duration of dry period in the atmospheric ground layer, i. e. from end of rain event to start of subsequent rain event [d]; see Equation A.13

Accordingly, the photochemical oxidation rate coefficient in the atmospheric ground layer during daytime wet period, $k_{\mathrm{a,wet,OH}}$ [d⁻¹], is calculated as follows (Jolliet and Hauschild, 2005, Supporting Information, p. 2):

$$k_{\mathrm{a,wet,OH}} = k_{\mathrm{a,dry,OH}} \cdot \left(1 - RE_{\mathrm{a,wet,OH}}\right) \tag{A.11}$$

where

$k_{\mathrm{a,dry,OH}}$	:	photochemical oxidation rate coefficient in the atmopsheric ground layer during daytime dry period [d⁻¹]; see Equation A.10
$RE_{\mathrm{a,wet,OH}}$	:	reduction coefficient of OH radicals in the atmospheric ground layer during wet period [kg·m⁻³ per kg·m⁻³]; see Table B.1

The most important aspect in considering the intermittent character of rain for degradation in the atmospheric ground layer of the dynamiCROP model is to introduce the duration time of and between rain events. As a first step, the average duration of wet period in the atmospheric ground layer, i. e. from start to end of a rain event, $t_{\mathrm{rain,wet}}$ [d], is calculated as follows (Jolliet and Hauschild, 2005, Supporting Information, p. 2):

$$t_{\mathrm{rain,wet}} = t_{\mathrm{rain,int}} \cdot \frac{p_{\mathrm{rain}}}{p_{\mathrm{rain,wet}}} \tag{A.12}$$

where

$t_{\text{rain,int}}$: interval period between two consecutive rain events in the atmospheric ground layer [d]; see Table B.1

p_{rain} : average annual precipitation rate in the atmospheric ground layer [$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$]; see Table B.1

$p_{\text{rain,wet}}$: precipitation rate in the atmospheric ground layer during the wet period, i. e. intensity of a rain event [$\text{m} \cdot \text{d}^{-1}$]; see Table B.1

As a second step, also the average duration of dry period in the atmospheric ground layer, i. e. from the end of a rain event to the start of a subsequent rain event, $t_{\text{a,rain,dry}}$ [d], needs to be accounted for and is derived as follows (Jolliet and Hauschild, 2005, p. 4521):

$$t_{\text{rain,dry}} = t_{\text{rain,int}} - t_{\text{rain,wet}} \tag{A.13}$$

where

$t_{\text{rain,int}}$: interval period between two consecutive rain events in the atmospheric ground layer [d]; see Table B.1

$t_{\text{rain,wet}}$: average duration of wet period in the atmospheric ground layer, i. e. from start to end of rain event [d]; see Equation A.12

Degradation in root-zone soil layer

The bulk degradation rate coefficient in the root-zone soil layer can be calculated according to the general degradation Equation A.5 with compartment i referring to the root-zone soil layer.

Degradation in paddy water layer

Degradation in paddy water is exclusively relevant with respect to the assessment of the environmental fate of substances in paddy rice fields. The bulk degradation rate coefficient in the paddy water layer can be calculated according to the general degradation Equation A.5 with compartment i referring to the paddy water layer. Temperature has been considered as influencing the overall degradation in paddy water, since paddy wanter and freshwater temperatures are considered to be significantly different. For the influence of temperature on the degradation in water see for instance Oue and Kamii (2002) and Kuwagata et al. (2008).

If one has to take into account different temperatures between different water compartment types as influential parameter for the degradation processes, an empirical correction factor, based on the Arrhenius equation[4], can be introduced as follows (Schwarzenbach et al., 2003, p. 478), leading to the bulk degradation rate coefficient in the paddy water layer, $k_{\mathrm{pw,deg}}$ [d^{-1}]:

$$k_{\mathrm{pw,deg}} = \frac{\ln(2)}{t_{\frac{1}{2},\mathrm{pw}}} \cdot fc_{\mathrm{w,deg,T}} \tag{A.14}$$

where

$t_{\frac{1}{2},\mathrm{pw}}$: degradation half life in bulk paddy water layer [d]

$fc_{\mathrm{w,deg,T}}$: empirical correction factor of bulk degradation in water at temperature $T_{\mathrm{water_y}}$ compared to bulk degradation in the paddy water layer at temperature $T_{\mathrm{water_x}}$ $[(\mathrm{J{\cdot}mol^{-1}})/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}){\cdot}\mathrm{K^{-1}}]$; see Equation A.15

The related empirical correction factor of bulk degradation in water at temperature T_{w} compared to bulk degradation in the paddy water layer at temperature T_{pw}, $fc_{\mathrm{w,deg,T}}$ $[(\mathrm{J{\cdot}mol^{-1}})/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}){\cdot}\mathrm{K^{-1}}]$ is calculated as a function of the difference in water temperatures (Pingali and Roger, 1995, p. 10) and the respective activation energy for the degradation reaction process (Schwarzenbach et al., 2003, p. 478):

$$fc_{\mathrm{w,deg,T}} = \exp\left(\frac{EA_{\mathrm{w,deg}}}{R} \cdot \left(\frac{1}{T_{\mathrm{w}}} - \frac{1}{T_{\mathrm{pw}}}\right)\right) \tag{A.15}$$

where

$EA_{\mathrm{w,deg}}$: reaction activation energy for degradation in water [J·mol^{-1}]; see Table B.1

R : universal or molar gas constant [J·mol^{-1}·K^{-1}]; see Table B.1

T_{w} : daily mean temperatures of reference water compartment and
T_{pw} paddy water layer compartment, respectively [K]; see Table B.1

Note that when using the Arrhenius equation to calculate degradation rate coefficients in water of different temperatures, it is assumed that the reaction energy is temperature independent. However, according to Schwarzenbach et al. (2003, p. 478) this is a "reasonable first approximation if the temperature range considered is not too large, and if we are dealing with only one reaction that causes the compound to disappear". In general, an increase (decrease) of 10 K water temperature may accelerate (slow down) a degradation reaction by a factor of between two and six.

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[4] The Arrhenius equation relates the specific rate coefficient, i. e. in the present study applied to the bulk degradation rate coefficient in water, to the (difference in) absolute temperature (Perry and Green, 2008). This equation can be derived from theoretical considerations by using either one of two competing theories, i. e. the *collision theory* or the *transition state theory*.

Degradation in vegetation leaf/fruit surface deposit

Degradation in vegetation leaf/fruit surface deposit can be calculated as a function of the degradation half life in bulk soil according to a recently published regression equation between the degradation half life on vegetation surfaces, $t_{\frac{1}{2},\mathrm{vd}}$ [d], and the degradation half life in bulk soil from Thomas et al. (2011, p. 1531) (thereby correcting the constant relation factor between these two measures as described in Juraske et al. (2008, p. 1751)):

$$\log t_{\frac{1}{2},\mathrm{vd}} = a_{\mathrm{vd-ts}} \cdot \log t_{\frac{1}{2},\mathrm{ts}} + b_{\mathrm{vd-ts}} \tag{A.16}$$

where

$t_{\frac{1}{2},\mathrm{ts}}$	:	degradation half life in bulk root-zone soil layer [d]
$a_{\mathrm{vd-ts}}$	:	regression coefficient (slope) in linear relation between degradation in vegetation leaf/fruit surface deposit and degradation in bulk root-zone soil layer [–]; see Table B.1
$b_{\mathrm{vd-ts}}$	:	regression coefficient (y-intercept) in linear relation between degradation in vegetation leaf/fruit surface deposit and degradation in bulk root-zone soil layer [d]; see Table B.1

Incorporating Equation A.16 into the general degradation Equation A.5 with compartment i referring to the root-zone soil layer leads to the relation between the degradation rate coefficient in vegetation leaf/fruit surface deposit, $k_{\mathrm{vd,deg}}$ [d^{-1}], and the bulk degradation rate coefficient in the root-zone soil layer:

$$k_{\mathrm{vd,deg}} = fc_{\mathrm{ts,vd,deg}} \cdot k_{\mathrm{ts,deg}} \tag{A.17}$$

where

$k_{\mathrm{ts,deg}}$	:	degradation rate coefficient in bulk root-zone soil layer [d^{-1}]; see Table B.2
$fc_{\mathrm{ts,vd,deg}}$	:	correlation factor between degradation in vegetation leaf/fruit surface deposit and degradation in bulk root-zone soil layer [d·d^{-1}]

Degradation in vegetation leaf/fruit/stem/thick root

Degradation in vegetation (interior), i. e. leaf, fruit, stem and thick root, can be calculated similarly as the degradation in vegetation surface deposit compartments, i. e. as a function of the degradation half life in bulk soil according to a direct relation between the degradation half life in vegetation (interior), $t_{\frac{1}{2},\mathrm{v}}$ [d], and the degradation half life in bulk soil from Juraske et al. (2008, p. 1754):

$$t_{\frac{1}{2},\mathrm{v}} = \frac{t_{\frac{1}{2},\mathrm{ts}}}{fc_{\mathrm{ts,v,deg}}} \tag{A.18}$$

where
$t_{\frac{1}{2},\mathrm{ts}}$: degradation half life in bulk root-zone soil layer [d]
$fc_{\mathrm{ts,v,deg}}$: correlation factor between degradation in vegetation (interior) and degradation in bulk root-zone soil layer [d·d^{-1}]

Incorporating Equation A.18 into the general degradation Equation A.5 with compartment i referring to the root-zone soil layer leads to the relation between the degradation rate coefficient in vegetation (interior), i. e. leaf, fruit, stem and thick root, $k_{\mathrm{v,deg}}$ [d^{-1}], and the bulk degradation rate coefficient in the root-zone soil layer:

$$k_{\mathrm{v,deg}} = fc_{\mathrm{ts,v,deg}} \cdot k_{\mathrm{ts,deg}} \tag{A.19}$$

where
$k_{\mathrm{ts,deg}}$: degradation rate coefficient in bulk root-zone soil layer [d^{-1}]; see Table B.1
$fc_{\mathrm{ts,v,deg}}$: correlation factor between degradation in vegetation (interior) and degradation in bulk root-zone soil layer [d·d^{-1}]

A.3. Transfers from atmospheric ground layer

Wind drift described as part of the model's initial conditions (see Section 2.3.4).

Dry and wet deposition (advection, diffusion) from atmospheric ground layer to root-zone soil layer, paddy water layer, vegetation leaf/fruit surface deposit

Deposition from the atmospheric ground layer to adjacent compartments, i. e. root-zone soil layer, vegetation leaf/fruit surface deposit and in case of paddy rice also paddy water layer, can be described as the sum of two different, but related transfer rate coefficients during the dry and wet periods, i. e. by considering the intermittent character of rain events in the atmospheric ground layer. According to Jolliet and Hauschild (2005, p. 4519), the respective rate coefficients [d^{-1}] can be derived as follows:

$$k_{\mathrm{ts}\leftarrow\mathrm{a,dep}} = k_{\mathrm{pw}\leftarrow\mathrm{a,dep}} = \left(k_{\mathrm{a,dep,dry}} + \Delta k_{\mathrm{a,dep,wet,int}}\right) \cdot \mathrm{e}^{-(AI_{\mathrm{vl}}+AI_{\mathrm{vf}})\cdot c_{\mathrm{cap}}} \tag{A.20}$$

$$k_{\mathrm{vld}\leftarrow\mathrm{a,dep}} = \left(k_{\mathrm{a,dep,dry}} + \Delta k_{\mathrm{a,dep,wet,int}}\right) \cdot \left(1 - \mathrm{e}^{AI_{\mathrm{vl}}\cdot c_{\mathrm{cap}}}\right) \tag{A.21}$$

$$k_{\mathrm{vfd}\leftarrow\mathrm{a,dep}} = \left(k_{\mathrm{a,dep,dry}} + \Delta k_{\mathrm{a,dep,wet,int}}\right) \cdot \left(1 - \mathrm{e}^{AI_{\mathrm{vf}}\cdot c_{\mathrm{cap}}}\right) \tag{A.22}$$

where

$k_{\mathrm{ts}\leftarrow\mathrm{a,dep}}$, $k_{\mathrm{pw}\leftarrow\mathrm{a,dep}}$, $k_{\mathrm{vld}\leftarrow\mathrm{a,dep}}$, $k_{\mathrm{vfd}\leftarrow\mathrm{a,dep}}$: overall deposition rate coefficients from the atmospheric ground layer to root-zone soil layer, paddy water layer, vegetation leaf surface deposit and vegetation fruit surface deposit, respectively [d^{-1}]

$k_{\mathrm{a,dep,dry}}$: dry deposition rate coefficient in the atmospheric ground layer [d^{-1}]; see Equation A.23

$\Delta k_{\mathrm{a,dep,wet,int}}$: additional equivalent wet deposition rate coefficient in the atmospheric ground layer [d^{-1}]; see Equation A.24

LAI, FAI : area indices for vegetation leaf and fruit, respectively [m^{2}·m^{-2}]; see Table B.3

c_{cap} : substance capture coefficient, representing the interception efficacy of vegetation surfaces [kg·m^{-2} per kg·m^{-2}]; see Table B.3

The dry deposition rate coefficient in the atmospheric ground layer, $k_{\mathrm{a,dep,dry}}$ [d^{-1}], can be calculated as a function of the deposition velocities of suspended particles and gas phase, valid for the fractions of substance that are sorbed to suspended particles and available in the gas phase, respectively (Jolliet and Hauschild, 2005, p. 4514). Note that while the dry deposition of suspended particles along with the wet deposition of suspended particles/gas phase are advective processes, the dry deposition of the gas phase is considered a diffusive process. However, as both dry deposition rates can be described as a function of the respective deposition velocities, they can be summed up in the following equation. In this equation, the term $(fc_{\mathrm{a,dep,dry,pg}\rightarrow\mathrm{u}} \cdot u_{10})$ represents the deposition velocity of the gas phase in the atmospheric ground layer during the dry period (Fogg and Sangster, 2003, p. 39):

$$k_{\mathrm{a,dep,dry}} = fr\_V_{\mathrm{a,sus}} \cdot \frac{p_{\mathrm{a,dep,dry,sus}}}{h_{\mathrm{a}}} + \left(1 - fr\_V_{\mathrm{a,sus}}\right) \cdot \frac{fc_{\mathrm{a,dep,dry,pg}\rightarrow\mathrm{u}} \cdot u_{10}}{h_{\mathrm{a}}} \tag{A.23}$$

where

$fr\_V_{\mathrm{a,sus}}$: average fraction of substance in the atmospheric ground layer that is sorbed to suspended particles [L·L^{-1}]; see Equation A.8

$p_{\mathrm{a,dep,dry,sus}}$: deposition velocity of suspended particles in the atmospheric ground layer during the dry period [m·d^{-1}]; see Table B.1

h_{a} : vertical dimension (height) of the atmospheric ground layer [m]; see Table B.1

$fc_{\mathrm{a,dep,dry,pg\rightarrow u}}$: correlation factor between deposition velocity of the gas phase in the atmospheric ground layer during the dry period and the average wind velocity [m·d^{-1} per m·d^{-1}]

u_{10} : average wind velocity at 10 m above (soil/water) surface level [m·d^{-1}]; see Table B.1

The additional equivalent wet deposition rate coefficient in the atmospheric ground layer, $\Delta k_{\mathrm{a,dep,wet,int}}$ [d^{-1}], accounts for an additional deposition rate of suspended particles and the gas phase during the wet periods of rain events (Jolliet and Hauschild, 2005, p. 4519):

$$\Delta k_{\mathrm{a,dep,wet,int}} = \min\Bigg[\left(\frac{2}{t_{\mathrm{rain,dry}}} \cdot \frac{t_{\mathrm{rain,int}}}{t_{\mathrm{rain,dry}}} + \frac{k_{\mathrm{a,dep,dry}} \cdot t_{\mathrm{rain,wet}}}{t_{\mathrm{rain,dry}}}\right); \left(\left(k_{\mathrm{a,dep,wet}} - k_{\mathrm{a,dep,dry}}\right) \cdot \frac{t_{\mathrm{rain,dry}}}{t_{\mathrm{rain,int}}}\right)\Bigg] \tag{A.24}$$

where

$t_{\mathrm{rain,dry}}$: average duration of dry period in the atmospheric ground layer, i. e. from end of rain event to start of subsequent rain event [d]; see Equation A.13

$t_{\mathrm{rain,int}}$: interval period between two consecutive rain events in the atmospheric ground layer [d]; see Table B.1

$k_{\mathrm{a,dep,dry}}$: dry deposition rate coefficient in the atmospheric ground layer [d^{-1}]; see Equation A.23

$t_{\mathrm{rain,wet}}$: average duration of wet period in the atmospheric ground layer, i. e. from start to end of rain event [d]; see Equation A.12

$k_{\mathrm{a,dep,wet}}$: wet deposition rate coefficient in the atmospheric ground layer [d^{-1}]; see Equation A.25

The wet deposition rate coefficient in the atmospheric ground layer, $k_{\mathrm{a,dep,wet}}$ [d^{-1}], is calculated similarly to the dry deposition rate, i. e. as the sum of the deposition of suspended particles and gas phase (here in the wet period), both depending on their respective deposition velocities (Jolliet and Hauschild, 2005, p. 4514). In this equation, the term $(RE_{\mathrm{a,dep,wet,wash}} \cdot p_{\mathrm{a,dep,dry,sus}})$ represents the deposition velocity of particles in the atmospheric ground layer during the wet period (Jolliet and Hauschild, 2005, p. 4515), the term $(fc_{\mathrm{a,dep,dry,pg\rightarrow u}} \cdot u_{10})$ represents the deposition velocity of the gas phase in the atmospheric ground layer during the dry period (Fogg and Sangster, 2003, p. 39), and the term $\left(\frac{p_{\mathrm{rain,wet}}}{K_{\mathrm{a/w}}+fr\_V_{\mathrm{a,rain,paq}}}\right)$ represents the deposition velocity of the gas phase in the atmospheric ground layer during the precipitation phase of the wet period (Jolliet and Hauschild, 2005, p. 4515).

$$k_{\mathrm{a,dep,wet}} = fr\_V_{\mathrm{a,sus}} \cdot \frac{RE_{\mathrm{a,dep,wet,wash}} \cdot p_{\mathrm{a,dep,dry,sus}}}{h_{\mathrm{a}}} + \left(1 - fr\_V_{\mathrm{a,sus}}\right) \cdot \left(\frac{fc_{\mathrm{a,dep,dry,pg\rightarrow u}} \cdot u_{10}}{h_{\mathrm{a}}} + \frac{1}{h_{\mathrm{a}}} \cdot \frac{p_{\mathrm{rain,wet}}}{K_{\mathrm{a/w}} + fr\_V_{\mathrm{a,rain,paq}}}\right) \tag{A.25}$$

where

$fr\_V_{\mathrm{a,sus}}$: average fraction of substance in the atmospheric ground layer that is sorbed to suspended particles [L·L^{-1}]; see Equation A.8

$RE_{\mathrm{a,dep,wet,wash}}$: yearly average reduction (washout) coefficient of aerosols (particles) in the atmospheric ground layer [kg·m^{-3} per kg·m^{-3}]; see Table B.1

$p_{\mathrm{a,dep,dry,sus}}$: deposition velocity of suspended particles in the atmospheric ground layer during the dry period [m·d^{-1}]; see Table B.1

h_{a} : vertical dimension (height) of the atmospheric ground layer [m]; see Table B.1

$fc_{\mathrm{a,dep,dry,pg\rightarrow u}}$: correlation factor between deposition velocity of the gas phase in the atmospheric ground layer during the dry period and the average wind velocity [m·d^{-1} per m·d^{-1}]

u_{10} : average wind velocity at 10 m above (soil/water) surface level [m·d^{-1}]; see Table B.1

$p_{\mathrm{rain,wet}}$: precipitation rate in the atmospheric ground layer during the wet period, i. e. intensity of a rain event [m·d^{-1}]; see Table B.1

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

$fr\_V_{\mathrm{a,rain,paq}}$: fraction of volumetric water in the atmospheric ground layer at air/water droplet equilibrium [m^{3}·m^{-3}]; see Table B.1

Diffusion from atmospheric ground layer to vegetation leaf (interior) through stomata

According to Trapp and Matthies (1998, p. 121; 246) and Charles (2004, p. 77), the rate coefficient for diffusion from atmospheric ground layer to vegetation leaf (interior) through stomata, $k_{\mathrm{vl}\leftarrow\mathrm{a,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vl}\leftarrow\mathrm{a,diff}} = \frac{A_{\mathrm{vl}} \cdot \varphi_{\mathrm{a/vl}}}{K_{\mathrm{a/w}} \cdot V_{\mathrm{a}}} \tag{A.26}$$

where

A_{vl}	:	area of vegetation leaf [m^2]; see Table B.3
$\varphi_{\mathrm{a/vl}}$	:	conductance (diffusion velocity) between atmospheric ground layer and vegetation leaf (interior) [m·d^{-1}]; see Equation A.27
$K_{\mathrm{a/w}}$	:	partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2
V_{a}	:	volume of the atmospheric ground layer [m^3]; see Table B.1

In the following equation, the term $\left(\varphi_{\mathrm{a}} \cdot K_{\mathrm{a/w}}\right)$ represents the permeability of the boundary between the atmospheric ground layer and vegetation leaf, i. e. the conductance though the boundary layer related to water (Trapp, 2007; Trapp and Mc Farlane, 1995).

$$\varphi_{\mathrm{a/vl}} = \left(\frac{1}{\varphi_{\mathrm{sto}} + \varphi_{\mathrm{cut,w}}} + \frac{1}{\varphi_{\mathrm{a}} \cdot K_{\mathrm{a/w}}}\right)^{-1} \tag{A.27}$$

where

φ_{sto}	:	conductance (diffusion velocity) through vegetation leaf stomata [m·d^{-1}]; see Equation A.62
$\varphi_{\mathrm{cut,w}}$	:	conductance (diffusion velocity) through cuticle related to water [m·d^{-1}]; see Equation A.64
φ_{a}	:	conductance (diffusion velocity) through atmospheric ground layer boundary [m·d^{-1}]; see Equation A.28
$K_{\mathrm{a/w}}$	:	partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

$$\varphi_{\mathrm{a}} = \frac{D_{\mathrm{a,H_2O}}}{\Delta l_{\mathrm{a}}} \cdot \left(\frac{MW_{\mathrm{H_2O}}}{MW}\right)^{\frac{1}{2}} \tag{A.28}$$

where

$D_{\mathrm{a,H_2O}}$: diffusion coefficient of water vapor in the atmospheric ground layer [m^2·d^{-1}]; see Table B.1

Δl_{a} : diffusion path length (thickness) of the atmospheric ground layer boundary [m]; Table B.1

$MW_{\mathrm{H_2O}}$: molecular weight of water [g·mol^{-1}]; see Table B.1

MW : molecular weight [g·mol^{-1}]; see Table B.2

A.4. Transfers from root-zone soil layer

Generally, environmental factors such as temperature also influence the rate of uptake of a xenobiotic chemical (Pingali and Roger, 1995, p. 238). However, since there is only rare if any information available for these factors in the context of plant uptake modeling, these factors are disregarded in the present assessment.

Volatilization (diffusion) from root-zone soil layer to atmospheric ground layer

According to Rosenbaum et al. (2004, Part IV, p. 24), the rate coefficient for volatilization from root-zone soil layer to the atmospheric ground layer, $k_{\mathrm{a\leftarrow ts,volat}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{a\leftarrow ts,volat}} = \frac{A_{\mathrm{ts}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{a/ts}}}{K_{\mathrm{ts/a}} \cdot M_{\mathrm{ts}}} \tag{A.29}$$

where

A_{ts} : area of the root-zone soil layer [m^2]; see Table B.1

$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

$\varphi_{\mathrm{a/comp}}$: conductance (diffusion velocity) between atmospheric ground layer and root-zone soil layer [m·d^{-1}]; see Equation A.30

$K_{\mathrm{ts/a}}$: partition coefficient between the bulk root-zone soil layer and air [L·kg^{-1}]; see Equation A.31

M_{ts} : mass of the root-zone soil layer [kg]; see Table B.1

The conductance (diffusion velocity) between the atmospheric ground layer and an adjacent compartment, i. e. root-zone soil layer or paddy water layer, $\varphi_{\mathrm{a/comp}}$ [m·d^{-1}], according to Rosenbaum et al. (2004, Part IV, p. 24), Schwarzenbach et al. (2003, p. 919) and Schwarzenbach et al. (1993, p. 238):

$$\varphi_{\mathrm{a/comp}} = \left(\frac{1}{\varphi_{\mathrm{comp}}} + \frac{1}{\varphi_{\mathrm{a}} \cdot K_{\mathrm{a/w}}} \right)^{-1} \tag{A.30}$$

where

φ_{comp} : conductance (diffusion velocity) through bulk compartment layer boundary [m·d^{-1}]; for root-zone soil layer boundary see Equation A.38 and for paddy water layer boundary see Equation A.50

φ_{a} : conductance (diffusion velocity) through atmospheric ground layer boundary [m·d^{-1}]; see Equation A.28

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

The partition coefficient between the bulk root-zone soil layer and air, $K_{\mathrm{ts/a}}$ [L·kg^{-1}], according to the concepts of correlated partition coefficients as described in Mackay (2001, p. 85):

$$K_{\mathrm{ts/a}} = \frac{K_{\mathrm{ts/w}}}{K_{\mathrm{a/w}}} \tag{A.31}$$

where

$K_{\mathrm{ts/w}}$: partition coefficient between the root-zone soil layer and water [L·kg^{-1}]; see Equation A.32

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

In the following equation, the term ($\rho_{\mathrm{ts,ps}} \cdot \mathit{fr\_V}_{\mathrm{ts,ps}}$) represents the density of dry bulk root-zone soil layer. The partition coefficient between the root-zone soil layer and water, $K_{\mathrm{ts/w}}$ [L·kg^{-1}], according to Trapp and Matthies (1998, p. 41) and Charles (2004, p. 64):

$$K_{\mathrm{ts/w}} = \frac{K_{\mathrm{d,ts}} \cdot \rho_{\mathrm{ts,ps}} \cdot \mathit{fr\_V}_{\mathrm{ts,ps}}}{\rho_{\mathrm{w}}} + \mathit{fr\_V}_{\mathrm{ts,paq}} + \mathit{fr\_V}_{\mathrm{ts,pg}} \cdot K_{\mathrm{a/w}} \tag{A.32}$$

where

$K_{\mathrm{d,ts}}$: partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water [L·kg^{-1}]; see Equation A.33

$\rho_{\mathrm{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$\mathit{fr\_V}_{\mathrm{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

ρ_{w} : density of water [kg·L^{-1}]; see Table B.1

$\mathit{fr\_V}_{\mathrm{ts,paq}}$: fraction of volumetric water in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$\mathit{fr\_V}_{\mathrm{ts,pg}}$: fraction of volumetric gas in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

The partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water, $K_{\mathrm{d,ts}}$ [L·kg^{-1}], according to Trapp and Matthies (1998, p. 42):

$$K_{\mathrm{d,ts}} = fr\_M_{\mathrm{ts,oc}} \cdot K_{\mathrm{oc/w}} \tag{A.33}$$

where

$fr\_M_{\mathrm{ts,oc}}$: fraction of mass of organic carbon (fraction of organic matter) in bulk root-zone soil layer (organic carbon content) [kg·kg^{-1}]; see Table B.1

$K_{\mathrm{oc/w}}$: partition coefficient between organic carbon in root-zone soil layer and water [L·kg^{-1}]; see Equation A.4

Run off (advection) from root-zone soil layer to freshwater body

According to Rosenbaum et al. (2004, Part IV, p. 15-16) and Charles (2004, p. 88-89), the rate coefficient for run off from root-zone soil layer to the freshwater body as loss from the considered compartmental system, $k_{\mathrm{fb}\leftarrow\mathrm{ts,run}}$ [d^{-1}], can be derived as follows (How to arrive at this equation is explained in Section A.12, Equation A.90.):

$$k_{\mathrm{fb}\leftarrow\mathrm{ts,run}} = \frac{(fc_{\mathrm{ts,paq}} + fc_{\mathrm{ts,ps}} \cdot fr\_M_{\mathrm{ts,run,ps}}) \cdot p_{\mathrm{rain}} \cdot fr\_p_{\mathrm{rain,run}}}{h_{\mathrm{ts}}} \tag{A.34}$$

where

$fc_{\mathrm{ts,paq}}$: correction factor between the aqueous and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.35

$fc_{\mathrm{ts,ps}}$: correction factor between the solid and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.36

$fr\_M_{\mathrm{ts,run,ps}}$: fraction of mass of root-zone soil layer solids in run off water [kg·kg^{-1}]; see Table B.1

p_{rain} : average annual precipitation rate in the atmospheric ground layer [m^3·m^{-2}·d^{-1}]; see Table B.1

$fr\_p_{\mathrm{rain,run}}$: fraction of average annual precipitation rate in the atmospheric ground layer that undergoes run off [m^3·m^{-2}·d^{-1} per m^3·m^{-2}·d^{-1}]; see Table B.1

h_{ts} : vertical dimension (depth) of the root-zone soil layer [m]; see Table B.1

The correction factor between the aqueous and the bulk phase of the root-zone soil layer, $fc_{\mathrm{ts,paq}}$ [L·L^{-1}], according to Rosenbaum et al. (2004, Part II, p. 17) and as implemented in the Impact 2002 model (Pennington et al., 2005):

$$fc_{\mathrm{ts,paq}} = \frac{1}{fr\_V_{\mathrm{ts,paq}} + fr\_V_{\mathrm{ts,pg}} \cdot K_{\mathrm{a/w}} + fr\_V_{\mathrm{ts,ps}} \cdot \rho_{\mathrm{ts,ps}} \cdot K_{\mathrm{d,ts}}} \tag{A.35}$$

where

$fr\_V_{\mathrm{ts,paq}}$: fraction of volumetric water in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,pg}}$: fraction of volumetric gas in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

$fr\_V_{\mathrm{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$\rho_{\mathrm{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$K_{\mathrm{d,ts}}$: partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water [L·kg^{-1}]; see Equation A.33

The correction factor between the solid and the bulk phase of the root-zone soil layer, $fc_{\mathrm{ts,ps}}$ [L·L^{-1}], according to Rosenbaum et al. (2004, Part II, p. 17) and as implemented in the Impact 2002 model (Pennington et al., 2005):

$$fc_{\mathrm{ts,ps}} = \frac{1}{fr\_V_{\mathrm{ts,paq}} + fr\_V_{\mathrm{ts,pg}} \cdot K_{\mathrm{a/w}}} \cdot \frac{1}{\rho_{\mathrm{ts,ps}} \cdot K_{\mathrm{d,ts}}} + fr\_V_{\mathrm{ts,ps}} \tag{A.36}$$

where

$fr\_V_{\mathrm{ts,paq}}$: fraction of volumetric water in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,pg}}$: fraction of volumetric gas in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

$\rho_{\mathrm{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$K_{\mathrm{d,ts}}$: partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water [L·kg^{-1}]; see Equation A.33

$fr\_V_{\mathrm{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

Leaching (advection, diffusion) from root-zone soil layer to saturated subsoil (groundwater layer)

Main parameters influencing leaching processes are the amount of precipitation, timing of rainfall and extreme rain events in relation to application date (Nolan et al., 2008). According to Rosenbaum et al. (2004, Part IV, p. 17), which is in line with Brandes et al. (1996, p. 80), the rate coefficient for leaching from root-zone soil layer to the saturated subsoil (groundwater layer) as loss from the considered compartmental system, $k_{\mathrm{us}\leftarrow\mathrm{ts,leach}}$ [d^{-1}], can be derived as follows (How to arrive at this equation is explained in Section A.12, Equation A.93.):

$$k_{\mathrm{us}\leftarrow\mathrm{ts,leach}} = \frac{fc_{\mathrm{ts,paq}} \cdot (p_{\mathrm{rain}} \cdot fr\_p_{\mathrm{rain,leach}} \cdot fr\_V_{\mathrm{ts,paq}} - \varphi_{\mathrm{ts}})}{h_{\mathrm{ts}}} \tag{A.37}$$

where

$fc_{\mathrm{ts,paq}}$: correction factor between the aqueous and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.35

p_{rain} : average annual precipitation rate in the atmospheric ground layer [m^{3}·m^{-2}·d^{-1}]; see Table B.1

$fr\_p_{\mathrm{rain,leach}}$: fraction of average annual precipitation rate in the atmospheric ground layer that undergoes leaching [m^{3}·m^{-2}·d^{-1} per m^{3}·m^{-2}·d^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,paq}}$: fraction of volumetric water in the bulk root-zone soil layer [L·L^{-1}]; see Table B.1

φ_{ts} : conductance (diffusion velocity) through the root-zone soil layer [m·d^{-1}]; see Equation A.38

h_{ts} : vertical dimension (depth) of the root-zone soil layer [m]; see Table B.1

The conductance (diffusion velocity) through the root-zone soil layer, φ_{ts} [m·d^{-1}], according to Trapp and Matthies (1998, p. 94-95), Trapp (2007, p. 384-85) and Rosenbaum et al. (2004, Part IV, p. 19):

$$\varphi_{\mathrm{ts}} = \frac{D_{\mathrm{ts}}}{\Delta l_{\mathrm{ts}}} \tag{A.38}$$

where

D_{ts} : (effective) diffusion coefficient in the bulk root-zone soil layer [m^{2}·d^{-1}]; see Equation A.85

Δl_{ts} : diffusion path length (thickness) of the root-zone soil layer boundary [m]; see Table B.1

Resuspension (advection) and diffusion from root-zone soil layer to paddy water layer

According to Rosenbaum et al. (2004, Part II, p. 18), the rate coefficient for resuspension and diffusion from root-zone soil layer to the paddy water layer (based on the approach for resuspension and diffusion from sediment to water), $k_{\text{pw}\leftarrow\text{ts,resus}}$ [d^{-1}], can be derived as follows:

$$k_{\text{pw}\leftarrow\text{ts,resus}} = \frac{A_{\text{pw}} \cdot (p_{\text{ts,resus}} + \varphi_{\text{ts,pw}})}{V_{\text{ts}}} \tag{A.39}$$

where

A_{pw} : area of the paddy water layer [m^2]; see Table B.1

$p_{\text{ts,resus}}$: resuspension velocity from root-zone soil layer to paddy water layer [m·d^{-1}]; see Equation A.40

$\varphi_{\text{ts,pw}}$: diffusion velocity from root-zone soil layer to paddy water layer [m·d^{-1}]; see Equation A.42

V_{ts} : volume of the root-zone soil layer [m^3]; see Table B.1

In the following equation, the term ($p_{\text{pw,ps}} \cdot C_{\text{pw,sus}}$) represents the mean root-zone soil layer accumulation rate of suspended particles from the paddy water layer, $\phi_{\text{pw,ts,sus}}$ [kg·m·L^{-1}·d^{-1}], and the term ($\rho_{\text{ts,ps}} \cdot fr\_V_{\text{ts,ps}}$) represents the density of dry bulk root-zone soil layer. The resuspension velocity from root-zone soil layer to paddy water layer, $p_{\text{ts,resus}}$ [m·d^{-1}], according to Rosenbaum et al. (2004, Part II, p. 18):

$$p_{\text{ts,resus}} = \frac{p_{\text{pw,ps}} \cdot C_{\text{pw,sus}} \cdot fr\_m_{\text{ts,sed,resus}}}{\rho_{\text{ts,ps}} \cdot fr\_V_{\text{ts,ps}}} \cdot fr\_M_{\text{ts,ps}} \tag{A.40}$$

where

$p_{\text{pw,ps}}$: sedimentation velocity of suspended particles from the paddy water layer to the root-zone soil layer [m·d^{-1}]; see Table B.1

$C_{\text{pw,sus}}$: concentration of suspended particles per unit volume of bulk paddy water layer [kg·L^{-1}]; see Table B.1

$fr\_m_{\text{ts,sed,resus}}$: fraction of substance mass deposited from paddy water layer to root-zone soil layer that undergoes resuspension from root-zone soil layer to paddy water layer [kg·kg^{-1}]; see Table B.1

$\rho_{\text{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$fr\_V_{\text{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$fr\_M_{\text{ts,ps}}$: fraction of mass of bulk root-zone soil layer that is solid phase [kg·kg^{-1}]; see Equation A.41

The fraction of mass of bulk root-zone soil layer that is (solid phase), $fr\_M_{\mathrm{ts,ps}}$ [kg·kg^{-1}], according to Rosenbaum et al. (2004, Part II, p. 17):

$$fr\_M_{\mathrm{ts,ps}} = \left(1 + \frac{1}{K_{\mathrm{d,ts}} \cdot \rho_{\mathrm{ts,ps}}} \cdot \frac{1 - fr\_V_{\mathrm{ts,ps}}}{fr\_V_{\mathrm{ts,ps}}}\right)^{-1} \tag{A.41}$$

where

$K_{\mathrm{d,ts}}$: partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water [L·kg^{-1}]; see Equation A.33

$\rho_{\mathrm{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

The diffusion velocity from root-zone soil layer to paddy water layer, $\varphi_{\mathrm{ts,pw}}$ [m·d^{-1}], according to Rosenbaum et al. (2004, Part II, p. 18):

$$\varphi_{\mathrm{ts,pw}} = \varphi_{\mathrm{ts,pw,paq}} \cdot fr\_M_{\mathrm{ts,paq}} \tag{A.42}$$

where

$\varphi_{\mathrm{ts,pw,paq}}$: diffusion velocity from root-zone soil layer aqueous phase to paddy water layer [m·d^{-1}]; see Table B.1

$fr\_M_{\mathrm{ts,paq}}$: fraction of mass of bulk root-zone soil layer that is aqueous phase [kg·kg^{-1}]; see Equation A.43

The fraction of mass of bulk root-zone soil layer that is aqueous phase, $fr\_M_{\mathrm{ts,paq}}$ [kg·kg^{-1}], according to Rosenbaum et al. (2004, Part II, p. 17):

$$fr\_M_{\mathrm{ts,paq}} = \left(1 + K_{\mathrm{d,ts}} \cdot \rho_{\mathrm{ts,ps}} \cdot \frac{fr\_V_{\mathrm{ts,ps}}}{1 - fr\_V_{\mathrm{ts,ps}}}\right)^{-1} \tag{A.43}$$

where

$K_{\mathrm{d,ts}}$: partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water [L·kg^{-1}]; see Equation A.33

$\rho_{\mathrm{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

Root uptake (advection, diffusion) from root-zone soil layer to vegetation thick root

Root uptake into vegetation is referring to both advective plant uptake driven by transpiration as well as diffusion. However, for root crops, such as potatoes, only diffusion is considered according to Trapp et al. (2007); Juraske et al. (2011) and, in addition, diffusion into root crops is based on a specific radial diffusion model as introduced by Schwarzenbach et al. (2003). While root uptake from root-zone soil layer to all vegetation thick roots but root crops is formulated in Equation A.44, root uptake from root-zone soil layer to root crops is formulated in Equation A.46.

According to Juraske et al. (2009a, p. 684), Trapp (2002, p. 204) and Trapp and Mc Farlane (1995, p. 118-20), the rate coefficient for root uptake from root-zone soil layer to vegetation thick root, $k_{\mathrm{vr}\leftarrow\mathrm{ts,conv}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vr}\leftarrow\mathrm{ts,conv}} = \frac{(A_{\mathrm{vr}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{vr}} + Q_{\mathrm{xyl}}) \cdot K_{\mathrm{w/ts}}}{M_{\mathrm{ts}}} \tag{A.44}$$

where

A_{vr} : area of vegetation thick root [m^2]; see Table B.3

$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{vr} : conductance (diffusion velocity) through thick root [m·d^{-1}]; see Equation A.83

Q_{xyl} : acropetal transpiration stream (flow rate) in xylem of vegetation [L·d^{-1}]; see Equation A.77

$K_{\mathrm{w/ts}}$: partition coefficient between water and the bulk root-zone soil layer [kg·L^{-1}]; see Equation A.45

M_{ts} : mass of the root-zone soil layer [kg]; see Table B.1

In the following equation, the term $(\rho_{\mathrm{ts,ps}} \cdot fr\_V_{\mathrm{ts,ps}})$ represents the density of dry bulk root-zone soil layer, while the term $(\rho_{\mathrm{ts,ps}} \cdot fr\_V_{\mathrm{ts,ps}} + fr\_V_{\mathrm{ts,paq}})$ represents the density of wet root-zone soil layer, respectively. The partition coefficient between water and the bulk root-zone soil layer, $K_{\mathrm{w/ts}}$ [kg·L^{-1}], according to Trapp (2007, p. 369):

$$K_{\mathrm{w/ts}} = \frac{\rho_{\mathrm{ts,ps}} \cdot fr\_V_{\mathrm{ts,ps}} + fr\_V_{\mathrm{ts,paq}}}{K_{\mathrm{d,ts}} \cdot \rho_{\mathrm{ts,ps}} \cdot fr\_V_{\mathrm{ts,ps}} + fr\_V_{\mathrm{ts,paq}} + fr\_V_{\mathrm{ts,pg}} \cdot K_{\mathrm{a/w}}} \tag{A.45}$$

where

$\rho_{\mathrm{ts,ps}}$: density of dry root-zone soil layer matrix (particles) [kg·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,ps}}$: fraction of volumetric particles in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,paq}}$: fraction of volumetric water in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$K_{\mathrm{d,ts}}$: partition coefficient between bulk root-zone soil layer matrix (particles) fraction and water [L·kg^{-1}]; see Equation A.33

$fr\_V_{\mathrm{ts,paq}}$: fraction of volumetric water in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$fr\_V_{\mathrm{ts,pg}}$: fraction of volumetric gas in bulk root-zone soil layer [L·L^{-1}]; see Table B.1

$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

Whereas taproots (e. g. carrot), tuberous roots (e. g. sweet potato) and bulbs (e. g. onion) are part of the root system, stem rhizomes (e. g. ginger) and stem tubers (e. g. potato) are not connected to the root system and the transpiration stream, but are part of the stem that is loaded from vegetation leaves via phloem (Burton, 1989). For all root crops, however, translocation downward in phloem is considered negligible for organic substances, suggesting that the main uptake route is most likely to occur through the root-zone soil layer (Kleier, 1988). According to Juraske et al. (2011, p. S10), Trapp et al. (2007, p. 3107) and Paraíba and Kataguiri (2008, p. 1248), the rate coefficient for root uptake from root-zone soil layer to vegetation thick root of root crops, $k_{\mathrm{vr}\leftarrow\mathrm{ts,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vr}\leftarrow\mathrm{ts,diff}} = \frac{fc_{\mathrm{D,vr,tis}} \cdot D_{\mathrm{vr,tis}} \cdot M_{\mathrm{vr}}}{{r_{\mathrm{vr}}}^2 \cdot \rho_{\mathrm{vr}} \cdot K_{\mathrm{ts/w}} \cdot M_{\mathrm{ts}}} \tag{A.46}$$

where

$fc_{\mathrm{D,vr,tis}}$: empirical correction factor for radial diffusion model [–]; see Table B.1

$D_{\mathrm{vr,tis}}$: (effective) diffusion coefficient in the tissue of vegetation thick root [m^2·d^{-1}]; see Equation A.85

M_{vr} : mass of vegetation thick root [kg]; see Table B.3

r_{vr} : mean radius of vegetation thick root [m]; see Table B.3

ρ_{vr} : density of bulk vegetation thick root [kg·L^{-1}]; see Table B.3

$K_{\mathrm{ts/w}}$: partition coefficient between the root-zone soil layer and water [L·kg^{-1}]; see Equation A.32

M_{ts} : mass of the root-zone soil layer [kg]; see Table B.1

A.5. Transfers from paddy water layer

Paddy rice involves an additional compartment to be considered in the calculation of inter- and intramedia fate processes, namely the paddy water layer as shown in Figure A.1.

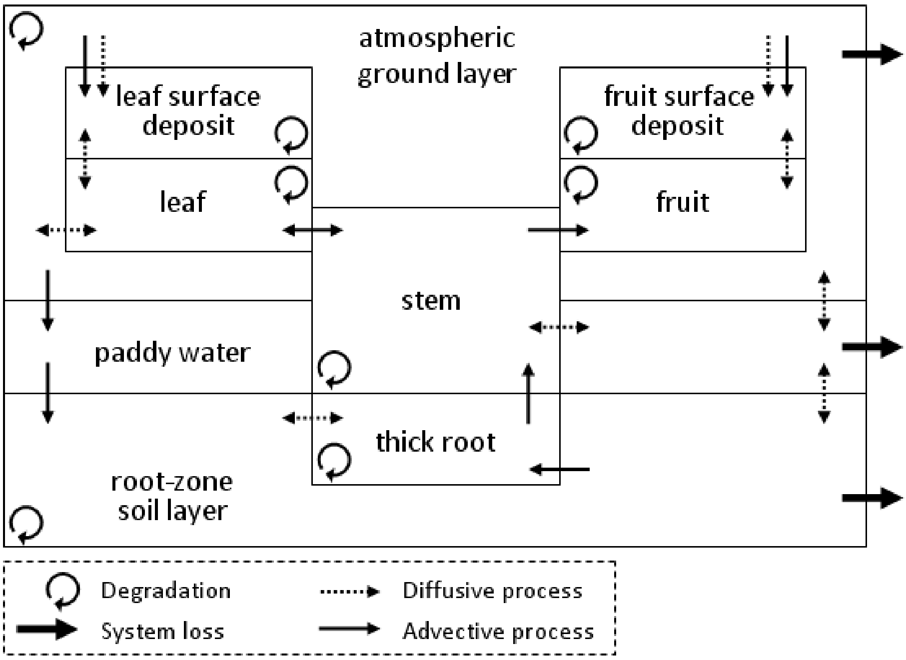

Figure A.1.: Graphical representation of model setup consisting of environmental compartments (atmospheric ground layer, root-zone soil layer, paddy water layer), rice crop components (leaf and fruit surface deposit, leaf, fruit, stem, and thick root) and processes within/between compartments for paddy rice.

All subsequent processes, hence, are exclusively relevant for paddy rice.

Volatilization (diffusion) from paddy water layer to atmospheric ground layer

Volatilization was recognized more than 20 years ago as an important process for the loss of pesticides from the areas where they are applied. Consequently, information on the potential volatility of a pesticide is needed to understand its environmental fate and is therefore required by international registration authorities including Europe and the United States (Ferrari et al., 2005, p. 2968). High temperature decreases adsorption and favor desorption of pesticides, which may result in higher quantities of pesticides dissolved in soil water and a faster dispersion (Pingali and Roger, 1995, p. 121).

The volatilization velocity needs to be further described by the chemical's mass fractions in bulk water, i. e. aqueous phase, sediment solids (particles) and suspended colloidal organic matter (solid, but dissolved in water and, thus, not undergoing deposition or volatilization (Schwarzenbach et al., 1993, 2003), as well as by the diffusion velocities through the two phase boundary layers as described in Schwarzenbach et al. (1993, 2003). According to Inao and Kitamura (1999, p. 40-41) and Trapp and Matthies (1998, p. 70; 266-67), the rate coefficient for volatilization from paddy water layer to the atmospheric ground layer, $k_{\mathrm{a}\leftarrow\mathrm{pw,volat}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{a}\leftarrow\mathrm{pw,volat}} = \frac{A_{\mathrm{a}} \cdot fr\_m_{\mathrm{pw,paq}} \cdot \varphi_{\mathrm{a/pw}}}{V_{\mathrm{pw}}} \tag{A.47}$$

where

A_{a} : area of the atmospheric ground layer [m^2]; see Table B.1

$fr\_m_{\mathrm{pw,paq}}$: fraction of mass of substance in aqueous phase (dissolved) of the paddy water layer [kg·kg^{-1}]; see Equation A.48

$\varphi_{\mathrm{a/comp}}$: conductance (diffusion velocity) between atmospheric ground layer and paddy water layer [m·d^{-1}]; see Equation A.30

V_{pw} : volume of the paddy water layer [m^3]; see Table B.1

The fraction of mass of substance in aqueous phase (dissolved) of the paddy water layer, $fr\_m_{\mathrm{pw,paq}}$ [kg·kg^{-1}], according to Schwarzenbach et al. (2003, p. 1068), Schwarzenbach et al. (1993, p. 587 ff.) and Trapp and Matthies (1998, p. 267 ff.):

$$fr\_m_{\mathrm{pw,paq}} = \frac{1}{1 + C_{\mathrm{pw,coc}} \cdot K_{\mathrm{coc/w}} + C_{\mathrm{pw,sus}} \cdot fr\_M_{\mathrm{pw,coc}} \cdot K_{\mathrm{coc/w}}} \tag{A.48}$$

where

$C_{\mathrm{pw,coc}}$: concentration of colloidal organic carbon per unit volume of bulk paddy water layer [kg·L^{-1}]; see Table B.1

$K_{\mathrm{coc/w}}$: partition coefficient between colloidal organic carbon in paddy water and water [L·kg^{-1}]; see Equation A.49

$C_{\mathrm{pw,sus}}$: concentration of suspended particles per unit volume of bulk paddy water layer [kg·L^{-1}]; see Table B.1

$fr\_M_{\mathrm{pw,coc}}$: fraction of mass of colloidal organic carbon in paddy water suspended particles phase [kg·kg^{-1}]; see Table B.1

The partition coefficient between colloidal organic carbon in the paddy water layer and water[5], $K_{\mathrm{coc/w}}$ [L·kg^{-1}], according to Schwarzenbach et al. (2003, p. 301), Schwarzenbach et al. (1993, p. 275) and Ruffino and Zanetti (2009, p. 509):

$$\log K_{\mathrm{coc/w}} = a_{\mathrm{coc/w-o/w}} \cdot \log K_{\mathrm{o/w}} + b_{\mathrm{coc/w-o/w}} \tag{A.49}$$

where

$a_{\mathrm{coc/w-o/w}}$: regression coefficient (slope) in linear relation between $K_{\mathrm{coc/w}}$ and $K_{\mathrm{o/w}}$ [L·kg^{-1}]; see Table B.1

$b_{\mathrm{coc/w-o/w}}$: regression coefficient (y-intercept) in linear relation between $K_{\mathrm{coc/w}}$ and $K_{\mathrm{o/w}}$ [L·kg^{-1}]; see Table B.1

$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.1

The conductance (diffusion velocity) through the paddy water layer boundary, φ_{pw} [m·d^{-1}], according to Schwarzenbach et al. (2003, p. 813, 916-17); Schwarzenbach et al. (1993, p. 200) and Trapp (2007, p. 385):

$$\varphi_{\mathrm{pw}} = \frac{D_{\mathrm{w,O_2}}}{\Delta l_{\mathrm{pw}}} \cdot \left(\frac{MW_{\mathrm{O_2}}}{MW}\right)^{\frac{1}{2}} \tag{A.50}$$

where

$D_{\mathrm{w,O_2}}$: diffusion coefficient of gaseous oxygen in water (at +25°C) [m^2·d^{-1}]; see Table B.1

Δl_{pw} : diffusion path length (thickness) of the paddy water layer boundary [m]; see Table B.1

$MW_{\mathrm{O_2}}$: molecular weight of oxygen [g·mol^{-1}]; see Table B.1

MW : molecular weight [g·mol^{-1}]; see Table B.2

Outflow from paddy water layer to freshwater body

According to Inao (2003, p. 26), the rate coefficient for outflow from paddy water layer to the freshwater body as loss from the considered compartmental system, $k_{\mathrm{fb}\leftarrow\mathrm{pw,loss}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{fb}\leftarrow\mathrm{pw,loss}} = \frac{p_{\mathrm{pw,fb}}}{h_{\mathrm{pw}}} \tag{A.51}$$

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[5] Note that $K_{\mathrm{coc/w}}$ is different from $K_{\mathrm{oc/w}}$, which is the partition coefficient between soil organic carbon and water and, thus, refers to processes in soil (Schwarzenbach et al., 2003, p. 301).

where

$p_{\text{pw,fb}}$: outflow velocity of water in paddy water layer that flows into freshwater body [m·d^{-1}]; see Table B.1

h_{pw} : vertical dimension (depth) of the paddy water layer [m]; see Table B.1

Sedimentation and adsorption (advection) and diffusion from paddy water layer to root-zone soil layer

According to Inao and Kitamura (1999, p. 40-41) and Rosenbaum et al. (2004, Part II, p. 11), the rate coefficient for sedimentation, adsorption and diffusion from paddy water layer to the root-zone soil layer, $k_{\text{ts}\leftarrow\text{pw,conv}}$ [d^{-1}], can be derived as follows (How to arrive at this equation is explained in Section A.12, Equation A.96.)

$$k_{\text{ts}\leftarrow\text{pw,conv}} = \frac{A_{\text{ts}} \cdot \big(p_{\text{pw,ps}} \cdot fr\_m_{\text{pw,ps}} + p_{\text{pw,ts}} + \varphi_{\text{pw/ts,paq}} \cdot (1 - fr\_m_{\text{pw,ps}})\big)}{V_{\text{pw}}} \tag{A.52}$$

where

A_{ts} : area of the root-zone soil layer [m^2]; see Table B.1

$p_{\text{pw,ps}}$: sedimentation velocity of suspended particles from the paddy water layer to the root-zone soil layer [m·d^{-1}]; see Table B.1

$fr\_m_{\text{pw,ps}}$: fraction of mass of substance in solid phase (sorbed to particles) of the paddy water layer [kg·kg^{-1}]; see Equation A.48

$p_{\text{pw,ts}}$: penetration velocity from the paddy water layer to the root-zone soil layer [m·d^{-1}]; see Table B.1

$\varphi_{\text{pw/ts,paq}}$: conductance (diffusion velocity) between aqueous phase of paddy water layer and root-zone soil layer [m·d^{-1}]; see Table B.1

V_{pw} : volume of the paddy water layer [m^3]; see Table B.1

The fraction of mass of substance in solid phase (sorbed to particles) of the paddy water layer, $fr\_m_{\text{pw,ps}}$ [kg·kg^{-1}], according to Rosenbaum et al. (2004, Part II, p. 12):

$$fr\_m_{\text{pw,ps}} = \frac{C_{\text{pw,sus}} \cdot fr\_M_{\text{pw,coc}} \cdot K_{\text{coc/w}}}{1 + C_{\text{pw,coc}} \cdot K_{\text{coc/w}} + C_{\text{pw,sus}} \cdot fr\_M_{\text{pw,coc}} \cdot K_{\text{coc/w}}} \tag{A.53}$$

where

$C_{\mathrm{pw,sus}}$: concentration of suspended particles per unit volume of bulk paddy water layer [kg·L^{-1}]; see Table B.1

$fr\_M_{\mathrm{pw,coc}}$: fraction of mass of colloidal organic carbon in paddy water suspended particles phase [kg·kg^{-1}]; see Table B.1

$C_{\mathrm{pw,coc}}$: concentration of colloidal organic carbon per unit volume of bulk paddy water layer [kg·L^{-1}]; see Table B.1

$K_{\mathrm{coc/w}}$: partition coefficient between colloidal organic carbon in paddy water and water [L·kg^{-1}]; see Equation A.49

Diffusion from paddy water layer to vegetation stem

According to Trapp (2007, p. 371), the rate coefficient for diffusion from paddy water layer to vegetation stem (based on a similar approach for diffusion through thick roots), $k_{\mathrm{vs}\leftarrow\mathrm{pw,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vs}\leftarrow\mathrm{pw,diff}} = \frac{A_{\mathrm{vs,pw}} \cdot \varphi_{\mathrm{vs,pw}}}{V_{\mathrm{pw}}} \tag{A.54}$$

where

$A_{\mathrm{vs,pw}}$: area of vegetation stem that is in contact with the paddy water layer [m^2]; see Equation A.71

$\varphi_{\mathrm{vs,pw}}$: conductance (diffusion velocity) through vegetation stem that is in contact with the paddy water layer [m·d^{-1}]; see Equation A.72

V_{pw} : volume of the paddy water layer [m^3]; see Table B.1

A.6. Transfers from plant leaf surface deposit

Penetration (diffusion) from vegetation leaf surface deposit to vegetation leaf (interior)

According to Juraske (2007, p. 1103) and Charles (2004, p. 84), the rate coefficient for diffusion from vegetation leaf surface deposit to vegetation leaf (interior), $k_{\mathrm{vl}\leftarrow\mathrm{vld,diff}}$ [d^{-1}], can be derived as follows (How to arrive at this equation is explained in Section A.12, Equation A.100.):

$$k_{\mathrm{vl}\leftarrow\mathrm{vld,diff}} = \frac{A_{\mathrm{vl}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{vld}}} = k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}} \tag{A.55}$$

where

A_{vl} : area of vegetation leaf [m^2]; see Table B.3

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

V_{vld} : volume of vegetation leaf surface deposit [m^3]; see Table B.3

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\text{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

The conductance of vegetation cuticles does not depend on solubilities of substances in the cuticle and in water, since solute concentrations in the cuticle rather than concentrations of aqueous donor solutions were used to deduce the following equation (Buchholz et al., 1998, p. 323). The conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior), φ_{cut} [m·d^{-1}], according to Buchholz et al. (1998, p. 324), Charles (2004, p. 80) and Satchivi et al. (2006, p. 87):

$$\varphi_{\text{cut}} = \Delta l_{\text{cut}} \cdot k_{\text{cut}} \cdot K_{\text{cuw/w}} \tag{A.56}$$

where

Δl_{cut} : diffusion path length (thickness) of the limiting barrier of the cuticle [m]; see Table B.1

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\text{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

Solute mobilities were originally derived as a function of the molar volume rather than a function of molecular weight, as e. g. in approaches of Juraske (2007, p. 1103), Schreiber (2005, p. 1070), Schreiber and Schönherr (2009, p. 187), Buchholz et al. (1998, p. 324) and Schönherr and Schreiber (2004, p. 409). However, as the molecular weight is a parameter that is easily available for almost all substances, the molar volume must often be determined. This is why the solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane, k_{cut} [d^{-1}], based on molecular weights as described in Schönherr and Schreiber (2004, p. 409) and Buchholz et al. (1998, p. 324) has been applied:

$$\log k_{\text{cut}} = \log k_{\text{cut},\text{V}_0} + SL_{\text{cut}} \cdot MW \tag{A.57}$$

where

$k_{\mathrm{cut,V_0}}$: solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane for volume of 0 mol [d^{-1}]; see Table B.1

SL_{cut} : solute size selectivity of cuticular membrane [mol·g^{-1}]; see Table B.1

MW : molecular weight [g·mol^{-1}]; see Table B.2

The partition coefficient between cuticular wax and water, $K_{\mathrm{cuw/w}}$ [kg·m^{-3} per kg·m^{-3}], according to Satchivi et al. (2006, p. 86), Schreiber and Schönherr (2009, p. 150) and Riederer and Müller (2006, p. 257):

$$\log K_{\mathrm{cuw/w}} = a_{\mathrm{cuw/w-cut/w}} \cdot \log K_{\mathrm{cut/w}} + b_{\mathrm{cuw/w-cut/w}} \tag{A.58}$$

where

$a_{\mathrm{cuw/w-cut/w}}$: regression coefficient (slope) in linear relation between $K_{\mathrm{cuw/w}}$ and $K_{\mathrm{cut/w}}$ [–]; see Table B.1

$b_{\mathrm{cuw/w-cut/w}}$: regression coefficient (y-intercept) in linear relation between $K_{\mathrm{cuw/w}}$ and $K_{\mathrm{cut/w}}$ [kg·m^{-3} per kg·m^{-3}]; see Table B.1

$K_{\mathrm{cut/w}}$: partition coefficient between cuticle and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.59

The partition coefficient between cuticle and water, $K_{\mathrm{cut/w}}$ [kg·m^{-3} per kg·m^{-3}], according to Schreiber and Schönherr (2009, p. 149), Schönherr and Riederer (1989, p. 45), Trapp and Mc Farlane (1995, p. 161), Kerler and Schönherr (1988a, p. 1) and Charles (2004, p. 84):

$$\log K_{\mathrm{cut/w}} = a_{\mathrm{cut/w-o/w}} \cdot \log K_{\mathrm{o/w}} + b_{\mathrm{cut/w-o/w}} \tag{A.59}$$

where

$a_{\mathrm{cut/w-o/w}}$: regression coefficient (slope) in linear relation between $K_{\mathrm{cut/w}}$ and $K_{\mathrm{o/w}}$ [–]; see Table B.1

$b_{\mathrm{cut/w-o/w}}$: regression coefficient (y-intercept) in linear relation between $K_{\mathrm{cut/w}}$ and $K_{\mathrm{o/w}}$ [kg·m^{-3} per kg·m^{-3}]; see Table B.1

$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.1

A.7. Transfers from plant fruit surface deposit

Penetration (diffusion) from vegetation fruit surface deposit to vegetation fruit (interior) via fruit lemma

According to an own approach of fruit resistances in series for protected fruits and based on an approach for diffusion through vegetation leaves according to Juraske (2007, p. 1103) and Charles (2004, p. 84), the rate coefficient for diffusion from vegetation fruit surface deposit to vegetation fruit (interior) via fruit lemma, $k_{\mathrm{vf}\leftarrow\mathrm{led,diff}}$ [d^{-1}], can be derived as follows (How to arrive at this equation is explained in Section A.12, Equation A.102.):

$$k_{\mathrm{vf}\leftarrow\mathrm{led,diff}} = \left(\frac{2}{k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}}} + \frac{K_{\mathrm{lem/cut}} \cdot M_{\mathrm{lem}}}{A_{\mathrm{lem}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}} \right)^{-1} \tag{A.60}$$

where

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\mathrm{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

$K_{\mathrm{lem/cut}}$: partition coefficient between vegetation fruit lemma and cuticle (equals $K_{\mathrm{vl/cut}}$, partition coefficient between vegetation leaf and cuticle) [L·kg^{-1}]; see Equation A.66

M_{lem} : mass of vegetation fruit lemma [kg]; see Table B.3

A_{lem} : area of vegetation fruit lemma [m^2]; see Table B.3

$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

A.8. Transfers from plant leaf (interior)

Transpiration (diffusion) from vegetation leaf (interior) to atmospheric ground layer through stomata

According to Trapp and Matthies (1998, p. 121; 246) and Charles (2004, p. 77-78), the rate coefficient for transpiration from vegetation leaf (interior) to the atmospheric ground layer, $k_{\mathrm{a}\leftarrow\mathrm{vl,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{a}\leftarrow\mathrm{vl,diff}} = \frac{A_{\mathrm{vl}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{a/vl}} \cdot K_{\mathrm{a/w}}}{K_{\mathrm{vl/w}} \cdot M_{\mathrm{vl}}} \tag{A.61}$$

where
A_{vl} : area of vegetation leaf [m^2]; see Table B.3
$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]
$\varphi_{\mathrm{a/vl}}$: conductance (diffusion velocity) between atmospheric ground layer and vegetation leaf (interior) [m·d^{-1}]; see Equation A.27
$K_{\mathrm{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2
$K_{\mathrm{vl/w}}$: partition coefficient between vegetation leaf and water [L·kg^{-1}]; see Equation A.63
M_{vl} : mass of vegetation leaf [kg]; see Table B.3

The conductance (diffusion velocity) through vegetation leaf stomata, φ_{sto} [m·d^{-1}], according to Trapp (2007, p. 386):

$$\varphi_{\mathrm{sto}} = \frac{Q_{\mathrm{vl,xyl}} \cdot \rho_{\mathrm{w}}}{A_{\mathrm{vl}} \cdot (C_{\mathrm{a,H_2O}} - rh \cdot C_{\mathrm{a,H_2O}})} \cdot \left(\frac{MW_{\mathrm{H_2O}}}{MW}\right)^{\frac{1}{2}} \tag{A.62}$$

where
$Q_{\mathrm{vl,xyl}}$: acropetal transpiration stream (flow rate) in xylem of vegetation that flows into vegetation leaf [L·d^{-1}]; see Equation A.76
ρ_{w} : density of water [kg·L^{-1}]; see Table B.1
A_{vl} : area of vegetation leaf [m^2]; see Table B.1
$C_{\mathrm{a,H_2O}}$: saturation water concentration in the atmospheric ground layer [kg·m^{-3}]; see Table B.1
rh : average relative humidity in the atmospheric ground layer [Pa·Pa^{-1}]; see Table B.1
$MW_{\mathrm{H_2O}}$: molecular weight of water [g·mol^{-1}]; see Table B.1
MW : molecular weight [g·mol^{-1}]; see Table B.2

The following equation for the partitioning coefficient between vegetation compartments and water is valid for $K_{\mathrm{vl/w}}$, $K_{\mathrm{vs/w}}$ and $K_{\mathrm{vr/w}}$, i. e. for vegetation leaf, stem and thick root compartments, respectively. Note that according to Trapp (2007, 369-70), this partition coefficient for the vegetation thick root compartment is also referred to as "root concentration factor". The partition coefficient between vegetation compartments and water, $K_{\mathrm{v,comp/w}}$ $[\mathrm{L{\cdot}kg^{-1}}]$, according to Trapp and Matthies (1998, p. 118, 271-72) and Trapp (2007, p. 370, 373):

$$K_{\mathrm{v,comp/w}} = \left(fr\_V_{\mathrm{v,paq}} + fr\_V_{\mathrm{v,pli}} \cdot \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{o}}} \cdot {K_{\mathrm{o/w}}}^{fc_{\mathrm{v,pli/o}}} \right) \cdot \frac{\rho_{\mathrm{v}}}{\rho_{\mathrm{w}}} \tag{A.63}$$

where

$fr\_V_{\mathrm{v,paq}}$: fraction of volumetric water in vegetation compartment $[\mathrm{L{\cdot}kg^{-1}}]$; see Table B.3

$fr\_V_{\mathrm{v,pli}}$: fraction of volumetric lipids in vegetation compartment $[\mathrm{L{\cdot}kg^{-1}}]$; see Table B.3

ρ_{w} : density of water $[\mathrm{kg{\cdot}L^{-1}}]$; see Table B.1

ρ_{o} : density of n–octanol $[\mathrm{kg{\cdot}L^{-1}}]$; see Table B.1

$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water $[\mathrm{kg{\cdot}m^{-3}}$ per $\mathrm{kg{\cdot}m^{-3}}]$; see Equation A.1

$fc_{\mathrm{v,pli/o}}$: (empirical) correction exponent for differences between vegetation compartment lipids and n–octanol; differs between vegetation thick root and other vegetation compartments [–]

ρ_{v} : density of bulk vegetation compartment $[\mathrm{kg{\cdot}L^{-1}}]$; see Table B.3

The conductance (diffusion velocity) through the vegetation cuticle related to water (also known as permeability), $\varphi_{\mathrm{cut,w}}$ $[\mathrm{m{\cdot}d^{-1}}]$ can be described according to Trapp (2007, p. 387):

$$\log \varphi_{\mathrm{cut,w}} = a_{\mathrm{cut,w-cut/w}} \cdot \log K_{\mathrm{cut/w}} + b_{\mathrm{cut,w-cut/w}} \tag{A.64}$$

where

$a_{\mathrm{cut,w-cut/w}}$: regression coefficient (slope) in linear relation between $\varphi_{\mathrm{cut,w}}$ and $K_{\mathrm{cut/w}}$ $[\mathrm{m{\cdot}d^{-1}}]$; see Table B.1

$b_{\mathrm{cut,w-cut/w}}$: regression coefficient (y-intercept) in linear relation between $\varphi_{\mathrm{cut,w}}$ and $K_{\mathrm{cut/w}}$ $[\mathrm{m{\cdot}d^{-1}}]$; see Table B.1

$K_{\mathrm{cut/w}}$: partition coefficient between cuticle and water $[\mathrm{kg{\cdot}m^{-3}}$ per $\mathrm{kg{\cdot}m^{-3}}]$; see Equation A.59

Diffusion from vegetation leaf (interior) to vegetation leaf surface deposit

According to Charles (2004, p. 85), the rate coefficient for diffusion from vegetation leaf (interior) to vegetation leaf surface deposit, $k_{\text{vld}\leftarrow\text{vl,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\text{vld}\leftarrow\text{vl,diff}} = \frac{A_{\text{vl}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{cut,w}}}{K_{\text{vl/cut}} \cdot M_{\text{vl}}} \tag{A.65}$$

where
A_{vl} : area of vegetation leaf [m^2]; see Table B.3
$fc_{\text{L to m}^3}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]
$\varphi_{\text{cut,w}}$: conductance (diffusion velocity) of cuticle related to water [m·d^{-1}]; see Equation A.64
$K_{\text{vl/cut}}$: partition coefficient between vegetation leaf and cuticle [L·kg^{-1}]; see Equation A.66
M_{vl} : mass of vegetation leaf [kg]; see Table B.3

The partition coefficient between vegetation leaf and cuticle, $K_{\text{vl/cut}}$ [L·kg^{-1}], according to Trapp and Mc Farlane (1995, p. 156-57):

$$K_{\text{vl/cut}} = \frac{K_{\text{vl/w}}}{K_{\text{cut/w}}} \tag{A.66}$$

where
$K_{\text{vl/w}}$: partition coefficient between vegetation leaf and water [L·kg^{-1}]; see Equation A.63
$K_{\text{cut/w}}$: partition coefficient between cuticle and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.59

Basipetal assimilation (advection) from vegetation leaf to vegetation stem via phloem

Only the part of the phloem flow rate in vegetation is considered which flows into the vegetation fruit compartment. However, if one would like to consider the total phloem flow rate in vegetation, i. e. to also account for the part that flows towards the roots, $Q_{\text{vf,phlo}}$ must be replaced by Q_{phlo} (see Equation A.68) in the following equation. According to Trapp and Mc Farlane (1995, p. 121), the rate coefficient for basipetal assimilation from vegetation leaf (interior) to vegetation stem, $k_{\text{vs}\leftarrow\text{vl,adv}}$ [d^{-1}], can be derived as follows:

$$k_{\text{vs}\leftarrow\text{vl,adv}} = \frac{Q_{\text{vf,phlo}}}{K_{\text{vl/w}} \cdot M_{\text{vl}}} \tag{A.67}$$

where

$Q_{\mathrm{vf,phlo}}$: basipetal assimilation stream (flow rate) in phloem of vegetation that flows into vegetation fruit $[\mathrm{L}\cdot\mathrm{d}^{-1}]$; see Equation A.68

$K_{\mathrm{vl/w}}$: partition coefficient between vegetation leaf and water $[\mathrm{L}\cdot\mathrm{kg}^{-1}]$; see Equation A.63

M_{vl} : mass of vegetation leaf [kg]; see Table B.3

The basipetal assimilation stream (flow rate) in phloem of vegetation that flows into vegetation fruit, $Q_{\mathrm{vf,phlo}}$ $[\mathrm{L}\cdot\mathrm{d}^{-1}]$, according to Trapp et al. (2003, p. 20) and Trapp (2007, p. 374-75):

$$Q_{\mathrm{vf,phlo}} = \frac{M_{\mathrm{vf}} \cdot fc_{\mathrm{phlo}\rightarrow\mathrm{vf,M}} \cdot (1 - fr\_V_{\mathrm{vf,paq}})}{\bar{t}_{\mathrm{vf,app}\rightarrow\mathrm{harv}}} \tag{A.68}$$

where

M_{vf} : mass of vegetation fruit [kg]; see Table B.3

$fc_{\mathrm{phlo}\rightarrow\mathrm{vf,M}}$: correlation factor between basipetal assimilation stream (flow rate) in phloem of vegetation and dry mass of vegetation fruit [–]; see Table B.1

$fr\_V_{\mathrm{vf,paq}}$: fraction of volumetric water in vegetation fruit $[\mathrm{L}\cdot\mathrm{kg}^{-1}]$; see Table B.1

$\bar{t}_{\mathrm{vf,app}\rightarrow\mathrm{harv}}$: average time period between ‘from when vegetation fruit starts to grow to application (of substance)’ and ‘from when vegetation fruit starts to grow to harvest (of vegetation fruit compartment)’ [d]; see Table B.1

A.9. Transfers from plant fruit (interior)

Diffusion from vegetation fruit (interior) to vegetation fruit surface deposit via fruit lemma

According to Charles (2004, p. 85), the rate coefficient for diffusion from vegetation fruit (interior) to vegetation fruit surface deposit (based on the approach for diffusion from leaves), $k_{\mathrm{led}\leftarrow\mathrm{vf,diff}}$ $[\mathrm{d}^{-1}]$, can be derived as follows (How to arrive at this equation is explained in Section A.12, Equation A.108.)

$$k_{\mathrm{led}\leftarrow\mathrm{vf,diff}} = \left(\frac{K_{\mathrm{vf/cut}} \cdot (M_{\mathrm{vf}} + M_{\mathrm{lem}})}{A_{\mathrm{vf}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}} + \frac{1}{k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}}} \right)^{-1} \tag{A.69}$$

where

$K_{\text{vf/cut}}$: partition coefficient between vegetation fruit and cuticle (equals $K_{\text{vl/cut}}$, partition coefficient between vegetation leaf and cuticle) [L·kg^{-1}]; see Equation A.66

M_{vf} : mass of vegetation fruit [kg]; see Table B.3

M_{lem} : mass of vegetation fruit lemma [kg]; see Table B.3

A_{vf} : area of vegetation fruit [m^2]; see Table B.3

$fc_{\text{L to m}^3}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\text{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

A.10. Transfers from plant stem (including branches)

Diffusion from vegetation stem to paddy water layer

According to an own approach of stem resistances in series when in contact with water and based on an approach for diffusion through vegetation thick roots according to Trapp et al. (2007, p. 3105), the rate coefficient for diffusion from vegetation stem to the paddy water layer, $k_{\text{pw}\leftarrow\text{vs,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\text{pw}\leftarrow\text{vs,diff}} = \frac{A_{\text{vs,pw}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{vs,pw}}}{K_{\text{vs/w}} \cdot M_{\text{vs}}} \tag{A.70}$$

where

$A_{\text{vs,pw}}$: area of vegetation stem that is in contact with the paddy water layer [m^2]; see Equation A.71

$fc_{\text{L to m}^3}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

$\varphi_{\text{vs,pw}}$: conductance (diffusion velocity) through vegetation stem that is in contact with the paddy water layer [m·d^{-1}]; see Equation A.72

$K_{\text{vs/w}}$: partition coefficient between vegetation stem and water [L·kg^{-1}]; see Equation A.63 (note that only non-woody vegetation is considered here as no woody vegetation is known to grow in paddy water)

M_{vs} : mass of vegetation stem [kg]; see Table B.3

In the following equation, the term $(V_{\mathrm{vs}}/(\pi \cdot h_{\mathrm{vs}}))^{\frac{1}{2}}$ represents the mean radius of the vegetation stem, r_{vs} [m]. The area of vegetation stem that is in contact with the paddy water layer (based on general geometric formulations for cylindric objects), $A_{\mathrm{vs,pw}}$ [m^2], according to Perry and Green (2008, p. 3-7):

$$A_{\mathrm{vs,pw}} = 2 \cdot \pi \cdot \left(\frac{V_{\mathrm{vs}}}{\pi \cdot h_{\mathrm{vs}}} \right)^{\frac{1}{2}} \cdot h_{\mathrm{pw}} \tag{A.71}$$

where
V_{vs} : volume of vegetation stem [m^3]; see Table B.3
h_{vs} : vertical dimension (height) of vegetation stem [m]; see Table B.3
h_{pw} : vertical dimension (depths) of the paddy water layer [m]; see Table B.1

The conductance (diffusion velocity) through vegetation stem that is in contact with the paddy water layer, $\varphi_{\mathrm{vs,pw}}$ [m·d^{-1}], according to Trapp (2007, p. 373, 385):

$$\varphi_{\mathrm{vs,pw}} = \left(\frac{1}{\varphi_{\mathrm{cut}}} + \frac{1}{\varphi_{\mathrm{vs,cew}}} + \frac{1}{\varphi_{\mathrm{vs,mem}}} \right)^{-1} \tag{A.72}$$

where
φ_{cut} : conductance (diffusion velocity) through cuticle [m·d^{-1}]; see Equation A.56
$\varphi_{\mathrm{vs,cew}}$: conductance (diffusion velocity) through epidermal cell wall of vegetation stem [m·d^{-1}]; see Equation A.73
$\varphi_{\mathrm{vs,mem}}$: conductance (diffusion velocity) through bio- or plasma-membrane of vegetation stem [m·d^{-1}]; see Equation A.74

The conductance (diffusion velocity) through the epidermal cell wall of vegetation stem, $\varphi_{\mathrm{vs,cew}}$ [m·d^{-1}], according to Trapp (2000, p. 770):

$$\varphi_{\mathrm{vs,cew}} = \frac{D_{\mathrm{vs,cew}}}{\Delta l_{\mathrm{vs,cew}}} \tag{A.73}$$

where
$D_{\mathrm{vs,cew}}$: (effective) diffusion coefficient in the epidermal cell wall of vegetation stem [m^2·d^{-1}]; see Table B.1
$\Delta l_{\mathrm{vs,cew}}$: diffusion path length (thickness) of the epidermal cell wall of vegetation stem [m]; see Table B.1

The conductance (diffusion velocity) through the bio- or plasma-membrane of vegetation stem, $\varphi_{\mathrm{vs,mem}}$ [m·d^{-1}], according to Trapp (2007, p. 385), Trapp (2004, p. 34) and Grayson and Kleier (1990, p. 70):

$$\varphi_{\mathrm{v,mem}} = \frac{D_{\mathrm{v,mem}} \cdot K_{\mathrm{o/w}}}{\Delta l_{\mathrm{v,mem}}} \tag{A.74}$$

where

$D_{\mathrm{v,mem}}$: diffusion coefficient in the bio- or plasma-membrane of vegetation compartment [m^2·d^{-1}]; see Table B.1

$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water [kg·m^{-3}per kg·m^{-3}]; see Equation A.1

$\Delta l_{\mathrm{v,mem}}$: diffusion path length (thickness) of the bio- or plasma-membrane of vegetation compartment [m]; see Table B.1

Acropetal transpiration (advection) from vegetation stem to vegetation leaf via xylem

According to Trapp (2007, p. 373), the rate coefficient for acropetal transpiration from vegetation stem to vegetation leaf via xylem, $k_{\mathrm{vl\leftarrow vs,adv}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vl\leftarrow vs,adv}} = \frac{Q_{\mathrm{vl,xyl}}}{K_{\mathrm{vs/w}} \cdot M_{\mathrm{vs}}} \tag{A.75}$$

where

$Q_{\mathrm{vl,xyl}}$: acropetal transpiration stream (flow rate) in xylem of vegetation that flows into vegetation leaf [L·d^{-1}]; see Equation A.76

$K_{\mathrm{vs/w}}$: partition coefficient between vegetation stem and water [L·kg^{-1}]; for non-woody vegetation see Equation A.63 and for woody vegetation see Equation A.78

M_{vs} : mass of vegetation stem [kg]; see Table B.3

The following equation is only relevant, if fruits with stomata are considered, such as sweet cherry fruits (Peschel et al., 2003). The acropetal transpiration stream (flow rate) in xylem of vegetation that flows into vegetation leaf, $Q_{\mathrm{vl,xyl}}$ [L·d^{-1}], according to Trapp (2007, p. 374):

$$Q_{\mathrm{vl,xyl}} = Q_{\mathrm{xyl}} \cdot \frac{A_{\mathrm{vl}}}{A_{\mathrm{vl}} + A_{\mathrm{vf}}} \tag{A.76}$$

where
Q_{xyl} : acropetal transpiration stream (flow rate) in xylem of vegetation [L·d^{-1}]; see Equation A.77
A_{vl} : area of vegetation leaf [m^2]; see Table B.3
A_{vf} : area of vegetation fruit [m^2]; see Table B.3

While xylem in vegetation stem is *endarch*, i. e. it grows from the outside towards the center of the stem, the xylem in vegetation thick roots is *exarch*, i. e. it grows from the inside of the root towards the periphery (Jeffrey, 2007, p. 20-23). The acropetal transpiration stream (flow rate) in xylem of vegetation, Q_{xyl} [L·d^{-1}], according to Charles (2004, p. 86):

$$Q_{\text{xyl}} = \frac{M_{\text{v}} \cdot ET_{\text{v}}}{\bar{t}_{\text{app}\rightarrow\text{harv}}} \tag{A.77}$$

where
M_{v} : mass of vegetation [kg]; see Table B.3
ET_{v} : transpiration coefficient of vegetation (inverse of water use efficiency of vegetation) [L·kg^{-1}]; see Table B.3
$\bar{t}_{\text{app}\rightarrow\text{harv}}$: average time period between ‘from when vegetation starts to grow to application (of substance)’ and ‘from when vegetation starts to grow to harvest (of vegetation compartment)’ [d]; see Table B.1

The partition coefficient between woody vegetation stem and water, $K_{\text{vs,wood/w}}$ [L·kg^{-1}], according to Trapp (2007, p. 372):

$$K_{\text{vs,wood/w}} = \frac{\rho_{\text{vs,dry}}}{\rho_{\text{vs,wet}}} \cdot K_{\text{wood/w}} + fr\_V_{\text{vs,paq}} + fr\_V_{\text{vs,pg}} \cdot K_{\text{a/w}} \tag{A.78}$$

where
$\rho_{\text{vs,dry}}$: density of dry (woody) vegetation stem [kg·L^{-1}]; see Table B.3
$\rho_{\text{vs,wet}}$: density of wet (woody) vegetation stem [kg·L^{-1}]; see Table B.3
$K_{\text{wood/w}}$: partition coefficient between wood fraction of vegetation stem and water [L·kg^{-1}]; see Equation A.79
$fr\_V_{\text{vs,paq}}$: fraction of volumetric water in vegetation stem [L·kg^{-1}]; see Table B.3
$fr\_V_{\text{vs,pg}}$: fraction of volumetric gas in vegetation stem [L·kg^{-1}]; see Table B.3
$K_{\text{a/w}}$: partition coefficient between air and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.2

The partition coefficient between the wood fraction of woody vegetation stem and water, $K_{\mathrm{wood/w}}$ [L·kg^{-1}], according to Trapp et al. (2001, p. 1536) and Trapp (2007, p. 372):

$$\log K_{\mathrm{wood/w}} = a_{\mathrm{wood/w-o/w}} \cdot \log K_{\mathrm{o/w}} + b_{\mathrm{wood/w-o/w}} \tag{A.79}$$

where

$a_{\mathrm{wood/w-o/w}}$: regression coefficient (slope) in linear relation between $K_{\mathrm{wood/w}}$ and $K_{\mathrm{o/w}}$ [L·kg^{-1}]; see Table B.1

$b_{\mathrm{wood/w-o/w}}$: regression coefficient (y-intercept) in linear relation between $K_{\mathrm{wood/w}}$ and $K_{\mathrm{o/w}}$ [L·kg^{-1}]; see Table B.1

$K_{\mathrm{o/w}}$: partition coefficient between n–octanol and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.1

Basipetal assimilation and acropetal transpiration (advection) from vegetation stem to vegetation fruit via phloem and xylem

According to Trapp (2007, p. 374-75) and Juraske et al. (2009a, p. 685), the rate coefficient for basipetal assimilation and acropetal transpiration from vegetation stem to vegetation fruit via phloem and xylem, $k_{\mathrm{vf\leftarrow vs,adv}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vf\leftarrow vs,adv}} = \frac{Q_{\mathrm{vf,xyl}} + Q_{\mathrm{vf,phlo}}}{K_{\mathrm{vs/w}} \cdot M_{\mathrm{vs}}} \tag{A.80}$$

where

$Q_{\mathrm{vf,xyl}}$: acropetal transpiration stream (flow rate) in xylem of vegetation that flows into vegetation fruit [L·d^{-1}]; see Equation A.81

$Q_{\mathrm{vf,phlo}}$: basipetal assimilation stream (flow rate) in phloem of vegetation that flows into vegetation fruit [L·d^{-1}]; see Equation A.68

$K_{\mathrm{vs/w}}$: partition coefficient between vegetation stem and water [L·kg^{-1}]; for non-woody vegetation see Equation A.63 and for woody vegetation see Equation A.78

M_{vs} : mass of vegetation stem [kg]; see Table B.3

The acropetal transpiration stream (flow rate) in xylem of vegetation that flows into vegetation fruit, $Q_{\mathrm{vf,xyl}}$ [L·d^{-1}], according to Trapp (2007, p. 374):

$$Q_{\mathrm{vf,xyl}} = Q_{\mathrm{xyl}} \cdot \frac{A_{\mathrm{vf}}}{A_{\mathrm{vl}} + A_{\mathrm{vf}}} \tag{A.81}$$

where

Q_{xyl} : acropetal transpiration stream (flow rate) in xylem of vegetation [L·d^{-1}]; see Equation A.77

A_{vf} : area of vegetation fruit [m^2]; see Table B.3

A_{vl} : area of vegetation leaf [m^2]; see Table B.3

Transfer from stem to root via phloem flow is considered negligible according to current literature, e. g. Trapp (2007). As a special case, for root-crops like potato no flow towards root is to be considered at all Trapp et al. (2007); Juraske et al. (2011).

A.11. Transfers from plant thick root

Diffusion from vegetation thick root to root-zone soil layer

Diffusion from vegetation thick root to root-zone soil layer is generally based on conductance (diffusion velocity) through vegetation thick root. However, for root crops, such as potatoes, this process is based on a specific radial diffusion model as introduced by Schwarzenbach et al. (2003). While the diffusion from all vegetation thick roots to root-zone soil layer is formulated in Equation A.82, the diffusion from root crops into root-zone soil layer is formulated in Equation A.88.

According to Trapp et al. (2007, p. 3105), the rate coefficient for diffusion from vegetation thick root to the root-zone soil layer, $k_{\mathrm{ts}\leftarrow\mathrm{vr,diff}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{ts}\leftarrow\mathrm{vr,diff}} = \frac{A_{\mathrm{vr}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{vr}}}{K_{\mathrm{vr/w}} \cdot M_{\mathrm{vr}}} \tag{A.82}$$

where

A_{vr} : area of vegetation thick root [m^2]; see Table B.3

$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{vr} : conductance (diffusion velocity) through vegetation thick root [m·d^{-1}]; see Equation A.83

$K_{\mathrm{vr/w}}$: partition coefficient between vegetation thick root and water [L·kg^{-1}]; see Equation A.63

M_{vr} : mass of vegetation thick root [kg]; see Table B.3

The conductance (diffusion velocity) through vegetation thick root, φ_{vr} [m·d^{-1}], according to Trapp (2007, p. 385):

$$\varphi_{\mathrm{vr}} = \left(\frac{1}{\varphi_{\mathrm{vr,tis}}} + \frac{1}{\varphi_{\mathrm{vr,mem}}}\right)^{-1} \tag{A.83}$$

where

$\varphi_{\mathrm{vr,tis}}$: conductance (diffusion velocity) through tissue of vegetation thick root [m·d^{-1}]; see Equation A.84

$\varphi_{\mathrm{vr,mem}}$: conductance (diffusion velocity) through bio- or plasma-membrane of vegetation thick root [m·d^{-1}]; see Equation A.74

The conductance (diffusion velocity) through tissue of vegetation thick root, $\varphi_{\mathrm{vr,tis}}$ [m·d^{-1}], according to Trapp (2007, p. 385):

$$\varphi_{\mathrm{vr,tis}} = \frac{D_{\mathrm{vr,tis}}}{\Delta l_{\mathrm{vr,tis}}} \tag{A.84}$$

where

$D_{\mathrm{vr,tis}}$: (effective) diffusion coefficient in the tissue of vegetation thick root [m^2·d^{-1}]; see Equation A.85

$\Delta l_{\mathrm{vr,tis}}$: diffusion path length (thickness) of the tissue of vegetation thick root [m]; see Table B.3

The following set of equations for deducing the (effective) diffusion coefficient in porous compartments, such as root-zone soil and vegetation thick root tissue, is valid for D_{ts} and $D_{\mathrm{vr,tis}}$, respectively. The (effective) diffusion coefficient in porous compartments, D_{comp} [m^2·d^{-1}], according to Trapp (2007, p. 385):

$$D_{\mathrm{comp}} = D_{\mathrm{comp,pg}} + D_{\mathrm{comp,paq}} \tag{A.85}$$

where

$D_{\mathrm{comp,pg}}$: (effective) diffusion coefficient in gas phase of porous compartment [m^2·d^{-1}]; see Equation A.86

$D_{\mathrm{comp,paq}}$: (effective) diffusion coefficient in aqueous phase of porous compartment [m^2·d^{-1}]; see Equation A.87

In the following equation, the first fraction term represents the mass fraction of substance of concern in air or gas phase of porous compartments (Trapp, 2007, p. 384), the terms between the first and the last fraction terms represent the diffusion coefficient in air or gas phase of porous compartments as a function of water vapor properties and the molecular weights of the substance of concern and water, respectively (Trapp, 2007, p. 385; Schwarzenbach et al., 2003, p. 803; Schwarzenbach et al., 1993, p. 200; Baum, 1998, p. 250; Trapp and Matthies, 1998, p. 23), and the last fraction term represents the tortuosity in air or gas phase of porous compartments (Trapp, 2007, p. 385; Trapp and Matthies, 1998, p. 91). The (effective) diffusion coefficient in gas phase of porous compartments, $D_{\mathrm{comp,pg}}$ [$\mathrm{m^2 \cdot d^{-1}}$], according to Holzbecher (2007, p. 52) and Trapp (2007, p. 385):

$$D_{\mathrm{comp,pg}} = \frac{\mathit{fr\_V}_{\mathrm{comp,pg}} \cdot K_{\mathrm{a/w}}}{K_{\mathrm{comp/w}}} \cdot D_{\mathrm{a,H_2O}} \cdot \left(\frac{MW_{\mathrm{H_2O}}}{MW} \right)^{\frac{1}{2}} \cdot \frac{(\mathit{fr\_V}_{\mathrm{comp,pg}})^{\frac{10}{3}}}{(\mathit{fr\_V}_{\mathrm{comp,pg}} + \mathit{fr\_V}_{\mathrm{comp,paq}})^2} \tag{A.86}$$

where

$\mathit{fr\_V}_{\mathrm{comp,pg}}$: fraction of volumetric gas in porous compartment [$\mathrm{L \cdot kg^{-1}}$]; for root-zone soil layer see Table B.1 and for vegetation compartments see Table B.3

$K_{\mathrm{a/w}}$: partition coefficient between air and water [$\mathrm{kg \cdot m^{-3}}$ per $\mathrm{kg \cdot m^{-3}}$]; see Equation A.2

$K_{\mathrm{comp/w}}$: partition coefficient between bulk porous compartment and water [$\mathrm{L \cdot kg^{-1}}$]; for root-zone soil layer compartment see Equation A.32 and for vegetation thick root compartment see Equation A.63

$D_{\mathrm{a,H_2O}}$: diffusion coefficient of water vapor in the atmospheric ground layer [$\mathrm{m^2 \cdot d^{-1}}$]; see Table B.1

$MW_{\mathrm{H_2O}}$: molecular weight of water [$\mathrm{g \cdot mol^{-1}}$]; see Table B.1

MW : molecular weight [$\mathrm{g \cdot mol^{-1}}$]; see Table B.2

$\mathit{fr\_V}_{\mathrm{comp,paq}}$: fraction of volumetric water in porous compartment [$\mathrm{L \cdot kg^{-1}}$]; for root-zone soil layer see Table B.1 and for vegetation compartments see Table B.3

In the following equation, the first fraction term represents the mass fraction of substance of concern in water or aqueous phase of porous compartments (Trapp, 2007, p. 384), the terms between the first and the last fraction terms represent the diffusion coefficient in water or aqueous phase of porous compartments as a function of gaseous oxygen properties and the molecular weights of the substance of concern and oxygen, respectively (Trapp, 2007, p. 385; Schwarzenbach et al., 2003, p. 803; Schwarzenbach et al., 1993, p. 200; Baum, 1998, p. 250; Trapp and Matthies, 1998, p. 23), and the last fraction term represents the tortuosity in water or aqueous phase of porous compartments (Trapp, 2007, p. 385). The (effective) diffusion coefficient in aqueous phase of porous compartments, $D_{\mathrm{comp,paq}}$ [$\mathrm{m^2 \cdot d^{-1}}$], according to Holzbecher (2007, p. 52) and Trapp (2007, p. 384-85):

$$D_{\mathrm{comp,paq}} = \frac{\mathit{fr\_V}_{\mathrm{comp,paq}}}{K_{\mathrm{comp/w}}} \cdot D_{\mathrm{w,O_2}} \cdot \left(\frac{MW_{\mathrm{O_2}}}{MW} \right)^{\frac{1}{2}} \cdot \frac{(\mathit{fr\_V}_{\mathrm{comp,paq}})^{\frac{10}{3}}}{(\mathit{fr\_V}_{\mathrm{comp,pg}} + \mathit{fr\_V}_{\mathrm{comp,paq}})^2} \tag{A.87}$$

where

$fr\_V_{\mathrm{comp,paq}}$: fraction of volumetric water in porous compartment $[\mathrm{L\cdot kg^{-1}}]$; for root-zone soil layer see Table B.1 and for vegetation compartments see Table B.3

$K_{\mathrm{comp/w}}$: partition coefficient between bulk porous compartment and water $[\mathrm{L\cdot kg^{-1}}]$; for root-zone soil layer compartment see Equation A.32 and for vegetation thick root compartment see Equation A.63

$D_{\mathrm{w,O_2}}$: diffusion coefficient of gaseous oxygen in water (at $+25°\mathrm{C}$) $[\mathrm{m^2\cdot d^{-1}}]$; see Table B.1

$MW_{\mathrm{O_2}}$: molecular weight of oxygen $[\mathrm{g\cdot mol^{-1}}]$; see Table B.1

MW : molecular weight $[\mathrm{g\cdot mol^{-1}}]$; see Table B.2

$fr\_V_{\mathrm{comp,pg}}$: fraction of volumetric gas in porous compartment $[\mathrm{L\cdot kg^{-1}}]$; for root-zone soil layer see Table B.1 and for vegetation compartments see Table B.3

According to Juraske et al. (2011, p. S11) and Paraíba and Kataguiri (2008, p. 1249), the rate coefficient for diffusion from vegetation thick root to the root-zone soil layer for root crops, $k_{\mathrm{ts\leftarrow vr,diff}}$ $[\mathrm{d^{-1}}]$, can be derived as follows:

$$k_{\mathrm{ts\leftarrow vr,diff}} = \frac{fc_{\mathrm{D,vr,tis}} \cdot D_{\mathrm{vr,tis}} \cdot M_{\mathrm{ts}}}{r_{\mathrm{vr}}{}^2 \cdot \rho_{\mathrm{w}} \cdot K_{\mathrm{vr/w}} \cdot M_{\mathrm{vr}}} \tag{A.88}$$

where

$fc_{\mathrm{D,vr,tis}}$: empirical correction factor for radial diffusion model [–]; see Table B.1

$D_{\mathrm{vr,tis}}$: (effective) diffusion coefficient in the tissue of vegetation thick root $[\mathrm{m^2\cdot d^{-1}}]$; see Equation A.85

M_{ts} : mass of the root-zone soil layer [kg]; see Table B.1

r_{vr} : mean radius of vegetation thick root [m]; see Table B.3

ρ_{w} : density of water $[\mathrm{kg\cdot L^{-1}}]$; see Table B.1

$K_{\mathrm{vr/w}}$: partition coefficient between vegetation thick root and water $[\mathrm{L\cdot kg^{-1}}]$; see Equation A.63

M_{vr} : mass of vegetation thick root [kg]; see Table B.3

Acropetal transpiration (advection) from vegetation thick root to vegetation stem via xylem

According to Trapp (2007, p. 371) and Juraske et al. (2009a, p. 685), the rate coefficient for acropetal transpiration from vegetation thick root to vegetation stem via xylem, $k_{\mathrm{vs}\leftarrow\mathrm{vr,adv}}$ [d^{-1}], can be derived as follows:

$$k_{\mathrm{vs}\leftarrow\mathrm{vr,adv}} = \frac{Q_{\mathrm{xyl}}}{K_{\mathrm{vr/w}} \cdot M_{\mathrm{vr}}} \tag{A.89}$$

where

Q_{xyl} : acropetal transpiration stream (flow rate) in xylem of vegetation [L·d^{-1}]; see Equation A.77

$K_{\mathrm{vr/w}}$: partition coefficient between vegetation thick root and water [L·kg^{-1}]; see Equation A.63

M_{vr} : mass of vegetation thick root [kg]; see Table B.3

A.12. Complementary equations to fate processes in dynamiCROP

Complementary equations for run off

The main equation referring to the transfer from root-zone soil layer to surface (fresh) water via run off (Equation A.34) is deduced as follows:

$$k_{\mathrm{fb}\leftarrow\mathrm{ts,run}} = k_{\mathrm{fb}\leftarrow\mathrm{ts,run,paq}} + k_{\mathrm{fb}\leftarrow\mathrm{ts,run,ps}} \tag{A.90}$$

where

$k_{\mathrm{fb}\leftarrow\mathrm{ts,run,paq}}$: rate coefficient for run off from root-zone soil layer to the freshwater body (soil aqueous phase) [d^{-1}]; see Equation A.91

$k_{\mathrm{fb}\leftarrow\mathrm{ts,run,ps}}$: rate coefficient for run off from root-zone soil layer to the freshwater body (soil matrix) [d^{-1}]; see Equation A.92

with

$$k_{\mathrm{fb}\leftarrow\mathrm{ts,run,paq}} = \frac{fc_{\mathrm{ts,paq}} \cdot p_{\mathrm{rain}} \cdot fr\_p_{\mathrm{rain,run}}}{h_{\mathrm{ts}}} \tag{A.91}$$

where

$fc_{\text{ts,paq}}$: correction factor between the aqueous and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.35

p_{rain} : average annual precipitation rate in the atmospheric ground layer [m^{3}·m^{-2}·d^{-1}]; see Table B.1

$fr\_p_{\text{rain,run}}$: fraction of average annual precipitation rate in the atmospheric ground layer that undergoes run off [m^{3}·m^{-2}·d^{-1} per m^{3}·m^{-2}·d^{-1}]; see Table B.1

h_{ts} : vertical dimension (depth) of the root-zone soil layer [m]; see Table B.1

and with

$$k_{\text{fb}\leftarrow\text{ts,run,ps}} = \frac{fc_{\text{ts,ps}} \cdot fr\_M_{\text{ts,run,ps}} \cdot p_{\text{rain}} \cdot fr\_p_{\text{rain,run}}}{h_{\text{ts}}} \tag{A.92}$$

where

$fc_{\text{ts,ps}}$: correction factor between the solid and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.36

$fr\_M_{\text{ts,run,ps}}$: fraction of mass of root-zone soil layer solids in run off water [kg·kg^{-1}]; see Table B.1

p_{rain} : average annual precipitation rate in the atmospheric ground layer [m^{3}·m^{-2}·d^{-1}]; see Table B.1

$fr\_p_{\text{rain,run}}$: fraction of average annual precipitation rate in the atmospheric ground layer that undergoes run off [m^{3}·m^{-2}·d^{-1} per m^{3}·m^{-2}·d^{-1}]; see Table B.1

h_{ts} : vertical dimension (depth) of the root-zone soil layer [m]; see Table B.1

Integrating $k_{\text{fb}\leftarrow\text{ts,run,paq}}$ from Equation A.91 and $k_{\text{fb}\leftarrow\text{ts,run,ps}}$ from Equation A.92 into Equation A.90 leads to Equation A.34.

Complementary equations for leaching

The main equation referring to the transfer from root-zone soil layer to subsurface soil and further to groundwater via leaching (Equation A.37) is deduced as follows:

$$k_{\text{us}\leftarrow\text{ts,leach}} = k_{\text{us}\leftarrow\text{ts,leach,adv}} - k_{\text{us}\leftarrow\text{ts,leach,diff}} \tag{A.93}$$

where

$k_{\text{us}\leftarrow\text{ts,leach,adv}}$: rate coefficient for leaching from root-zone soil layer to the saturated subsoil (via advection) [d^{-1}]; see Equation A.94

$k_{\text{us}\leftarrow\text{ts,leach,diff}}$: rate coefficient for leaching from root-zone soil layer to the saturated subsoil (via diffusion) [d^{-1}]; see Equation A.95

with

$$k_{\text{us}\leftarrow\text{ts,leach,adv}} = \frac{fc_{\text{ts,paq}} \cdot p_{\text{rain}} \cdot fr\_p_{\text{rain,leach}} \cdot fr\_V_{\text{ts,paq}}}{h_{\text{ts}}} \tag{A.94}$$

where

$fc_{\text{ts,paq}}$: correction factor between the aqueous and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.35

p_{rain} : average annual precipitation rate in the atmospheric ground layer [m^3·m^{-2}·d^{-1}]; see Table B.1

$fr\_p_{\text{rain,leach}}$: fraction of average annual precipitation rate in the atmospheric ground layer that undergoes leaching [m^3·m^{-2}·d^{-1} per m^3·m^{-2}·d^{-1}]; see Table B.1

$fr\_V_{\text{ts,paq}}$: fraction of volumetric water in the bulk root-zone soil layer [L·L^{-1}]; see Table B.1

h_{ts} : vertical dimension (depth) of the root-zone soil layer [m]; see Table B.1

and with

$$k_{\text{us}\leftarrow\text{ts,leach,diff}} = \frac{fc_{\text{ts,paq}} \cdot \varphi_{\text{ts}}}{h_{\text{ts}}} \tag{A.95}$$

where

$fc_{\text{ts,paq}}$: correction factor between the aqueous and the bulk phase of the root-zone soil layer [L·L^{-1}]; see Equation A.35

φ_{ts} : conductance (diffusion velocity) through the root-zone soil layer [m·d^{-1}]; see Equation A.38

h_{ts} : vertical dimension (depth) of the root-zone soil layer [m]; see Table B.1

Integrating $k_{\text{us}\leftarrow\text{ts,leach,adv}}$ from Equation A.94 and $k_{\text{us}\leftarrow\text{ts,leach,diff}}$ from Equation A.95 into Equation A.93 leads to Equation A.37.

Complementary equations for transfer from paddy water

The main equation referring to the transfer from paddy water layer to root-zone soil layer via sedimentation, adsorption and diffusion (Equation A.52) is deduced as follows:

$$k_{\text{ts}\leftarrow\text{pw,conv}} = k_{\text{ts}\leftarrow\text{pw,conv,sed}} + k_{\text{ts}\leftarrow\text{pw,conv,sorp}} + k_{\text{ts}\leftarrow\text{pw,conv,diff}} \tag{A.96}$$

where

$k_{\text{ts}\leftarrow\text{pw,conv,sed}}$: rate coefficient from paddy water layer to the root-zone soil layer due to sedimentation [d^{-1}]; see Equation A.97

$k_{\text{ts}\leftarrow\text{pw,conv,sorp}}$: rate coefficient from paddy water layer to the root-zone soil layer due to adsorption [d^{-1}]; see Equation A.98

$k_{\text{ts}\leftarrow\text{pw,conv,diff}}$: rate coefficient from paddy water layer to the root-zone soil layer due to diffusion [d^{-1}]; see Equation A.99

with

$$k_{\text{ts}\leftarrow\text{pw,conv,sed}} = \frac{A_{\text{ts}} \cdot p_{\text{pw,ps}} \cdot fr\_m_{\text{pw,ps}}}{V_{\text{pw}}} \tag{A.97}$$

where

A_{ts} : area of the root-zone soil layer [m^2]; see Table B.1

$p_{\text{pw,ps}}$: sedimentation velocity of suspended particles from the paddy water layer to the root-zone soil layer [m·d^{-1}]; see Table B.1

$fr\_m_{\text{pw,ps}}$: fraction of mass of substance in solid phase (sorbed to particles) of the paddy water layer [kg·kg^{-1}]; see Equation A.48

V_{pw} : volume of the paddy water layer [m^3]; see Table B.1

and with

$$k_{\text{ts}\leftarrow\text{pw,conv,sorp}} = \frac{A_{\text{ts}} \cdot p_{\text{pw,ts}}}{V_{\text{pw}}} \tag{A.98}$$

where

A_{ts} : area of the root-zone soil layer [m^2]; see Table B.1

$p_{\text{pw,ts}}$: penetration velocity from the paddy water layer to the root-zone soil layer [m·d^{-1}]; see Table B.1

V_{pw} : volume of the paddy water layer [m^3]; see Table B.1

and with

$$k_{\text{ts}\leftarrow\text{pw,conv,diff}} = \frac{A_{\text{ts}} \cdot \varphi_{\text{pw/ts,paq}} \cdot (1 - fr\_m_{\text{pw,ps}})}{V_{\text{pw}}} \tag{A.99}$$

where

A_{ts} : area of the root-zone soil layer [m^2]; see Table B.1

$\varphi_{\mathrm{pw/ts,paq}}$: conductance (diffusion velocity) between aqueous phase of paddy water layer and root-zone soil layer [m·d^{-1}]; see Table B.1

$fr\_m_{\mathrm{pw,ps}}$: fraction of mass of substance in solid phase (sorbed to particles) of the paddy water layer [kg·kg^{-1}]; see Equation A.48

V_{pw} : volume of the paddy water layer [m^3]; see Table B.1

Integrating Equations A.97, A.98 and A.99 into Equation A.96 leads to Equation A.52.

Complementary equations for leaf surface diffusion

The main equation referring to the transfer from vegetation leaf surface deposit to vegetation leaf (interior) via diffusion (Equation A.55) is deduced as follows:

$$k_{\mathrm{vl}\leftarrow\mathrm{vld,diff}} = \frac{A_{\mathrm{vl}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{vld}}} \tag{A.100}$$

where

A_{vl} : area of vegetation leaf [m^2]; see Table B.3

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

V_{vld} : volume of vegetation leaf surface deposit [m^3]; see Table B.3

Eq. A.100 can be re-written with φ_{cut} deduced from Equation A.56:

$$k_{\mathrm{vl}\leftarrow\mathrm{vld,diff}} = \frac{A_{\mathrm{vl}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{vld}}} = \frac{A_{\mathrm{vl}} \cdot \Delta l_{\mathrm{cut}} \cdot k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}}}{V_{\mathrm{vld}}} = k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}} \tag{A.101}$$

where

A_{vl} : area of vegetation leaf [m^2]; see Table B.3

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

V_{vld} : volume of vegetation leaf surface deposit [m^3]; see Table B.3

Δl_{cut} : diffusion path length (thickness) of the limiting barrier of the cuticle [m]; see Table B.1

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\mathrm{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

Integrating φ_{cut} from Equation A.56 into Equation A.100 leads to Equation A.101 and, thus, finally leads to the structure of Equation A.55.

Complementary equations for fruit surface diffusion

The main equation referring to the transfer from vegetation fruit surface deposit to vegetation fruit (interior) via diffusion (Equation A.60) is deduced as follows:

$$k_{\mathrm{vf}\leftarrow\mathrm{led,diff}} = \left(\frac{1}{k_{\mathrm{lem}\leftarrow\mathrm{led}}} + \frac{1}{k_{\mathrm{vfd}\leftarrow\mathrm{lem}}} + \frac{1}{k_{\mathrm{vf}\leftarrow\mathrm{vfd}}}\right)^{-1} \tag{A.102}$$

where

$k_{\mathrm{lem}\leftarrow\mathrm{led}}$: rate coefficient for diffusion from vegetation fruit lemma surface deposit to vegetation fruit lemma interior [d^{-1}]; see Equation A.103

$k_{\mathrm{vfd}\leftarrow\mathrm{lem}}$: rate coefficient for diffusion from vegetation fruit lemma interior to vegetation fruit interior surface [d^{-1}]; see Equation A.104

$k_{\mathrm{vf}\leftarrow\mathrm{vfd}}$: rate coefficient for diffusion from vegetation fruit interior surface to vegetation fruit interior [d^{-1}]; see Equation A.105

with $k_{\mathrm{lem}\leftarrow\mathrm{led}}$, which can be deduced from the structure of Equation A.55:

$$k_{\mathrm{lem}\leftarrow\mathrm{led}} = \frac{A_{\mathrm{lem}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{led}}} = k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}} \tag{A.103}$$

where

A_{lem} : area of vegetation fruit lemma [m^2]; see Table B.3

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

V_{led} : volume of vegetation fruit lemma surface deposit [m^3]; see Table B.3

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\mathrm{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

and with

$$k_{\mathrm{vfd}\leftarrow\mathrm{lem}} = \frac{A_{\mathrm{lem}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}}{K_{\mathrm{lem/cut}} \cdot M_{\mathrm{lem}}} \tag{A.104}$$

where

A_{lem} : area of vegetation fruit lemma [m^2]; see Table B.3

$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

$K_{\mathrm{lem/cut}}$: partition coefficient between vegetation fruit lemma and cuticle (equals $K_{\mathrm{vl/cut}}$, partition coefficient between vegetation leaf and cuticle) [L·kg^{-1}]; see Equation A.66

M_{lem} : mass of vegetation fruit lemma [kg]; see Table B.3

and with $k_{\mathrm{vf}\leftarrow\mathrm{vfd}}$, which again can be deduced from the structure of Equation A.55:

$$k_{\mathrm{vf}\leftarrow\mathrm{vfd}} = \frac{A_{\mathrm{lem}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{led}}} = k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}} \tag{A.105}$$

where

A_{lem} : area of vegetation fruit lemma [m^2]; see Table B.3

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

V_{led} : volume of vegetation fruit lemma surface deposit [m^3]; see Table B.3

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\text{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

In order to fit into Equation A.102, both Equations A.103 and A.105 can be summarized as follows:

$$\frac{1}{k_{\text{lem}\leftarrow\text{led}}} + \frac{1}{k_{\text{vf}\leftarrow\text{vfd}}} = \frac{1}{k_{\text{cut}} \cdot K_{\text{cuw/w}}} + \frac{1}{k_{\text{cut}} \cdot K_{\text{cuw/w}}} = \frac{2}{k_{\text{cut}} \cdot K_{\text{cuw/w}}} \tag{A.106}$$

Furthermore, Equation A.104 can be transformed as follows in order to fit into Equation A.102:

$$\frac{1}{k_{\text{vfd}\leftarrow\text{lem}}} = \frac{K_{\text{lem/cut}} \cdot M_{\text{lem}}}{A_{\text{lem}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{cut}}} \tag{A.107}$$

Finally, integrating now Equations A.106 and A.107 into Equation A.102 leads to Equation A.60.

Complementary equations for fruit diffusion

The main equation referring to the transfer from vegetation fruit (interior) to vegetation fruit surface deposit via diffusion (Equation A.69) is deduced as follows:

$$k_{\text{led}\leftarrow\text{vf,diff}} = \left(\frac{1}{k_{\text{vfd}\leftarrow\text{vf}}} + \frac{1}{k_{\text{lem}\leftarrow\text{vfd}}} + \frac{1}{k_{\text{led}\leftarrow\text{lem}}} \right)^{-1} \tag{A.108}$$

where

$k_{\mathrm{vfd}\leftarrow\mathrm{vf}}$: rate coefficient for diffusion from vegetation fruit interior to vegetation fruit interior surface [d^{-1}]; see Equation A.109

$k_{\mathrm{lem}\leftarrow\mathrm{vfd}}$: rate coefficient for diffusion from vegetation fruit interior surface to vegetation fruit lemma interior [d^{-1}]; see Equation A.110

$k_{\mathrm{led}\leftarrow\mathrm{lem}}$: rate coefficient for diffusion from vegetation fruit lemma interior to vegetation fruit lemma surface deposit [d^{-1}]; see Equation A.111

with

$$k_{\mathrm{vfd}\leftarrow\mathrm{vf}} = \frac{A_{\mathrm{vf}} \cdot fc_{\mathrm{L\,to\,m^3}} \cdot \varphi_{\mathrm{cut}}}{K_{\mathrm{vf/cut}} \cdot M_{\mathrm{vf}}} \tag{A.109}$$

where

A_{vf} : area of vegetation fruit [m^2]; see Table B.3

$fc_{\mathrm{L\,to\,m^3}}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

$K_{\mathrm{vf/cut}}$: partition coefficient between vegetation fruit and cuticle (equals $K_{\mathrm{vl/cut}}$, partition coefficient between vegetation leaf and cuticle) [L·kg^{-1}]; see Equation A.66

M_{vf} : mass of vegetation fruit [kg]; see Table B.3

and with $k_{\mathrm{lem}\leftarrow\mathrm{vfd}}$, which can be deduced from the structure of Equation A.55:

$$k_{\mathrm{lem}\leftarrow\mathrm{vfd}} = \frac{A_{\mathrm{lem}} \cdot \varphi_{\mathrm{cut}}}{V_{\mathrm{vfd}}} = k_{\mathrm{cut}} \cdot K_{\mathrm{cuw/w}} \tag{A.110}$$

where

A_{lem} : area of vegetation fruit lemma [m^2]; see Table B.3

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

V_{vfd} : volume of vegetation fruit surface deposit [m^3]; see Table B.3

k_{cut} : solute mobility (desorption rate coefficient) of vegetation leaf/fruit surface deposit in cuticular membrane [d^{-1}]; see Equation A.57

$K_{\mathrm{cuw/w}}$: partition coefficient between cuticular wax and water [kg·m^{-3} per kg·m^{-3}]; see Equation A.58

and with

$$k_{\text{led}\leftarrow\text{lem}} = \frac{A_{\text{lem}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{cut}}}{K_{\text{lem/cut}} \cdot M_{\text{lem}}} \tag{A.111}$$

where

A_{lem} : area of vegetation fruit lemma [m^2]; see Table B.3

$fc_{\text{L to m}^3}$: conversion factor of 1,000 L per 1 m^3 [L·m^{-3}]

φ_{cut} : conductance (diffusion velocity) of cuticle in vegetation (boundary between vegetation leaf/fruit surface deposit and leaf/fruit interior) [m·d^{-1}]; see Equation A.56

$K_{\text{lem/cut}}$: partition coefficient between vegetation fruit lemma and cuticle (equals $K_{\text{vl/cut}}$, partition coefficient between vegetation leaf and cuticle) [L·kg^{-1}]; see Equation A.66

M_{lem} : mass of vegetation fruit lemma [kg]; see Table B.3

In order to fit into Equation A.108, both Equations A.109 and A.111 can be summarized as follows (under the precondition that on the one hand $K_{\text{vf/cut}} = K_{\text{lem/cut}}$ and on the other hand $A_{\text{vf}} = A_{\text{lem}}$ as demonstrated above):

$$\begin{aligned} \frac{1}{k_{\text{vfd}\leftarrow\text{vf}}} + \frac{1}{k_{\text{led}\leftarrow\text{lem}}} &= \frac{K_{\text{vf/cut}} \cdot M_{\text{vf}}}{A_{\text{vf}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{cut}}} + \frac{K_{\text{lem/cut}} \cdot M_{\text{lem}}}{A_{\text{lem}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{cut}}} \\ &= \frac{K_{\text{vf/cut}} \cdot (M_{\text{vf}} + M_{\text{lem}})}{A_{\text{vf}} \cdot fc_{\text{L to m}^3} \cdot \varphi_{\text{cut}}} \end{aligned} \tag{A.112}$$

Furthermore, Equation A.110 can be transformed as follows in order to fit into Equation A.108:

$$\frac{1}{k_{\text{lem}\leftarrow\text{vfd}}} = \frac{1}{k_{\text{cut}} \cdot K_{\text{cuw/w}}} \tag{A.113}$$

Finally, integrating now Equations A.112 and A.113 into Equation A.108 leads to Equation A.69.

B. dynamiCROP model parameters and variables

B.1. Invariant or generic dynamiCROP input data

In the following, all invariant, average or generic input parameters for the dynamiCROP model with respect to environmental or plant compartments are listed.

Table B.1.: Invariant, average or generic dynamiCROP model input data with respect to environmental and crop compartments.

Variable	Default Value	Reference(s)
A_{a}	$1\,\mathrm{m}^2$	(*default*)
$a_{\mathrm{coc/w-o/w}}$	$1.01\,\frac{\mathrm{L}}{\mathrm{kg}}$	Schwarzenbach et al. (1993, p. 274-75); Ruffino and Zanetti (2009, p. 512-13)
$a_{\mathrm{cut,w-cut/w}}$	$0.734\,\frac{\mathrm{m}}{\mathrm{d}}$	Riederer and Müller (2006, p. 296); Kerler and Schönherr (1988b, p. 10); Trapp and Mc Farlane (1995, p. 172)
$a_{\mathrm{cut/w-o/w}}$	0.97 [–]	Schreiber and Schönherr (2009, p. 149); Schönherr and Riederer (1989, p. 45); Juraske et al. (2007, p. 1104); Trapp (2004, p. 35)
$a_{\mathrm{cuw/w-cut/w}}$	0.889 [–]	Satchivi et al. (2006, p. 86)
$a_{\mathrm{oc/w-o/w}}$	$0.81\,\frac{\mathrm{L}}{\mathrm{kg}}$	EC European Commission (2003, p. III:26); Baum (1998, p. 167)
A_{pw}	$1\,\mathrm{m}^2$	(*default*)
$a_{\mathrm{sus/pg\text{-}o/a}}$	$-2.91\,\frac{\mathrm{kg/kg}}{\mathrm{kg/m^3}}$	Jolliet and Hauschild (2005, p. 4514); Harner and Bidleman (1998, p. 1501)
A_{ts}	$1\,\mathrm{m}^2$	(*default*)

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Table B.1 (continued)

Variable	Default Value	Reference(s)
$a_{\mathrm{vd-ts}}$	$0.51\ [-]$	Thomas et al. (2011, p. 1531)
$a_{\mathrm{wood/w-o/w}}$	$1.21\,\frac{\mathrm{kg/L}}{\mathrm{kg/L}}$	Trapp and Matthies (1998, p. 118, 136, 271); Trapp (2007, p. 370)
$b_{\mathrm{coc/w-o/w}}$	$-0.72\,\frac{\mathrm{L}}{\mathrm{kg}}$	Schwarzenbach et al. (1993, p. 274-75); Ruffino and Zanetti (2009, p. 512-13)
$b_{\mathrm{cut,w-cut/w}}$	$-11.26\,\frac{\mathrm{m}}{\mathrm{d}}$	Riederer and Müller (2006, p. 296); Kerler and Schönherr (1988b, p. 10); Trapp and Mc Farlane (1995, p. 172)
$b_{\mathrm{cut/w-o/w}}$	$0.057\,\frac{\mathrm{kg/m^3}}{\mathrm{kg/m^3}}$	Schreiber and Schönherr (2009, p. 149); Schönherr and Riederer (1989, p. 45); Juraske et al. (2007, p. 1104); Trapp (2004, p. 35)
$b_{\mathrm{cuw/w-cut/w}}$	$-0.576\,\frac{\mathrm{kg/m^3}}{\mathrm{kg/m^3}}$	Satchivi et al. (2006, p. 86)
$b_{\mathrm{oc/w-o/w}}$	$0.10\,\frac{\mathrm{L}}{\mathrm{kg}}$	EC European Commission (2003, p. III:26); Baum (1998, p. 167)
$b_{\mathrm{vd-ts}}$	$0.11\,\mathrm{d}$	Thomas et al. (2011, p. 1531)
$b_{\mathrm{wood/w-o/w}}$	$0.95\ [-]$	Trapp and Matthies (1998, p. 118); Trapp (2007, p. 373); Charles (2004, p. 198)
$C_{\mathrm{a,H_2O}}$	$0.01282\,\frac{\mathrm{kg}}{\mathrm{m^3}}$	Trapp (2007, p. 386)
$C_{\mathrm{a,HO^-/H^+}}$	$1.00\,\mathrm{E}{-07}\,\frac{\mathrm{mol}}{\mathrm{L}}$	US-EPA United States - Environmental Protection Agency (2008, HydroWin)
$\overline{C}_{\mathrm{a,OH}}$	$7.50\,\mathrm{E}{+11}\,\frac{\mathrm{mol}}{\mathrm{m^3}}$	US-EPA United States - Environmental Protection Agency (2008, AopWin); Seinfeld and Pandis (2006, p. 208); Calamari (1993, p. 15)
$C_{\mathrm{a,sus}}$	$60\,\frac{\mu\mathrm{g}}{\mathrm{m^3}}$	Boethling and Mackay (2000, p. 238); Harner and Bidleman (1998, p. 1497)
$C_{\mathrm{pw,coc}}$	$0.0016\,\frac{\mathrm{kg}}{\mathrm{m^3}}$	Schwarzenbach et al. (2003, p. 1069)

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Table B.1 (continued)

Variable	Default Value	Reference(s)
$C_{\mathrm{pw,sus}}$	$0.001\ \frac{\mathrm{kg}}{\mathrm{m}^3}$	Mackay (2001, p. 58-59); Schwarzenbach et al. (2003, p. 1065); Bachmann (2006, p. 139)
$D_{\mathrm{a,H_2O}}$	$2.22\ \frac{\mathrm{m}^2}{\mathrm{d}}$	Trapp and Matthies (1998, p. 138); Schwarzenbach et al. (2003, p. 802, 916-17); Schwarzenbach et al. (1993, p. 230, 238)
$D_{\mathrm{v,mem}}$	$8.64\,\mathrm{E}{-10}\ \frac{\mathrm{m}^2}{\mathrm{d}}$	Trapp (2004, p. 34)
$D_{\mathrm{vs,cew}}$	$8.64\,\mathrm{E}{-06}\ \frac{\mathrm{m}^2}{\mathrm{d}}$	Trapp (2000, p. 770)
$D_{\mathrm{w,O_2}}$	$1.73\,\mathrm{E}{-04}\ \frac{\mathrm{m}^2}{\mathrm{d}}$	Trapp (2007, p. 385); Schwarzenbach et al. (2003, p. 911, 916-17); Trapp and Matthies (1998, p. 138); Schwarzenbach et al. (1993, p. 238); Doran and Doran (1997, p. 154)
$EA_{\mathrm{w,deg}}$	$100\ \frac{\mathrm{kJ}}{\mathrm{mol{\cdot}kg}}$	Schwarzenbach et al. (2003, p. 478, 1210)
$fc_{\mathrm{a,dep,dry,pg\rightarrow u}}$	$0.013\ \frac{\mathrm{m/d}}{\mathrm{m/d}}$	Fogg and Sangster (2003, p. 39)
$fc_{\mathrm{D,vr,tis}}$	23 [–]	Schwarzenbach et al. (2003, p. 877, 880)
$fc_{\mathrm{phlo\rightarrow vf,M}}$	10 [–]	Trapp et al. (2003, p. 20); Trapp (2007, p. 374-75)
$fc_{\mathrm{ts,vd,deg}}$	$4\ \frac{\mathrm{d}}{\mathrm{d}}$	Juraske et al. (2008, p. 1754)
$fr\_C_{\mathrm{a,om}}$	$0.20\ \frac{\mathrm{kg/m^3}}{\mathrm{kg/m^3}}$	Turpin et al. (2000, p. 2983); Jolliet and Hauschild (2005, p. 4514)
$fr\_M_{\mathrm{pw,coc}}$	$0.167\ \frac{\mathrm{kg}}{\mathrm{kg}}$	Mackay (2001, p. 59); Schwarzenbach et al. (2003, p. 1065)
$fr\_M_{\mathrm{ts,oc}}$	$0.02\ \frac{\mathrm{kg}}{\mathrm{kg}}$	Jones et al. (2005, p. 662); Inao et al. (2001, p. 231); Trapp (2007, p. 375)
$fr\_M_{\mathrm{ts,run,ps}}$	$200\ \frac{\mathrm{mg}}{\mathrm{L}}$	Pennington et al. (2005, SI, Table 9); Rosenbaum et al. (2004, p. IV:49-50)
$fr\_m_{\mathrm{ts,sed,resus}}$	$0.40\ \frac{\mathrm{kg}}{\mathrm{kg}}$	Pennington et al. (2005, SI, Table 12); Rosenbaum et al. (2004, p. II:16)

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Table B.1 (continued)

Variable	Default Value	Reference(s)
$fr\_p_{\mathrm{rain,leach}}$	$0.269\,\frac{\mathrm{m/d}}{\mathrm{m/d}}$	Rosenbaum et al. (2004, p. IV:48); Trapp and Matthies (1998, p. 90)
$fr\_p_{\mathrm{rain,run}}$	$0.0673\,\frac{\mathrm{m/d}}{\mathrm{m/d}}$	Rosenbaum et al. (2004, p. IV:48); Trapp and Matthies (1998, p. 90)
$fr\_V_{\mathrm{a,rain,paq}}$	$5.55\,\mathrm{E}{-08}\,\frac{\mathrm{m^3}}{\mathrm{m^3}}$	Jolliet and Hauschild (2005, p. 4515)
$fr\_V_{\mathrm{ts,paq}}$	$0.30\,\frac{\mathrm{L}}{\mathrm{L}}$	Trapp and Matthies (1998, p. 255-56); Bachmann (2006, p. 94); Rosenbaum et al. (2004, p. IV:43); Pennington et al. (2005, SI, Table 9)
$fr\_V_{\mathrm{ts,pg}}$	$0.20\,\frac{\mathrm{L}}{\mathrm{L}}$	Trapp and Matthies (1998, p. 255-56); Bachmann (2006, p. 94); Rosenbaum et al. (2004, p. IV:43); Pennington et al. (2005, SI, Table 9)
$fr\_V_{\mathrm{ts,ps}}$	$0.50\,\frac{\mathrm{L}}{\mathrm{L}}$	Rosenbaum et al. (2004, p. V:9); Rosenbaum et al. (2004, p. IV:43); Pennington et al. (2005, SI, Table 9)
h_{a}	$1000\,\mathrm{m}$	Seinfeld and Pandis (2006, p. 7)
h_{pw}	$0.04\,\mathrm{m}$	Inao (2003, p. 322); Inao et al. (2008, p. 14-15); Capri and Karpouzas (2008, p. 2-3)
h_{ts}	$0.30\,\mathrm{m}$	Rosenbaum et al. (2004, p. IV:7-9)
$k_{\mathrm{a,deg,H_2O}}$	$178.76\,\frac{\mathrm{L}}{\mathrm{mol \cdot d}}$	US-EPA United States - Environmental Protection Agency (2008, HydroWin)
$k_{\mathrm{a},h\nu}$	$\sim 0\,\frac{1}{\mathrm{d}}$	Matthies et al. (2009, SI, p. 1); Calamari (1993, p. 14)
$k^*{}_{\mathrm{a,OH}}$	$4.52\,\mathrm{E}{-13}\,\frac{\mathrm{m^3}}{\mathrm{mol \cdot d}}$	US-EPA United States - Environmental Protection Agency (2008, AopWin)
$k_{\mathrm{cut,V_0}}$	$-1.58\,\frac{1}{\mathrm{d}}$	Schönherr and Schreiber (2004, p. 409); Buchholz et al. (1998, p. 324)

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Table B.1 (continued)

Variable	Default Value	Reference(s)
Δl_{a}	0.10 cm	Schwarzenbach et al. (1993, p. 242)
Δl_{cut}	1 µm	Baur et al. (1999, p. 834); Charles (2004, p. 82)
Δl_{pw}	0.20 mm	Schwarzenbach et al. (1993, p. 242)
Δl_{ts}	5 cm	Brandes et al. (1996, p. 78); Rosenbaum et al. (2004, p. IV:53-54)
M_{ts}	480 kg	Perry and Green (2008, p. 1-2, 1-5)
$MW_{\mathrm{H_2O}}$	$18.01\,\frac{\mathrm{g}}{\mathrm{mol}}$	Lyman et al. (1990, p. 16)
$MW_{\mathrm{O_2}}$	$31.99\,\frac{\mathrm{g}}{\mathrm{mol}}$	Lyman et al. (1990, p. 16)
$p_{\mathrm{a,dep,dry,sus}}$	$129.60\,\frac{\mathrm{m}}{\mathrm{d}}$	Seinfeld and Pandis (2006, p. 903, 905, 909)
$p_{\mathrm{pw,fb}}$	$0.0077\,\frac{\mathrm{m}^3}{\mathrm{m}^2\cdot\mathrm{d}}$	Inao and Kitamura (1999, p. 43)
$p_{\mathrm{pw,ps}}$	$0.684\,\frac{\mathrm{m}^3}{\mathrm{m}^2\cdot\mathrm{d}}$	Schwarzenbach et al. (2003, p. 1065); Rosenbaum et al. (2004, p. II:9)
$p_{\mathrm{pw,ts}}$	$0.0095\,\frac{\mathrm{m}^3}{\mathrm{m}^2\cdot\mathrm{d}}$	Inao and Kitamura (1999, p. 43)
p_{rain}	$767\,\frac{\mathrm{L}}{\mathrm{m}^2\cdot\mathrm{year}}$	Jolliet and Hauschild (2005, p. 4515); Trapp and Matthies (1998, p. 90); JRC Joint Research Center (2008, p. III:284)
$p_{\mathrm{rain,wet}}$	$31.20\,\frac{\mathrm{m}}{\mathrm{d}}$	Rowe (2001, p. 849-50); Jolliet and Hauschild (2005, p. 4515)
$\varphi_{\mathrm{pw/ts,paq}}$	$0.0024\,\frac{\mathrm{m}}{\mathrm{d}}$	Pennington et al. (2005, SI, Table 11); Rosenbaum et al. (2004, p. II:8)
$\varphi_{\mathrm{ts,pw,paq}}$	$0.0024\,\frac{\mathrm{m}}{\mathrm{d}}$	Pennington et al. (2005, SI, Table 11); Rosenbaum et al. (2004, p. II:8)
R	$8.314472\,\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}$	Mohr et al. (2008, p. 1238); Perry and Green (2008, p. 1-17)
$RE_{\mathrm{a,dep,wet,wash}}$	$2.00\,\mathrm{E}{+}05\,\frac{\mathrm{kg/m}^3}{\mathrm{kg/m}^3}$	Boethling and Mackay (2000, p. 337); Jolliet and Hauschild (2005, p. 4515)

(continued on next page)

Table B.1 (continued)

Variable	Default Value	Reference(s)
$RE_{\mathrm{a,wet,OH}}$	$0.40\,\frac{\mathrm{kg/m^3}}{\mathrm{kg/m^3}}$	Jolliet and Hauschild (2005, p. 4517, SI, p. 2)
rh	$0.50\,\frac{\mathrm{Pa}}{\mathrm{Pa}}$	Hens (2007, p. 147); Satchivi et al. (2006, p. 86)
ρ_{o}	$0.823\,\frac{\mathrm{kg}}{\mathrm{L}}$	Lide and Milne (1995, p. 1574-76)
$\rho_{\mathrm{ts,ps}}$	$2.60\,\frac{\mathrm{kg}}{\mathrm{L}}$	Bachmann (2006, p. 94-95); Rosenbaum et al. (2004, p. IV:43)
ρ_{w}	$0.999972\,\frac{\mathrm{kg}}{\mathrm{L}}$	Dorsey (1968); Lyman et al. (1990, p. 19-2); Baum (1998, p. 35)
SL_{cut}	$-0.011\,\frac{\mathrm{mol}}{\mathrm{g}}$	Schönherr and Schreiber (2004, p. 409); Buchholz et al. (1998, p. 324)
T_{pw}	$303.15\,\mathrm{K}$	Oue and Kamii (2002, p. 64-66); Kuwagata et al. (2008, p. 1758)
$t_{\mathrm{rain,int}}$	$3.33\,\mathrm{d}$	Jolliet and Hauschild (2005, p. 4516-18)
T_{w}	$285.15\,\mathrm{K}$	JRC Joint Research Center (2008, p. III-260)
u_{10}	$2\,\frac{\mathrm{m}}{\mathrm{s}}$	Schwarzenbach et al. (1993, p. 235)
V_{a}	$1000\,\mathrm{m^3}$	Perry and Green (2008, p. 3-7)
V_{pw}	$0.04\,\mathrm{m^3}$	Perry and Green (2008, p. 3-7)
V_{ts}	$0.30\,\mathrm{m^3}$	Perry and Green (2008, p. 3-7)

B.2. Variable dynamiCROP input data

In the following, input data for the dynamiCROP model are listed that are either substance- or crop-specific, i. e. varying between substances or crops, respectively.

Table B.2.: Substance-specific physicochemical properties required by the dynamiCROP model. Numerical values for a wide range of pesticides are given e. g. in AERU Agriculture and Environment Research Unit (2011).

Variable	Unit	Name
H	$\frac{\mathrm{Pa \cdot m^3}}{\mathrm{mol}}$	Henry's law constant
$k_{\mathrm{a,deg}}$	$\frac{1}{\mathrm{d}}$	degradation rate coefficient in air
$k_{\mathrm{ts,deg}}$	$\frac{1}{\mathrm{d}}$	degradation rate coefficient in soil
$k_{\mathrm{w,deg}}$	$\frac{1}{\mathrm{d}}$	degradation rate coefficient in water
$K_{\mathrm{a/w}}$	$\frac{\mathrm{kg/m^3}}{\mathrm{kg/m^3}}$	partition coefficient between air and water
$K_{\mathrm{o/w}}$	$\frac{\mathrm{kg/m^3}}{\mathrm{kg/m^3}}$	partition coefficient between n–octanol and water
$K_{\mathrm{oc/w}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	partition coefficient between soil organic carbon and water
MW	$\frac{\mathrm{g}}{\mathrm{mol}}$	molecular weight
P_{sat}	Pa	saturation vapor pressure
S_{w}	$\frac{\mathrm{g}}{\mathrm{m^3}}$	water solubility

Table B.3.: Crop-specific characteristics required by the dynamiCROP model. Numerical values for six crop types are given in Table 2.7.

Variable	Unit	Name
A_{lem}	$\mathrm{m^2}$	area of vegetation fruit lemma
A_{vf}	$\mathrm{m^2}$	area of vegetation fruit
A_{vl}	$\mathrm{m^2}$	area of vegetation leaf
A_{vr}	$\mathrm{m^2}$	area of vegetation thick root
c_{cap}	$\frac{\mathrm{kg/m^2}}{\mathrm{kg/m^2}}$	substance capture coefficient
$\Delta l_{\mathrm{vr,tis}}$	m	diffusion coefficient in vegetation thick root tissue
ET_{v}	$\frac{\mathrm{L}}{\mathrm{kg}}$	transpiration coefficient of vegetation
FAI	$\frac{\mathrm{m^2}}{\mathrm{m^2}}$	fruit area index

(continued on next page)

Table B.3 (continued)

Variable	Unit	Name
$fr\_V_{\mathrm{comp,paq}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	fraction of volumetric water in vegetation compartment
$fr\_V_{\mathrm{comp,pg}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	fraction of volumetric gas in vegetation compartment
$fr\_V_{\mathrm{v,paq}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	fraction of volumetric water in vegetation compartment
$fr\_V_{\mathrm{v,pli}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	fraction of volumetric lipid in vegetation compartment
$fr\_V_{\mathrm{vs,paq}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	fraction of volumetric water in vegetation stem
$fr\_V_{\mathrm{vs,pg}}$	$\frac{\mathrm{L}}{\mathrm{kg}}$	fraction of volumetric gas in vegetation stem
h_{vs}	m	height of vegetation stem
LAI	$\frac{\mathrm{m}^2}{\mathrm{m}^2}$	leaf area index
M_{lem}	kg	mass of vegetation fruit lemma
M_{v}	kg	mass of vegetation compartment
M_{vf}	kg	mass of vegetation fruit
M_{vl}	kg	mass of vegetation leaf
M_{vr}	kg	mass of vegetation thick root
M_{vs}	kg	mass of vegetation stem
r_{vr}	m	mean radius of vegetation thick root
ρ_{v}	$\frac{\mathrm{kg}}{\mathrm{L}}$	density of vegetation compartment
ρ_{vr}	$\frac{\mathrm{kg}}{\mathrm{L}}$	density of vegetation thick root
$\rho_{\mathrm{vs,dry}}$	$\frac{\mathrm{kg}}{\mathrm{L}}$	dry density of vegetation stem
$\rho_{\mathrm{vs,wet}}$	$\frac{\mathrm{kg}}{\mathrm{L}}$	wet density of vegetation stem
V_{led}	m^3	volume of vegetation fruit lemma
V_{vfd}	m^3	volume of vegetation fruit surface deposit
V_{vld}	m^3	volume of vegetation leaf surface deposit
V_{vs}	m^3	volume of vegetation stem

B.3. Acronyms and indices referring to compartments, phases and processes

In the following, acronyms and indices referring to compartments, compartment phases and environmental fate processes as considered in the present work are listed.

Table B.4.: Compartments acronyms employed throughout this document.

Acronym	Compartment
a	**a**ir or atmospheric ground layer
ws	**w**ater **s**ediment
ob	**o**cean/coastal water **b**ody
fb	**f**reshwater **b**ody
gw	**g**round**w**ater
pw	**p**addy **w**ater
n	**n**atural land
c	**c**ultivated or agricultural land
ts	**t**op**s**oil layer or root-zone soil layer
us	s**u**b**s**oil layer
v	**v**egetation or plant
vd	**v**egetation/plant surface **d**eposit
vl	**v**egetation/plant **l**eaf
vld	**v**egetation/plant **l**eaf surface **d**eposit
vf	**v**egetation/plant **f**ruit
vfd	**v**egetation/plant **f**ruit surface **d**eposit
vs	**v**egetation/plant **s**tem/trunk (including branches)
vr	**v**egetation/plant thick **r**oot
comp	generic/not specified **comp**artment

Table B.5.: Compartment phases or components acronyms employed throughout this document.

Acronym	Phase/Component
cew	**ce**ll **w**all (component of vegetation compartments)
coc	**c**olloidal **o**rganic **c**arbon (component in water)
cut	**cut**icle (component of vegetation leaf/fruit surface deposit)

(continued on next page)

Table B.5 (continued)

Acronym	Phase/Component
cuw	**cu**ticle **w**ax (component of vegetation leaf/fruit surface deposit)
led	**le**mma **d**eposit (vegetation fruit/fruit surface deposit interface)
lem	**lem**ma (vegetation fruit/fruit surface deposit interface)
mem	bio- or plasma-**mem**brane (component of vegetation compartments)
o	*n*–**oct**anol (reference compartment for fatty tissues)
oc	**o**rganic **c**arbon (fraction of organic matter) of compartment
om	**o**rganic **m**atter of compartment
pg	**p**hase of compartment which is **g**as
paq	**p**hase of compartment which is **aq**ueous
pli	**p**hase of compartment which is **li**pid
ps	**p**hase of compartment which is **s**olid
sto	**sto**mata (component of vegetation leaf)
sus	**sus**pended particles (component of air and water)
tis	**tis**sue (component of vegetation compartments)

Table B.6.: Process acronyms employed throughout this document.

Acronym	Process
adv	**adv**ective process
acc	**acc**umulation process
app	**app**lication (of substance) related process
conv	**conv**ective process**
deg	**deg**radation process
dep	**dep**osition process
diff	**diff**usive process
dry	**dry** (deposition) process
emi	**emi**ssion process
harv	**harv**est (of vegetation compartments) related process
int	**intermit**tent or **int**erval process
leach	**leach**ing process
loss	**loss** process (sum of dissolution*, degradation, etc.)
$h\nu$	light related process***
OH	process related to the highly reactive hydroxyl radical, OH·

(continued on next page)

Table B.6 (continued)

Acronym	Process
phlo	**phlo**em related (advective) process
rain	**rain** related (advective) process
resus	**resus**pension related (diffusive) process
run	**run** off related (advective) process
sed	**sed**imentation related (advective) process
sorp	ad- or de-**sorp**tion related (advective) process
volat	**volat**ilization related (diffusive) process
wash	**wash**out or **wash**off related (advective) process
wet	**wet** (deposition) process
xyl	**xyl**em related (advective) process

* Dissolution is defined as a kinetic process, i. e. as mixing of two phases with the formation of one new homogeneous phase, referred to as solution (IUPAC, 2009).

** Convection refers to the sum of advective and diffusive transfer processes (Incropera et al., 2007).

*** Light refers to the relationship $E = h\nu$, where E refers to the energy of a photon [J], h denotes Planck's constant [J·s] and ν is the frequency of the electromagnetic wave associated to the photon [s^{-1}](Mohr et al., 2008, p. 1200).

C. Case study background information

Table C.1.: ISO 3166-1 alpha-2 codes according to ISO International Organization for Standardization (2011) and official English names for European countries considered in the case study in Chapter 4.

ISO 3166-1	country	ISO 3166-1	country
AT	Austria	HU	Hungary
BE	Belgium (including Luxembourg, LU)	IE	Ireland
CY	Cyprus	IT	Italy
CZ	Czech Republic	LT	Lithuania
DE	Germany	LV	Latvia
DK	Denmark	NL	The Netherlands
EE	Estonia	PL	Poland
ES	Spain	PT	Portugal
FI	Finland	SE	Sweden
FR	France	SI	Slovenia
GB	United Kingdom	SK	Slovakia
GR	Greece		

Table C.2.: Substance name, CAS number, target class TC (F: fungicide, H: herbicide, I: insecticide, N: nematicide, A: acaricide, PGR: plant growth regulator), MW (g/mol), log Kaw (–), log Kow (–), log Koc (L/kg) and degradation half-lives t (d) in air, soil and plant for all substances considered in the present case study.

substance	CAS-RN	TC	MW	log Kaw	log Kow	log Koc	t_{air}	t_{soil}	t_{plant}
azoxystrobin	131860-33-8	F	403.4	−11.57	2.50	2.63	0.07	45	6.23
boscalid	188425-85-6	F	343.21	−7.67	2.96	2.91	1.10	200	4.80
captan	133-06-2	F	300.61	−6.55	2.50	1.99	0.04	8	2.50
carbendazim	10605-21-7	F	191.21	−6.05	1.48	2.35	0.05	22	1.56
chlorothalonil	1897-45-6	F	265.91	−4.87	2.94	2.93	1729	19	1.45
cymoxanil	57966-95-7	F	198.18	−11.19	0.67	1.64	1.78	25.3	1.67
cyprodinil	121552-61-2	F	225.29	−5.61	4.00	3.23	0.05	37	2.03
difenoconazole	119446-68-3	F	406.26	−9.14	4.36	3.54	0.50	46.8	2.29
dimethomorph	110488-70-5	F	387.86	−8.08	2.68	2.54	0.03	44	2.22
dinocap	131-72-6	F	364.18	−6.90	6.50	3.74	0.31	5.2	2.99
dithianon	3347-22-6	F	296.32	−9.00	3.20	3.56	0.48	35	1.97
dodine	2439-10-3	F	287.44	−9.16	1.25	6.63	0.10	13.25	1.20
famoxadone	131807-57-3	F	374.39	−6.05	4.80	3.99	0.19	20	1.48
fenarimol	60168-88-9	F	331.2	−6.54	3.69	3.09	2.72	74	2.89
fenhexamid	126833-17-8	F	302.2	−8.24	3.51	2.68	0.31	25	1.66
fenpropidin	67306-00-7	F	273.46	−5.17	2.60	3.58	0.09	109	3.52
fenpropimorph	67564-91-4	F	303.48	−4.26	4.50	3.38	0.08	19.6	1.47
fluazinam	79622-59-6	F	465.14	−2.53	4.03	4.22	163	16.4	1.34
flusilazole	85509-19-9	F	315.39	−4.46	3.87	3.22	1.74	94	3.27
folpet	133-07-3	F	296.56	−3.80	3.02	2.48	0.68	4.7	2.84
fosetyl	15845-66-6	F	110.05	−6.26	−0.70	4.38	0.55	30	1.83
hymexazol	10004-44-1	F	99.15	−6.94	0.30	0.34	0.05	30	1.83
iprodione	36734-19-7	F	330.17	−6.55	3.10	2.57	0.58	34	1.95
kresoxim-methyl	143390-89-0	F	313.35	−6.83	3.40	2.85	0.28	16	1.32
mancozeb	8018-01-7	F	271.3	−9.75	1.30	3.00	0.05	7	3.48
metalaxyl-m	70630-17-0	F	279.33	−7.84	1.71	2.82	0.40	54	2.46
metiram	9006-42-2	F	1088.6	−5.66	1.76	5.70	0.03	7	3.48
myclobutanil	88671-89-0	F	288.78	−6.76	2.89	2.71	1.52	35	1.97
oxadixyl	77732-09-3	F	278.3	−9.95	0.65	1.56	0.30	75	2.91
penconazole	66246-88-6	F	284.18	−6.47	3.72	3.34	1.33	25	1.66
prochloraz	67747-09-5	F	376.7	−6.17	3.53	3.35	0.14	140.2	4.01
propamocarb	24579-73-5	F	188.3	−7.20	0.84	0.78	0.11	35.4	1.99
propiconazole	60207-90-1	F	342.22	−6.77	3.72	3.04	0.46	29	1.79
propineb	12071-83-9	F	289.8	−5.72	−0.26	−0.11	0.16	3	2.26
pyrimethanil	53112-28-0	F	199.11	−6.13	2.84	2.48	0.05	22	1.56
tebuconazole	107534-96-3	F	307.82	−8.29	3.70	2.89	0.93	46	2.27
thiram	137-26-8	F	240.43	−6.48	1.73	3.98	0.03	15	1.28
tolylfluanid	731-27-1	F	347.27	−4.89	3.90	3.26	0.60	6	3.21

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Table C.2 (continued)

substance	CAS-RN	TC	MW	log Kaw	log Kow	log Koc	t_{air}	t_{soil}	t_{plant}
trifloxystrobin	141517-21-7	F	408.37	−6.04	4.50	3.38	1.75	7	3.48
vinclozolin	50471-44-8	F	286.11	−6.26	3.02	2.48	0.32	40.5	2.13
ziram	137-30-4	F	305.84	−5.64	1.65	1.44	0.08	30	1.83
2,4-D	94-75-7	H	221.04	−8.85	−0.83	1.75	1.61	10	4.17
acetochlor	34256-82-1	H	269.77	−8.06	4.14	2.19	0.22	10.6	1.07
aclonifen	74070-46-5	H	264.66	−6.19	4.37	3.85	0.84	37.9	2.06
alachlor	15972-60-8	H	269.77	−5.88	3.09	2.09	0.24	35	1.97
amitrole	61-82-5	H	84.08	−11.39	−0.97	2.05	1.94	5	2.93
atrazine	1912-24-9	H	215.68	−6.92	2.70	2.00	0.39	66	2.73
bentazone	25057-89-0	H	240.3	−12.70	−0.46	1.71	0.17	45	2.24
bromoxynil	1689-84-5	H	276.9	−6.84	1.04	2.24	51	1	1.29
chlorbufam	1967-16-4	H	223.7	−6.45	3.02	2.21	0.23	56	2.51
chloridazon	1698-60-8	H	221.6	−8.70	1.19	2.30	0.27	43.1	2.20
chlorotoluron	15545-48-9	H	212.68	−7.68	2.50	2.31	0.27	59	2.58
clomazone	81777-89-1	H	239.7	−5.78	2.54	2.46	0.49	42.5	2.18
clopyralid	1702-17-6	H	192	−7.84	−2.63	0.70	20	34	1.95
cycloxydim	101205-02-1	H	325.46	−4.80	2.29	1.77	0.08	0.58	0.98
desmedipham	13684-56-5	H	300.31	−8.27	3.39	4.02	0.12	17	1.37
dicamba	1918-00-9	H	221.04	−7.06	−1.88	1.08	3.58	4.2	2.68
dichlorprop	120-36-5	H	235.06	−6.52	2.29	2.23	0.94	14	1.24
dichlorprop-p	15165-67-0	H	235.06	−11.86	−0.56	1.64	0.94	14	1.24
dimethachlor	50563-36-5	H	255.74	−7.53	2.17	1.84	0.26	6.5	3.35
dimethenamid	87674-68-8	H	275.79	−6.72	2.20	2.03	0.20	13	1.19
dimethenamid-p	163515-14-8	H	275.8	−6.72	1.89	2.14	0.20	23	1.59
diquat	2764-72-9	H	184.24	−12.98	−4.60	2.58	2.98	40.2	2.12
EPTC	759-94-4	H	189.3	−3.02	3.20	2.48	0.34	18	1.41
ethofumesate	26225-79-6	H	286.34	−7.05	2.70	2.17	0.20	97	3.32
fluazifop-p-butyl	79241-46-6	H	383.36	−5.59	4.50	3.77	0.36	1	1.29
glufosinate	77182-82-2	H	198.2	−11.23	−4.01	2.88	0.35	7.4	3.58
glyphosate	1071-83-6	H	168.07	−18.18	−3.20	4.34	0.14	12	1.14
haloxyfop	69806-34-4	H	361.7	−6.91	3.38	1.88	0.41	55	2.49
imazamethabenz	100728-84-5	H	274.32	−11.61	3.30	1.96	0.65	75	2.91
isoproturon	34123-59-6	H	206.28	−8.42	2.50	2.09	0.89	12	1.14
isoxaflutole	141112-29-0	H	359.32	−7.62	2.32	2.05	1.83	2.3	1.97
lenacil	2164-08-1	H	234.29	−8.37	1.69	2.11	0.09	14.4	1.26
linuron	330-55-2	H	249.09	−5.60	3.00	2.79	1.03	87	3.14
MCPA	94-74-6	H	200.62	−7.96	−0.81	1.87	0.85	15	1.28
MCPB	94-81-5	H	228.67	−6.90	1.32	2.03	0.53	6.8	3.42
mecoprop	93-65-2	H	214.65	−8.85	−0.19	1.49	0.61	8.2	3.77
mecoprop-p	16484-77-8	H	214.65	−10.38	0.02	1.49	0.61	6.8	3.42
mesotrione	104206-82-8	H	339.32	−8.30	0.11	1.90	1.50	17	1.37
metamitron	41394-05-2	H	202.21	−10.34	0.85	1.91	0.55	19	1.45
metazachlor	67129-08-2	H	277.75	−6.74	2.49	2.13	0.18	15.6	1.31
metolachlor	51218-45-2	H	283.8	−6.38	3.40	2.30	0.19	15	1.28

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Table C.2 (continued)

substance	CAS-RN	TC	MW	log Kaw	log Kow	log Koc	t_{air}	t_{soil}	t_{plant}
metribuzin	21087-64-9	H	214.29	−8.83	1.65	1.58	0.59	11.5	1.12
molinate	2212-67-1	H	187.3	−4.46	2.86	2.28	0.35	12.5	1.17
napropamide	15299-99-7	H	271.36	−7.47	3.30	2.95	0.05	70	2.81
oxyfluorfen	42874-03-3	H	361.7	−4.48	4.86	4.09	0.93	186	4.63
paraquat	4685-14-7	H	186.25	−11.91	−4.50	6.00	0.50	41	2.14
pendimethalin	40487-42-1	H	281.31	−2.82	5.20	4.20	0.35	90	3.20
phenmedipham	13684-63-4	H	300.31	−10.85	3.59	2.95	0.07	37	2.03
prometryn	7287-19-6	H	241.36	−6.56	3.34	2.60	0.28	41	2.14
propachlor	1918-16-7	H	211.69	−5.37	1.60	1.90	0.51	5	2.93
propanil	709-98-8	H	218.08	−8.10	2.29	2.60	2.83	27.12	1.73
propyzamide	23950-58-5	H	256.13	−6.51	3.30	2.92	0.80	47	2.29
prosulfocarb	52888-80-9	H	251.39	−4.27	4.48	3.23	0.33	9.8	4.13
pyridate	55512-33-9	H	378.92	−7.30	0.50	4.76	0.64	0.6	0.99
quinmerac	90717-03-6	H	221.6	−7.82	−1.41	1.93	2.93	17.4	1.38
simazine	122-34-9	H	201.66	−7.89	2.30	2.11	0.97	60	2.60
s-metolachlor	87392-12-9	H	283.79	−6.05	3.05	2.35	0.19	14.5	1.26
sulcotrione	99105-77-8	H	328.77	−8.36	−1.70	1.56	1.43	25.3	1.67
terbuthylazine	5915-41-3	H	229.71	−5.79	3.40	2.34	0.97	75.1	2.91
terbutryn	886-50-0	H	241.36	−6.24	3.65	3.30	1.00	74	2.89
tralkoxydim	87820-88-0	H	329.43	−8.09	2.10	2.08	0.07	2.6	2.10
trifluralin	1582-09-8	H	335.28	−1.40	5.27	3.94	0.45	181	4.56
triflusulfuron	126535-15-7	H	492.43	−7.62	0.96	1.60	2.76	360	6.48
aldicarb	116-06-3	I	190.26	−6.66	1.15	1.48	1.16	2.4	2.01
beta-cyfluthrin	68359-37-5	I	434.29	−5.92	5.90	4.81	0.84	27.8	1.76
carbofuran	1563-66-2	I	221.26	−7.68	1.80	1.37	0.41	14	1.24
chlorfenvinphos	470-90-6	I	359.6	−7.66	3.80	2.83	0.19	37	2.03
chlorpyrifos	2921-88-2	I	350.89	−3.55	4.70	3.91	0.12	18	1.41
chlorpyrifos-methyl	5598-13-0	I	322.53	−3.72	4.00	3.67	0.18	2.5	2.06
cypermethrin	52315-07-8	I	416.3	−5.43	5.30	4.93	0.50	31	1.86
dazomet	533-74-4	I	162.27	−7.92	0.63	1.00	0.04	7	3.48
diafenthiuron	80060-09-9	I	384.58	−5.28	5.76	4.64	0.09	0.5	0.90
diazinon	333-41-5	I	304.35	−5.34	3.69	2.81	0.11	32.1	1.89
dimethoate	60-51-5	I	229.26	−7.39	0.70	1.48	0.14	2.6	2.10
ethoprophos	13194-48-4	I	242.3	−5.21	2.99	2.04	0.15	17	1.37
fenthion	55-38-9	I	278.33	−5.00	4.84	3.18	0.15	34	1.95
imidacloprid	138261-41-3	I	255.66	−10.39	0.57	2.35	0.07	48	2.50
lambda-cyhalothrin	91465-08-6	I	449.85	−5.13	6.90	5.20	0.32	25	1.66
methidathion	950-37-8	I	302.3	−7.12	2.57	2.60	0.07	10	1.04
methiocarb	2032-65-7	I	225.31	−6.97	3.18	2.82	0.79	1.4	1.53
methomyl	16752-77-5	I	162.21	−8.12	1.24	1.40	1.61	6.97	3.47
oxamyl	23135-22-0	I	219.26	−8.01	−0.44	1.23	0.47	6.6	3.37
parathion-methyl	298-00-0	I	263.21	−5.64	3.00	2.38	0.18	10	4.17

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Table C.2 (continued)

substance	CAS-RN	TC	MW	log Kaw	log Kow	log Koc	t_{air}	t_{soil}	t_{plant}
pirimiphos-methyl	29232-93-7	I	305.33	−3.42	3.90	3.04	0.07	39	2.09
spinosad	168316-95-8	I	739	−10.59	4.00	4.54	0.03	14	1.24
terbufos	13071-79-9	I	288.4	−2.96	4.51	2.70	0.04	5	2.93
thiamethoxam	153719-23-4	I	291.71	−12.71	−0.13	1.85	0.06	39	2.09
1,3-dichloropropene	542-75-6	N	110.97	−0.82	2.10	1.53	0.73	36.8	2.03
tebufenpyrad	119168-77-3	A	333.8	−6.25	4.93	3.78	0.20	14	1.24
chlormequat	7003-89-6	PGR	122.62	−10.07	−3.44	1.34	1.45	30	1.83
choline chloride	67-48-1	PGR	139.62	−14.24	−3.77	0.16	0.57	7	3.48
trinexapac-ethyl	95266-40-3	PGR	252.26	−6.70	−0.29	2.45	0.11	0.33	0.73

Table C.3.: NOEL (mg/$\text{kg}_{\text{applied}}$/d), receptor, exposure duration time, reference for NOEL, and cancer and non-cancer dose-response slope factors β (incidence risk/$\text{kg}_{\text{intake}}$) for all pesticides considered in the case study.

substance	NOEL	receptor	exposure	reference	$\beta_{\text{non-cancer}}$	β_{cancer}
1,3-dichloropropene	5	rat	subacute	(*2*)	1.3E-01	4.1E-02
2,4-D	1	rat	chronic	(*1*)	1.3E-01	0
acetochlor	10	rat	subacute	(*2*)	6.4E-02	n/a
aclonifen	50	rat	subacute	(*2*)	1.3E-02	n/a
alachlor	10	rat	subacute	(*2*)	6.4E-02	n/a
aldicarb	0.01	human	subacute	(*1*)	1.6E+01	0
amitrole	0.025	rat	chronic	(*3*)	5.1E+00	1.2E-01
atrazine	3.5	rat	chronic	(*1*)	3.6E-02	3.1E-02
azoxystrobin	10	dog	subchronic	(*3*)	9.1E-03	n/a
bentazone	25	rat	subacute	(*2*)	2.5E-02	n/a
beta-cyfluthrin	2.5	rat	chronic	(*1*)	5.1E-02	n/a
boscalid	5	rat	subacute	(*2*)	1.3E-01	n/a
bromoxynil	16.6	rat	chronic	(*2*)	7.7E-03	n/a
captan	12.5	rat	chronic	(*1*)	1.0E-02	9.7E-04
carbendazim	10	rat	subacute	(*2*)	6.4E-02	n/a
carbofuran	0.5	dog	chronic	(*1*)	9.1E-02	0
chlorbufam	2380	rat	subacute	(*2*)	2.7E-04	n/a
chlorfenvinphos	0.05	rat	chronic	(*3*)	2.5E+00	n/a
chloridazon	16	rat	chronic	(*2*)	7.9E-03	n/a
chlormequat	50	rat	chronic	(*2*)	2.5E-03	n/a
chlorothalonil	1.5	dog	chronic	(*1*)	3.0E-02	5.0E-04
chlorotoluron	5	rat	chronic	(*2*)	2.5E-02	n/a
chlorpyrifos	1.5	dog	chronic	(*1*)	3.0E-02	0
chlorpyrifos-methyl	0.1	rat	chronic	(*2*)	1.3E+00	n/a
choline chloride	3400	rat	subacute	(*2*)	1.9E-04	0
clomazone	4.3	rat	chronic	(*2*)	3.0E-02	n/a

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Table C.3 (continued)

substance	NOEL	receptor	exposure	reference	$\beta_{\text{non-cancer}}$	β_{cancer}
clopyralid	15	rat	chronic	(*2*)	8.5E-03	n/a
cycloxydim	10	dog	subacute	(*2*)	2.3E-02	n/a
cymoxanil	47.6	rat	subacute	(*2*)	1.3E-02	n/a
cypermethrin	1	dog	chronic	(*1*)	4.6E-02	n/a
cyprodinil	3	rat	chronic	(*2*)	4.2E-02	n/a
dazomet	0.5	rat	chronic	(*3*)	2.5E-01	n/a
desmedipham	3	rat	subacute	(*2*)	2.1E-01	n/a
diafenthiuron	0.3	dog	chronic	(*3*)	1.5E-01	n/a
diazinon	5	rat	subacute	(*2*)	1.3E-01	0
dicamba	110	rat	chronic	(*2*)	1.2E-03	n/a
dichlorprop	152	rat	subacute	(*2*)	4.2E-03	0
dichlorprop-p	152	rat	subacute	(*2*)	4.2E-03	0
difenoconazole	20	rat	subacute	(*2*)	3.2E-02	n/a
dimethachlor	12	rat	chronic	(*2*)	1.1E-02	n/a
dimethenamid	33.3	rat	subacute	(*2*)	1.9E-02	n/a
dimethenamid-p	33.3	rat	subacute	(*2*)	1.9E-02	n/a
dimethoate	0.18	dog	chronic	(*2*)	2.5E-01	0
dimethomorph	15	rat	subacute	(*2*)	4.2E-02	n/a
dinocap	18.2	rat	subacute	(*2*)	3.5E-02	n/a
diquat	0.22	rat	chronic	(*1*)	5.8E-01	n/a
dithianon	0.66	rat	chronic	(*3*)	1.9E-01	n/a
dodine	1.25	dog	chronic	(*1*)	3.7E-02	0
EPTC	2.5	rat	chronic	(*1*)	5.1E-02	n/a
ethofumesate	30	rat	chronic	(*3*)	4.2E-03	n/a
ethoprophos	0.1	rat	subacute	(*2*)	6.4E+00	n/a
famoxadone	3.3	rat	subacute	(*2*)	1.9E-01	n/a
fenarimol	1.1	rat	chronic	(*2*)	1.2E-01	n/a
fenhexamid	17.4	dog	chronic	(*3*)	2.6E-03	n/a
fenpropidin	20	rat	subacute	(*2*)	3.2E-02	n/a
fenpropimorph	0.3	rat	subacute	(*2*)	2.1E+00	n/a
fenthion	0.02	human	subacute	(*3*)	7.8E+00	0
fluazifop-p-butyl	0.3	rat	chronic	(*3*)	4.2E-01	n/a
fluazinam	3.48	dog	subacute	(*2*)	6.6E-02	n/a
flusilazole	6.25	rat	subacute	(*2*)	1.0E-01	n/a
folpet	44.5	rat	subacute	(*2*)	1.4E-02	1.3E-03
fosetyl	1424	rat	subacute	(*2*)	4.5E-04	3.1E-04
glufosinate-ammonium	64	rat	subacute	(*2*)	9.9E-03	n/a
glyphosate	10	rat	chronic	(*1*)	1.3E-02	n/a
haloxyfop	0.2	dog	subacute	(*2*)	1.1E+00	n/a
hymexazol	19	rat	chronic	(*2*)	6.7E-03	n/a
imazamethabenz	12.5	rat	chronic	(*2*)	1.0E-02	n/a
imidacloprid	13	rat	subacute	(*2*)	4.9E-02	n/a
iprodione	4.2	dog	chronic	(*1*)	1.1E-02	n/a
isoproturon	20	rat	subchronic	(*2*)	1.3E-02	n/a

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Table C.3 (continued)

substance	NOEL	receptor	exposure	reference	$\beta_{\text{non-cancer}}$	β_{cancer}
isoxaflutole	2	rat	chronic	(*2*)	6.4E-02	n/a
kresoxim-methyl	146	rat	subacute	(*2*)	4.4E-03	n/a
lambda-cyhalothrin	0.7	rat	subacute	(*2*)	9.1E-01	n/a
lenacil	12.5	rat	chronic	(*3*)	1.0E-02	n/a
linuron	2	rat	subacute	(*2*)	3.2E-01	n/a
mancozeb	0.6	dog	chronic	(*3*)	7.6E-02	n/a
MCPA	0.15	dog	chronic	(*1*)	3.0E-01	0
MCPB	12	dog	subchronic	(*1*)	7.6E-03	n/a
mecoprop	11.4	rat	subacute	(*2*)	5.6E-02	n/a
mecoprop-p	20	mouse	subacute	(*2*)	5.6E-02	n/a
mesotrione	0.24	rat	subacute	(*2*)	2.6E+00	n/a
metalaxyl-m	2.5	rat	subacute	(*2*)	2.5E-01	n/a
metamitron	56	rat	chronic	(*2*)	2.3E-03	n/a
metazachlor	3.6	rat	subacute	(*2*)	1.8E-01	n/a
methidathion	0.2	rat	chronic	(*2*)	6.4E-01	3.4E-01
methiocarb	1.3	rat	subacute	(*2*)	4.9E-01	n/a
methomyl	2.5	dog	chronic	(*1*)	1.8E-02	n/a
metiram	50	rat	subacute	(*2*)	1.3E-02	0
metolachlor	90	rat	subacute	(*2*)	7.1E-03	n/a
metribuzin	2.5	dog	chronic	(*1*)	1.8E-02	n/a
molinate	0.2	rat	subacute	(*1*)	3.2E+00	n/a
myclobutanil	2.49	rat	chronic	(*1*)	5.1E-02	n/a
napropamide	30	rat	chronic	(*1*)	4.2E-03	n/a
oxadixyl	19.7	rat	subacute	(*2*)	3.2E-02	n/a
oxamyl	0.93	dog	chronic	(*2*)	4.9E-02	0
oxyfluorfen	0.3	mouse	chronic	(*1*)	7.5E-01	n/a
paraquat	0.45	dog	chronic	(*1*)	1.0E-01	n/a
parathion-methyl	0.025	rat	chronic	(*1*)	5.1E+00	0
penconazole	3.8	rat	chronic	(*2*)	3.3E-02	n/a
pendimethalin	12.5	dog	chronic	(*1*)	3.7E-03	n/a
phenmedipham	25	rat	chronic	(*1*)	5.1E-03	n/a
pirimiphos-methyl	0.25	human	subacute	(*1*)	6.2E-01	n/a
prochloraz	0.9	dog	chronic	(*1*)	5.1E-02	5.2E-02
prometryn	3.75	dog	chronic	(*1*)	1.2E-02	n/a
propachlor	5.4	rat	chronic	(*2*)	2.4E-02	n/a
propamocarb	41	rat	chronic	(*1*)	3.1E-03	n/a
propanil	5	rat	chronic	(*1*)	2.5E-02	n/a
propiconazole	1.25	dog	chronic	(*1*)	3.7E-02	n/a
propineb	0.05	rat	chronic	(*3*)	2.5E+00	n/a
propyzamide	7.5	dog	chronic	(*1*)	6.1E-03	1.5E-02
prosulfocarb	1.9	rat	chronic	(*3*)	6.7E-02	n/a
pyridate	30	dog	subacute	(*2*)	7.6E-03	n/a
pyrimethanil	139	rat	subacute	(*2*)	4.6E-03	n/a
quinmerac	468.8	rat	subacute	(*2*)	1.4E-03	n/a

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Table C.3 (continued)

substance	NOEL	receptor	exposure	reference	$\beta_{\text{non-cancer}}$	β_{cancer}
simazine	0.52	rat	chronic	(*1*)	2.4E-01	0
s-metolachlor	15	dog	subacute	(*2*)	1.5E-02	n/a
spinosad	9	rat	subacute	(*2*)	7.1E-02	n/a
sulcotrione	0.5	rat	chronic	(*2*)	2.5E-01	n/a
tebuconazole	10.8	rat	subacute	(*2*)	5.9E-02	n/a
tebufenpyrad	48.5	rat	subacute	(*2*)	1.3E-02	n/a
terbufos	0.0025	rat	chronic	(*3*)	5.1E+01	n/a
terbuthylazine	0.22	rat	chronic	(*2*)	5.8E-01	n/a
terbutryn	0.1	rat	chronic	(*1*)	1.3E+00	n/a
thiamethoxam	2	rat	chronic	(*3*)	6.4E-02	n/a
thiram	5	rat	chronic	(*1*)	2.5E-02	0
tolylfluanid	50	rat	subacute	(*2*)	1.3E-02	n/a
tralkoxydim	4.4	rat	subacute	(*2*)	1.4E-01	n/a
trifloxystrobin	6.4	rat	subacute	(*2*)	9.9E-02	n/a
trifluralin	2.4	rat	subacute	(*2*)	2.6E-01	6.2E-03
triflusulfuron	6.9	rat	subacute	(*2*)	9.2E-02	n/a
trinexapac-ethyl	34	rat	subacute	(*2*)	1.9E-02	n/a
vinclozolin	2.8	rat	subacute	(*2*)	2.3E-01	n/a
ziram	1	rat	chronic	(*3*)	1.3E-01	2.8E-02

(*1*) US-EPA United States - Environmental Protection Agency (2011b); Huijbregts et al. (2005); (*2*) AERU Agriculture and Environment Research Unit (2011); Tomlin (2009); (*3*) OCSEH Office of Chemical Safety and Environmental Health (2010).

Table C.4.: Crop-specific human cancer toxicity characterization factors CF (DALY per $\text{kg}_{\text{applied}}$) for ingestion of pesticide residues from food crop consumption for all pesticides considered in the present case study.

substance	CF_{wheat}	CF_{rice}	$\text{CF}_{\text{tomato}}$	CF_{apple}	$\text{CF}_{\text{potato}}$	$\text{CF}_{\text{lettuce}}$
1,3-dichloropropene	2.0 E −07	3.1 E −05	2.0 E −05	1.5 E −06	3.3 E −07	5.1 E −08
2,4-D	0	0	0	0	0	0
acetochlor	n/a	n/a	n/a	n/a	n/a	n/a
aclonifen	n/a	n/a	n/a	n/a	n/a	n/a
alachlor	n/a	n/a	n/a	n/a	n/a	n/a
aldicarb	0	0	0	0	0	0
amitrole	1.8 E −08	5.0 E −04	1.1 E −03	1.9 E −04	6.1 E −09	8.7 E −04
atrazine	6.7 E −07	2.2 E −04	1.3 E −04	1.7 E −05	2.4 E −07	1.3 E −03
azoxystrobin	n/a	n/a	n/a	n/a	n/a	n/a
bentazone	n/a	n/a	n/a	n/a	n/a	n/a
beta-cyfluthrin	n/a	n/a	n/a	n/a	n/a	n/a
boscalid	n/a	n/a	n/a	n/a	n/a	n/a
bromoxynil	n/a	n/a	n/a	n/a	n/a	n/a
captan	7.9 E −11	5.3 E −07	2.1 E −06	2.5 E −07	3.8 E −10	5.9 E −06
carbendazim	n/a	n/a	n/a	n/a	n/a	n/a
carbofuran	0	0	0	0	0	0
chlorbufam	n/a	n/a	n/a	n/a	n/a	n/a
chlorfenvinphos	n/a	n/a	n/a	n/a	n/a	n/a
chloridazon	n/a	n/a	n/a	n/a	n/a	n/a
chlormequat	n/a	n/a	n/a	n/a	n/a	n/a
chlorothalonil	8.3 E −08	1.6 E −07	1.6 E −06	2.5 E −09	3.1 E −10	1.2 E −06
chlorotoluron	n/a	n/a	n/a	n/a	n/a	n/a
chlorpyrifos	0	0	0	0	0	0
chlorpyrifos-methyl	n/a	n/a	n/a	n/a	n/a	n/a
choline chloride	0	0	0	0	0	0
clomazone	n/a	n/a	n/a	n/a	n/a	n/a
clopyralid	n/a	n/a	n/a	n/a	n/a	n/a
cycloxydim	n/a	n/a	n/a	n/a	n/a	n/a
cymoxanil	n/a	n/a	n/a	n/a	n/a	n/a
cypermethrin	n/a	n/a	n/a	n/a	n/a	n/a
cyprodinil	n/a	n/a	n/a	n/a	n/a	n/a
dazomet	n/a	n/a	n/a	n/a	n/a	n/a
desmedipham	n/a	n/a	n/a	n/a	n/a	n/a
diafenthiuron	n/a	n/a	n/a	n/a	n/a	n/a
diazinon	0	0	0	0	0	0
dicamba	n/a	n/a	n/a	n/a	n/a	n/a
dichlorprop	0	0	0	0	0	0
dichlorprop-p	0	0	0	0	0	0

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Table C.4 (continued)

substance	CF_{wheat}	CF_{rice}	CF_{tomato}	CF_{apple}	CF_{potato}	$CF_{lettuce}$
difenoconazole	n/a	n/a	n/a	n/a	n/a	n/a
dimethachlor	n/a	n/a	n/a	n/a	n/a	n/a
dimethenamid	n/a	n/a	n/a	n/a	n/a	n/a
dimethenamid-p	n/a	n/a	n/a	n/a	n/a	n/a
dimethoate	0	0	0	0	0	0
dimethomorph	n/a	n/a	n/a	n/a	n/a	n/a
dinocap	n/a	n/a	n/a	n/a	n/a	n/a
diquat	n/a	n/a	n/a	n/a	n/a	n/a
dithianon	n/a	n/a	n/a	n/a	n/a	n/a
dodine	0	0	0	0	0	0
EPTC	n/a	n/a	n/a	n/a	n/a	n/a
ethofumesate	n/a	n/a	n/a	n/a	n/a	n/a
ethoprophos	n/a	n/a	n/a	n/a	n/a	n/a
famoxadone	n/a	n/a	n/a	n/a	n/a	n/a
fenarimol	n/a	n/a	n/a	n/a	n/a	n/a
fenhexamid	n/a	n/a	n/a	n/a	n/a	n/a
fenpropidin	n/a	n/a	n/a	n/a	n/a	n/a
fenpropimorph	n/a	n/a	n/a	n/a	n/a	n/a
fenthion	0	0	0	0	0	0
fluazifop-p-butyl	n/a	n/a	n/a	n/a	n/a	n/a
fluazinam	n/a	n/a	n/a	n/a	n/a	n/a
flusilazole	n/a	n/a	n/a	n/a	n/a	n/a
folpet	1.5 E −10	1.2 E −06	1.1 E −05	1.4 E −06	3.8 E −11	2.0 E −07
fosetyl	1.4 E −07	1.1 E −06	5.2 E −07	1.5 E −06	8.7 E −12	7.4 E −08
glufosinate-ammonium	n/a	n/a	n/a	n/a	n/a	n/a
glyphosate	n/a	n/a	n/a	n/a	n/a	n/a
haloxyfop	n/a	n/a	n/a	n/a	n/a	n/a
hymexazol	n/a	n/a	n/a	n/a	n/a	n/a
imazamethabenz	n/a	n/a	n/a	n/a	n/a	n/a
imidacloprid	n/a	n/a	n/a	n/a	n/a	n/a
iprodione	n/a	n/a	n/a	n/a	n/a	n/a
isoproturon	n/a	n/a	n/a	n/a	n/a	n/a
isoxaflutole	n/a	n/a	n/a	n/a	n/a	n/a
kresoxim-methyl	n/a	n/a	n/a	n/a	n/a	n/a
lambda-cyhalothrin	n/a	n/a	n/a	n/a	n/a	n/a
lenacil	n/a	n/a	n/a	n/a	n/a	n/a
linuron	n/a	n/a	n/a	n/a	n/a	n/a
mancozeb	n/a	n/a	n/a	n/a	n/a	n/a
MCPA	0	0	0	0	0	0
MCPB	n/a	n/a	n/a	n/a	n/a	n/a
mecoprop	n/a	n/a	n/a	n/a	n/a	n/a
mecoprop-p	n/a	n/a	n/a	n/a	n/a	n/a
mesotrione	n/a	n/a	n/a	n/a	n/a	n/a
metalaxyl-m	n/a	n/a	n/a	n/a	n/a	n/a

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Table C.4 (continued)

substance	CF_{wheat}	CF_{rice}	CF_{tomato}	CF_{apple}	CF_{potato}	$CF_{lettuce}$
metamitron	n/a	n/a	n/a	n/a	n/a	n/a
metazachlor	n/a	n/a	n/a	n/a	n/a	n/a
methidathion	4.0 E −07	5.1 E −06	9.5 E −05	1.7 E −09	7.1 E −08	3.4 E −04
methiocarb	n/a	n/a	n/a	n/a	n/a	n/a
methomyl	n/a	n/a	n/a	n/a	n/a	n/a
metiram	0	0	0	0	0	0
metolachlor	n/a	n/a	n/a	n/a	n/a	n/a
metribuzin	n/a	n/a	n/a	n/a	n/a	n/a
molinate	n/a	n/a	n/a	n/a	n/a	n/a
myclobutanil	n/a	n/a	n/a	n/a	n/a	n/a
napropamide	n/a	n/a	n/a	n/a	n/a	n/a
oxadixyl	n/a	n/a	n/a	n/a	n/a	n/a
oxamyl	0	0	0	0	0	0
oxyfluorfen	n/a	n/a	n/a	n/a	n/a	n/a
paraquat	n/a	n/a	n/a	n/a	n/a	n/a
parathion-methyl	0	0	0	0	0	0
penconazole	n/a	n/a	n/a	n/a	n/a	n/a
pendimethalin	n/a	n/a	n/a	n/a	n/a	n/a
phenmedipham	n/a	n/a	n/a	n/a	n/a	n/a
pirimiphos-methyl	n/a	n/a	n/a	n/a	n/a	n/a
prochloraz	2.5 E −05	7.7 E −04	1.0 E −03	2.2 E −04	3.6 E −08	1.7 E −03
prometryn	n/a	n/a	n/a	n/a	n/a	n/a
propachlor	n/a	n/a	n/a	n/a	n/a	n/a
propamocarb	n/a	n/a	n/a	n/a	n/a	n/a
propanil	n/a	n/a	n/a	n/a	n/a	n/a
propiconazole	n/a	n/a	n/a	n/a	n/a	n/a
propineb	n/a	n/a	n/a	n/a	n/a	n/a
propyzamide	1.0 E −06	2.9 E −05	9.7 E −05	2.0 E −06	1.7 E −08	1.0 E −04
prosulfocarb	n/a	n/a	n/a	n/a	n/a	n/a
pyridate	n/a	n/a	n/a	n/a	n/a	n/a
pyrimethanil	n/a	n/a	n/a	n/a	n/a	n/a
quinmerac	n/a	n/a	n/a	n/a	n/a	n/a
simazine	0	0	0	0	0	0
s-metolachlor	n/a	n/a	n/a	n/a	n/a	n/a
spinosad	n/a	n/a	n/a	n/a	n/a	n/a
sulcotrione	n/a	n/a	n/a	n/a	n/a	n/a
tebuconazole	n/a	n/a	n/a	n/a	n/a	n/a
tebufenpyrad	n/a	n/a	n/a	n/a	n/a	n/a
terbufos	n/a	n/a	n/a	n/a	n/a	n/a
terbuthylazine	n/a	n/a	n/a	n/a	n/a	n/a
terbutryn	n/a	n/a	n/a	n/a	n/a	n/a
thiamethoxam	n/a	n/a	n/a	n/a	n/a	n/a
thiram	0	0	0	0	0	0
tolylfluanid	n/a	n/a	n/a	n/a	n/a	n/a

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Table C.4 (continued)

substance	CF$_{\text{wheat}}$	CF$_{\text{rice}}$	CF$_{\text{tomato}}$	CF$_{\text{apple}}$	CF$_{\text{potato}}$	CF$_{\text{lettuce}}$
tralkoxydim	n/a	n/a	n/a	n/a	n/a	n/a
trifloxystrobin	n/a	n/a	n/a	n/a	n/a	n/a
trifluralin	7.4 E −07	1.0 E −04	8.1 E −05	2.9 E −05	7.5 E −09	1.4 E −07
triflusulfuron	n/a	n/a	n/a	n/a	n/a	n/a
trinexapac-ethyl	n/a	n/a	n/a	n/a	n/a	n/a
vinclozolin	n/a	n/a	n/a	n/a	n/a	n/a
ziram	2.2 E −08	2.9 E −05	9.7 E −06	5.1 E −07	3.1 E −07	3.7 E −04

Table C.5.: Crop-specific human non-cancer toxicity characterization factors CF (DALY per kg$_{\text{applied}}$) for ingestion of pesticide residues from food crop consumption for all pesticides considered in the present case study.

substance	CF$_{\text{wheat}}$	CF$_{\text{rice}}$	CF$_{\text{tomato}}$	CF$_{\text{apple}}$	CF$_{\text{potato}}$	CF$_{\text{lettuce}}$
1,3-dichloropropene	7.9 E −08	1.2 E −05	7.7 E −06	5.9 E −07	1.3 E −07	2.0 E −08
2,4-D	5.0 E −07	4.0 E −04	4.1 E −04	1.3 E −04	1.3 E −08	6.8 E −04
acetochlor	3.2 E −16	7.4 E −08	8.5 E −08	9.1 E −11	2.5 E −08	1.8 E −05
aclonifen	1.2 E −08	2.3 E −06	2.2 E −06	1.4 E −07	1.0 E −09	1.8 E −06
alachlor	2.6 E −09	1.9 E −05	1.0 E −05	5.1 E −07	7.6 E −08	2.9 E −04
aldicarb	3.6 E −11	4.9 E −05	3.6 E −04	2.8 E −05	2.9 E −10	6.1 E −05
amitrole	5.6 E −09	1.6 E −04	3.6 E −04	6.1 E −05	1.9 E −09	2.8 E −04
atrazine	1.8 E −07	6.0 E −05	3.5 E −05	4.6 E −06	6.5 E −08	3.6 E −04
azoxystrobin	2.1 E −06	7.5 E −05	1.4 E −04	5.6 E −05	3.0 E −09	4.1 E −04
bentazone	1.8 E −08	5.0 E −06	1.0 E −05	8.7 E −07	2.5 E −08	3.6 E −05
beta-cyfluthrin	1.7 E −10	3.6 E −06	1.8 E −06	9.6 E −08	4.1 E −10	7.1 E −07
boscalid	4.9 E −05	1.1 E −03	1.4 E −03	3.5 E −04	4.7 E −08	2.5 E −03
bromoxynil	2.2 E −18	7.4 E −09	1.5 E −07	2.8 E −09	3.0 E −17	4.0 E −09
captan	2.0 E −10	1.3 E −06	5.1 E −06	6.1 E −07	9.5 E −10	1.5 E −05
carbendazim	2.6 E −07	1.9 E −06	2.2 E −06	1.3 E −08	6.0 E −09	1.9 E −05
carbofuran	2.1 E −09	1.3 E −05	1.1 E −06	1.3 E −08	4.5 E −07	6.8 E −04
chlorbufam	4.7 E −10	2.3 E −07	1.9 E −07	1.7 E −08	3.2 E −10	1.8 E −06
chlorfenvinphos	8.6 E −08	4.2 E −04	1.5 E −03	2.1 E −05	1.0 E −06	3.3 E −03
chloridazon	4.9 E −07	1.4 E −05	5.0 E −06	2.7 E −07	5.2 E −09	2.5 E −05
chlormequat	3.0 E −08	9.9 E −06	1.0 E −04	5.0 E −05	2.9 E −08	1.9 E −04
chlorothalonil	5.9 E −07	1.1 E −06	1.1 E −05	1.7 E −08	2.2 E −09	8.7 E −06
chlorotoluron	1.0 E −06	3.4 E −05	2.5 E −05	2.1 E −06	2.1 E −08	1.4 E −04
chlorpyrifos	3.2 E −09	3.0 E −06	3.4 E −06	5.4 E −08	1.3 E −08	3.4 E −06
chlorpyrifos-methyl	1.3 E −11	1.5 E −05	1.3 E −04	1.2 E −05	7.2 E −12	2.8 E −07
choline chloride	1.4 E −10	2.1 E −07	5.7 E −07	1.4 E −07	7.1 E −11	8.3 E −07
clomazone	2.5 E −06	2.1 E −05	2.7 E −05	9.0 E −07	1.8 E −08	9.2 E −05
clopyralid	4.3 E −08	1.2 E −05	1.1 E −04	5.4 E −05	5.3 E −08	1.6 E −04
cycloxydim	1.8 E −24	1.5 E −11	1.6 E −09	7.5 E −12	5.6 E −27	2.9 E −19
cymoxanil	6.5 E −09	7.5 E −06	8.9 E −07	3.4 E −08	2.1 E −08	4.9 E −05

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Table C.5 (continued)

substance	CF_{wheat}	CF_{rice}	$\text{CF}_{\text{tomato}}$	CF_{apple}	$\text{CF}_{\text{potato}}$	$\text{CF}_{\text{lettuce}}$
cypermethrin	7.4 E −10	2.1 E −06	1.1 E −06	8.4 E −08	2.6 E −10	5.4 E −07
cyprodinil	1.7 E −08	6.4 E −06	1.8 E −05	3.2 E −07	8.1 E −09	2.1 E −05
dazomet	6.5 E −08	3.1 E −04	9.0 E −04	2.2 E −04	5.8 E −08	1.3 E −03
desmedipham	2.2 E −07	1.9 E −06	1.5 E −05	7.3 E −07	1.7 E −09	7.1 E −06
diafenthiuron	2.4 E −25	2.1 E −11	2.2 E −09	5.7 E −12	2.3 E −22	3.3 E −11
diazinon	9.1 E −08	1.4 E −04	6.1 E −04	5.1 E −06	4.2 E −07	1.4 E −03
dicamba	5.0 E −10	1.6 E −05	3.6 E −05	5.7 E −06	6.8 E −10	2.3 E −05
dichlorprop	7.6 E −09	1.8 E −07	7.0 E −08	1.4 E −10	1.1 E −09	4.0 E −06
dichlorprop-p	3.9 E −11	5.3 E −08	1.8 E −07	2.6 E −09	2.9 E −09	6.4 E −06
difenoconazole	8.8 E −09	9.6 E −06	1.1 E −05	6.9 E −07	5.5 E −09	1.2 E −05
dimethachlor	3.4 E −09	1.0 E −05	2.4 E −05	5.4 E −06	6.5 E −10	4.1 E −05
dimethenamid	6.7 E −09	7.8 E −07	5.6 E −08	2.8 E −10	5.7 E −09	2.0 E −05
dimethenamid-p	2.0 E −07	3.3 E −06	1.0 E −06	1.9 E −08	1.1 E −08	4.2 E −05
dimethoate	3.8 E −12	4.8 E −06	2.9 E −05	2.4 E −06	3.1 E −11	7.9 E −06
dimethomorph	7.0 E −07	2.1 E −05	3.4 E −05	9.3 E −07	1.7 E −08	1.2 E −04
dinocap	3.3 E −10	8.8 E −06	3.8 E −05	6.9 E −06	1.1 E −10	6.6 E −05
diquat	1.4 E −06	1.8 E −04	1.1 E −02	6.4 E −03	2.4 E −07	6.1 E −02
dithianon	7.2 E −07	7.5 E −06	3.0 E −05	4.5 E −07	2.2 E −09	1.4 E −05
dodine	8.5 E −12	1.8 E −07	7.9 E −09	3.5 E −08	3.7 E −14	4.2 E −10
EPTC	8.8 E −09	8.5 E −07	6.1 E −06	8.0 E −09	1.5 E −08	4.0 E −06
ethofumesate	1.1 E −07	1.3 E −05	9.7 E −06	1.8 E −06	5.8 E −09	5.2 E −05
ethoprophos	7.3 E −09	1.1 E −04	3.2 E −05	3.4 E −07	1.8 E −06	5.1 E −03
famoxadone	2.8 E −09	2.9 E −06	2.4 E −06	6.9 E −08	8.7 E −09	2.3 E −06
fenarimol	1.2 E −06	1.2 E −04	2.6 E −04	1.8 E −05	3.4 E −08	2.7 E −04
fenhexamid	1.1 E −10	1.7 E −07	8.1 E −07	2.9 E −09	8.3 E −10	3.0 E −06
fenpropidin	2.8 E −06	8.5 E −05	1.2 E −04	2.3 E −05	1.9 E −09	1.0 E −05
fenpropimorph	5.4 E −10	2.9 E −05	8.5 E −05	3.6 E −07	2.7 E −07	1.3 E −04
fenthion	1.2 E −09	4.8 E −05	4.8 E −05	1.8 E −06	2.4 E −07	8.2 E −05
fluazifop-p-butyl	4.5 E −18	2.6 E −08	7.0 E −07	1.2 E −08	2.1 E −18	6.8 E −08
fluazinam	3.5 E −05	2.8 E −04	6.4 E −05	2.2 E −05	1.4 E −09	1.9 E −04
flusilazole	5.7 E −06	3.1 E −04	3.3 E −04	4.6 E −05	3.4 E −08	2.7 E −04
folpet	1.2 E −10	9.6 E −07	8.8 E −06	1.1 E −06	3.1 E −11	1.7 E −07
fosetyl	2.0 E −08	1.4 E −07	7.1 E −08	2.0 E −07	1.2 E −12	1.0 E −08
glufosinate-ammonium	2.4 E −08	3.4 E −05	2.5 E −04	5.2 E −05	6.6 E −10	2.7 E −04
glyphosate	7.2 E −09	2.9 E −07	1.2 E −05	4.4 E −06	5.1 E −12	2.2 E −05
haloxyfop	2.0 E −07	8.0 E −04	5.9 E −04	6.3 E −05	3.2 E −06	1.0 E −02
hymexazol	6.3 E −09	4.7 E −06	6.5 E −07	3.6 E −08	3.8 E −08	2.6 E −05
imazamethabenz	1.2 E −08	1.3 E −05	1.1 E −05	1.7 E −06	2.5 E −08	1.2 E −04
imidacloprid	2.9 E −07	7.3 E −06	2.8 E −05	2.2 E −06	1.3 E −08	6.3 E −05
iprodione	5.1 E −08	5.1 E −06	1.2 E −05	1.5 E −07	9.2 E −09	4.6 E −05
isoproturon	1.6 E −09	3.5 E −07	3.4 E −08	9.2 E −11	3.2 E −09	1.1 E −05
isoxaflutole	1.1 E −12	1.5 E −06	8.8 E −06	6.1 E −07	2.2 E −12	2.8 E −06
kresoxim-methyl	4.3 E −10	2.8 E −08	7.4 E −07	2.1 E −10	4.0 E −10	1.4 E −06
lambda-cyhalothrin	1.2 E −10	3.1 E −05	1.5 E −05	6.3 E −07	3.6 E −10	5.2 E −06

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Table C.5 (continued)

substance	$\mathrm{CF}_{\mathrm{wheat}}$	$\mathrm{CF}_{\mathrm{rice}}$	$\mathrm{CF}_{\mathrm{tomato}}$	$\mathrm{CF}_{\mathrm{apple}}$	$\mathrm{CF}_{\mathrm{potato}}$	$\mathrm{CF}_{\mathrm{lettuce}}$
lenacil	1.9 E −08	5.6 E −07	7.3 E −08	3.6 E −10	2.8 E −09	1.1 E −05
linuron	7.8 E −05	9.1 E −04	1.4 E −03	1.2 E −04	1.4 E −07	1.3 E −03
mancozeb	2.3 E −08	3.9 E −05	9.8 E −05	2.0 E −05	1.6 E −10	8.3 E −05
MCPA	3.8 E −09	4.3 E −06	6.1 E −06	6.7 E −08	1.6 E −07	6.0 E −04
MCPB	8.1 E −09	1.1 E −05	3.0 E −05	6.7 E −06	4.4 E −10	2.4 E −05
mecoprop	1.1 E −07	3.2 E −04	5.1 E −04	1.4 E −04	2.1 E −08	5.7 E −04
mecoprop-p	1.5 E −08	1.0 E −04	2.3 E −04	5.3 E −05	7.2 E −09	2.4 E −04
mesotrione	8.3 E −08	1.3 E −04	3.5 E −03	4.7 E −04	1.7 E −06	2.8 E −03
metalaxyl-m	2.3 E −05	5.3 E −04	6.9 E −04	2.0 E −05	6.2 E −08	4.5 E −04
metamitron	7.7 E −10	5.2 E −07	4.5 E −08	8.7 E −10	1.5 E −09	4.4 E −06
metazachlor	6.1 E −08	1.1 E −05	1.7 E −06	9.9 E −09	6.3 E −08	2.4 E −04
methidathion	9.1 E −08	1.2 E −06	2.2 E −05	3.9 E −10	1.6 E −08	7.7 E −05
methiocarb	2.0 E −16	2.4 E −08	4.0 E −07	1.4 E −08	2.1 E −16	5.9 E −08
methomyl	1.7 E −07	5.4 E −04	1.2 E −03	2.9 E −04	5.3 E −08	1.7 E −03
metiram	4.4 E −11	6.8 E −08	2.2 E −05	7.3 E −06	2.2 E −13	5.3 E −05
metolachlor	2.7 E −13	1.9 E −07	1.6 E −07	3.0 E −10	2.8 E −09	8.2 E −06
metribuzin	5.3 E −10	7.7 E −07	1.6 E −08	1.1 E −10	9.6 E −09	2.0 E −05
molinate	1.3 E −07	6.3 E −06	1.4 E −05	8.9 E −09	1.5 E −07	3.2 E −04
myclobutanil	3.2 E −07	4.5 E −06	1.7 E −05	1.6 E −07	5.2 E −09	2.8 E −05
napropamide	1.1 E −07	4.1 E −06	9.7 E −06	5.3 E −07	1.2 E −09	1.2 E −05
oxadixyl	2.9 E −06	1.7 E −04	6.5 E −05	1.1 E −05	1.1 E −07	4.0 E −04
oxamyl	2.6 E −08	1.3 E −04	2.0 E −04	4.4 E −05	8.4 E −09	1.8 E −04
oxyfluorfen	4.9 E −05	3.9 E −03	2.9 E −03	1.1 E −03	1.2 E −07	9.2 E −03
paraquat	1.2 E −06	6.8 E −06	1.2 E −03	7.5 E −04	1.1 E −11	7.1 E −03
parathion-methyl	1.4 E −06	7.8 E −04	2.7 E −03	7.4 E −04	5.5 E −08	3.0 E −03
penconazole	2.5 E −08	7.5 E −07	5.1 E −06	2.0 E −08	1.4 E −09	4.1 E −06
pendimethalin	8.2 E −09	5.2 E −06	3.4 E −06	7.3 E −07	4.6 E −10	3.4 E −07
phenmedipham	5.1 E −09	7.6 E −07	3.6 E −06	4.2 E −08	1.2 E −09	5.5 E −06
pirimiphos-methyl	2.1 E −08	2.2 E −05	7.2 E −05	1.2 E −06	3.4 E −08	2.8 E −05
prochloraz	1.1 E −05	3.4 E −04	4.5 E −04	9.8 E −05	1.6 E −08	7.4 E −04
prometryn	1.5 E −08	4.1 E −06	9.2 E −06	1.9 E −07	6.2 E −09	3.1 E −05
propachlor	1.9 E −09	6.2 E −06	5.3 E −05	8.4 E −06	5.5 E −10	4.6 E −06
propamocarb	1.6 E −08	1.5 E −05	2.4 E −06	1.7 E −07	6.9 E −08	6.5 E −05
propanil	5.8 E −07	5.3 E −06	1.5 E −05	6.6 E −08	7.0 E −09	3.5 E −05
propiconazole	9.0 E −09	2.7 E −06	1.5 E −05	8.3 E −08	6.4 E −09	2.0 E −05
propineb	8.1 E −12	4.6 E −06	6.9 E −05	6.8 E −06	6.4 E −10	2.5 E −06
propyzamide	1.0 E −07	2.8 E −06	9.5 E −06	2.0 E −07	1.7 E −09	1.0 E −05
prosulfocarb	6.9 E −08	7.2 E −05	2.1 E −04	6.0 E −05	3.9 E −09	2.9 E −04
pyridate	1.6 E −23	5.2 E −11	1.1 E −09	4.7 E −12	4.8 E −24	1.1 E −11
pyrimethanil	1.2 E −08	2.7 E −07	7.6 E −07	2.5 E −09	1.3 E −09	6.1 E −06
quinmerac	1.8 E −12	4.3 E −08	3.2 E −06	6.4 E −07	8.4 E −10	3.5 E −06
simazine	9.6 E −06	4.5 E −04	2.2 E −04	2.4 E −05	3.2 E −07	1.8 E −03
s-metolachlor	3.4 E −10	2.3 E −07	4.6 E −07	4.6 E −10	3.6 E −09	1.3 E −05
spinosad	1.1 E −08	1.8 E −06	1.8 E −04	5.5 E −05	2.0 E −10	2.6 E −05

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Table C.5 (continued)

substance	$\mathrm{CF}_{\mathrm{wheat}}$	$\mathrm{CF}_{\mathrm{rice}}$	$\mathrm{CF}_{\mathrm{tomato}}$	$\mathrm{CF}_{\mathrm{apple}}$	$\mathrm{CF}_{\mathrm{potato}}$	$\mathrm{CF}_{\mathrm{lettuce}}$
sulcotrione	6.8 E −07	8.1 E −05	2.5 E −03	1.2 E −03	4.8 E −07	9.4 E −03
tebuconazole	8.7 E −09	5.7 E −06	1.6 E −05	3.8 E −07	5.9 E −09	2.5 E −05
tebufenpyrad	3.3 E −12	3.8 E −08	5.3 E −08	2.4 E −10	5.8 E −10	7.4 E −08
terbufos	3.6 E −08	1.0 E −03	6.1 E −03	9.0 E −04	1.1 E −07	1.8 E −04
terbuthylazine	2.0 E −06	8.9 E −04	1.0 E −03	1.2 E −04	8.0 E −07	4.6 E −03
terbutryn	4.4 E −05	1.5 E −03	2.7 E −03	2.2 E −04	2.4 E −07	2.5 E −03
thiamethoxam	5.8 E −08	2.1 E −05	7.4 E −05	6.9 E −06	8.8 E −08	1.7 E −04
thiram	2.0 E −08	9.7 E −07	8.7 E −06	7.0 E −07	2.4 E −10	1.1 E −06
tolylfluanid	1.8 E −09	4.6 E −06	2.0 E −05	3.8 E −06	6.8 E −11	1.8 E −05
tralkoxydim	1.0 E −11	5.7 E −06	2.6 E −05	2.2 E −06	1.4 E −11	1.2 E −05
trifloxystrobin	9.8 E −09	4.2 E −05	1.8 E −04	4.0 E −05	1.6 E −09	3.1 E −04
trifluralin	1.7 E −06	2.3 E −04	1.9 E −04	6.7 E −05	1.7 E −08	3.3 E −07
triflusulfuron	3.0 E −04	4.8 E −03	5.5 E −03	4.1 E −03	4.4 E −07	1.6 E −02
trinexapac-ethyl	5.8 E −31	1.1 E −13	1.7 E −11	1.3 E −14	1.1 E −26	5.2 E −15
vinclozolin	4.0 E −07	3.7 E −05	5.6 E −05	1.5 E −06	5.2 E −08	2.8 E −04
ziram	3.7 E −08	4.8 E −05	1.6 E −05	8.6 E −07	5.3 E −07	6.3 E −04

Table C.6.: Human cancer and non-cancer toxicity characterization factors CF (DALY per $\mathrm{kg}_{\mathrm{applied}}$) for pesticide intake caused by the fractions lost via air (wind drift) and soil (run off, leaching) for all pesticides considered in the present case study.

substance	$\mathrm{CF}_{\mathrm{cancer,air}}$	$\mathrm{CF}_{\mathrm{cancer,soil}}$	$\mathrm{CF}_{\mathrm{non\text{-}cancer,air}}$	$\mathrm{CF}_{\mathrm{non\text{-}cancer,soil}}$
1,3-dichloropropene	1.8 E −08	2.0 E −08	4.5 E −06	3.7 E −06
2,4-D	0	0	7.6 E −07	2.8 E −07
acetochlor	n/a	n/a	n/a	n/a
aclonifen	n/a	n/a	n/a	n/a
alachlor	n/a	n/a	n/a	n/a
aldicarb	0	0	1.8 E −05	8.5 E −06
amitrole	9.0 E −07	2.9 E −07	1.2 E −06	4.0 E −07
atrazine	3.0 E −07	1.6 E −07	3.5 E −07	1.9 E −07
azoxystrobin	n/a	n/a	n/a	n/a
bentazone	n/a	n/a	5.8 E −08	1.0 E −07
beta-cyfluthrin	n/a	n/a	1.8 E −06	7.2 E −09
boscalid	n/a	n/a	n/a	n/a
bromoxynil	n/a	n/a	5.2 E −07	6.2 E −08
captan	4.1 E −09	7.8 E −09	4.3 E −08	8.2 E −08
carbendazim	n/a	n/a	2.3 E −08	3.7 E −08
carbofuran	0	0	3.3 E −06	2.4 E −06
chlorbufam	n/a	n/a	n/a	n/a

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Table C.6 (continued)

substance	$CF_{cancer,air}$	$CF_{cancer,soil}$	$CF_{non\text{-}cancer,air}$	$CF_{non\text{-}cancer,soil}$
chlorfenvinphos	n/a	n/a	1.9 E −05	3.4 E −05
chloridazon	n/a	n/a	n/a	n/a
chlormequat	n/a	n/a	6.7 E −08	2.2 E −08
chlorothalonil	1.7 E −08	3.8 E −09	5.2 E −07	1.2 E −07
chlorotoluron	n/a	n/a	n/a	n/a
chlorpyrifos	0	0	1.8 E −06	3.0 E −06
chlorpyrifos-methyl	n/a	n/a	5.1 E −06	1.7 E −06
choline chloride	0	0	n/a	n/a
clomazone	n/a	n/a	n/a	n/a
clopyralid	n/a	n/a	n/a	n/a
cycloxydim	n/a	n/a	n/a	n/a
cymoxanil	n/a	n/a	n/a	n/a
cypermethrin	n/a	n/a	8.1 E −07	3.3 E −09
cyprodinil	n/a	n/a	n/a	n/a
dazomet	n/a	n/a	n/a	n/a
desmedipham	n/a	n/a	n/a	n/a
diafenthiuron	n/a	n/a	n/a	n/a
diazinon	0	0	3.0 E −06	1.8 E −06
dicamba	n/a	n/a	5.2 E −07	1.8 E −07
dichlorprop	0	0	n/a	n/a
dichlorprop-p	0	0	n/a	n/a
difenoconazole	n/a	n/a	n/a	n/a
dimethachlor	n/a	n/a	n/a	n/a
dimethenamid	n/a	n/a	n/a	n/a
dimethenamid-p	n/a	n/a	n/a	n/a
dimethoate	0	0	1.7 E −07	2.8 E −07
dimethomorph	n/a	n/a	n/a	n/a
dinocap	n/a	n/a	6.1 E −07	5.0 E −10
diquat	n/a	n/a	4.6 E −06	1.9 E −08
dithianon	n/a	n/a	3.5 E −07	1.5 E −08
dodine	0	0	4.1 E −09	4.5 E −11
EPTC	n/a	n/a	3.8 E −08	5.0 E −08
ethofumesate	n/a	n/a	n/a	n/a
ethoprophos	n/a	n/a	6.1 E −06	5.2 E −06
famoxadone	n/a	n/a	n/a	n/a
fenarimol	n/a	n/a	2.9 E −06	7.4 E −07
fenhexamid	n/a	n/a	n/a	n/a
fenpropidin	n/a	n/a	n/a	n/a
fenpropimorph	n/a	n/a	n/a	n/a

(continued on next page)

Table C.6 (continued)

substance	$CF_{cancer,air}$	$CF_{cancer,soil}$	$CF_{non\text{-}cancer,air}$	$CF_{non\text{-}cancer,soil}$
fenthion	0	0	1.2 E −06	5.5 E −07
fluazifop-p-butyl	n/a	n/a	n/a	n/a
fluazinam	n/a	n/a	n/a	n/a
flusilazole	n/a	n/a	n/a	n/a
folpet	2.5 E −08	2.8 E −08	8.5 E −08	9.8 E −08
fosetyl	9.9 E −10	2.4 E −11	5.8 E −10	1.4 E −11
glufosinate-ammonium	n/a	n/a	1.8 E −07	2.4 E −08
glyphosate	n/a	n/a	7.3 E −09	1.7 E −08
haloxyfop	n/a	n/a	n/a	n/a
hymexazol	n/a	n/a	n/a	n/a
imazamethabenz	n/a	n/a	n/a	n/a
imidacloprid	n/a	n/a	3.2 E −07	2.5 E −08
iprodione	n/a	n/a	5.2 E −07	8.1 E −07
isoproturon	n/a	n/a	n/a	n/a
isoxaflutole	n/a	n/a	n/a	n/a
kresoxim-methyl	n/a	n/a	1.6 E −08	8.6 E −11
lambda-cyhalothrin	n/a	n/a	n/a	n/a
lenacil	n/a	n/a	n/a	n/a
linuron	n/a	n/a	4.6 E −06	7.0 E −07
mancozeb	n/a	n/a	3.3 E −08	2.4 E −08
MCPA	0	0	2.0 E −06	4.1 E −07
MCPB	n/a	n/a	7.8 E −08	2.9 E −08
mecoprop	n/a	n/a	1.1 E −06	6.9 E −07
mecoprop-p	n/a	n/a	n/a	n/a
mesotrione	n/a	n/a	n/a	n/a
metalaxyl-m	n/a	n/a	n/a	n/a
metamitron	n/a	n/a	n/a	n/a
metazachlor	n/a	n/a	n/a	n/a
methidathion	7.3 E −07	2.3 E −06	7.0 E −07	2.2 E −06
methiocarb	n/a	n/a	3.2 E −07	7.4 E −08
methomyl	n/a	n/a	2.3 E −06	7.4 E −07
metiram	0	0	2.2 E −07	1.2 E −11
metolachlor	n/a	n/a	4.7 E −08	3.7 E −08
metribuzin	n/a	n/a	1.8 E −07	1.0 E −07
molinate	n/a	n/a	1.2 E −06	2.1 E −06
myclobutanil	n/a	n/a	2.3 E −07	3.0 E −08
napropamide	n/a	n/a	5.4 E −09	8.0 E −09
oxadixyl	n/a	n/a	n/a	n/a
oxamyl	0	0	4.6 E −07	4.8 E −07

(continued on next page)

Table C.6 (continued)

substance	$CF_{cancer,air}$	$CF_{cancer,soil}$	$CF_{non\text{-}cancer,air}$	$CF_{non\text{-}cancer,soil}$
oxyfluorfen	n/a	n/a	2.6 E −05	4.5 E −07
paraquat	n/a	n/a	5.4 E −07	2.2 E −09
parathion-methyl	0	0	1.5 E −06	4.5 E −07
penconazole	n/a	n/a	5.8 E −07	6.0 E −08
pendimethalin	n/a	n/a	3.3 E −08	1.9 E −09
phenmedipham	n/a	n/a	6.3 E −08	9.5 E −10
pirimiphos-methyl	n/a	n/a	1.7 E −07	1.7 E −07
prochloraz	9.2 E −07	2.9 E −06	1.7 E −06	5.4 E −06
prometryn	n/a	n/a	8.6 E −08	2.7 E −08
propachlor	n/a	n/a	6.1 E −08	3.6 E −08
propamocarb	n/a	n/a	3.1 E −08	4.7 E −08
propanil	n/a	n/a	6.9 E −07	2.2 E −07
propiconazole	n/a	n/a	3.6 E −07	7.1 E −08
propineb	n/a	n/a	4.9 E −07	8.6 E −09
propyzamide	2.6 E −07	1.2 E −07	1.1 E −07	5.0 E −08
prosulfocarb	n/a	n/a	n/a	n/a
pyridate	n/a	n/a	n/a	n/a
pyrimethanil	n/a	n/a	n/a	n/a
quinmerac	n/a	n/a	n/a	n/a
simazine	0	0	4.1 E −06	1.5 E −06
s-metolachlor	n/a	n/a	n/a	n/a
spinosad	n/a	n/a	n/a	n/a
sulcotrione	n/a	n/a	n/a	n/a
tebuconazole	n/a	n/a	2.9 E −07	5.4 E −08
tebufenpyrad	n/a	n/a	n/a	n/a
terbufos	n/a	n/a	3.9 E −06	1.4 E −05
terbuthylazine	n/a	n/a	n/a	n/a
terbutryn	n/a	n/a	2.1 E −05	3.4 E −06
thiamethoxam	n/a	n/a	n/a	n/a
thiram	0	0	1.2 E −08	4.0 E −08
tolylfluanid	n/a	n/a	n/a	n/a
tralkoxydim	n/a	n/a	n/a	n/a
trifloxystrobin	n/a	n/a	n/a	n/a
trifluralin	5.7 E −08	1.5 E −08	5.6 E −07	1.5 E −07
triflusulfuron	n/a	n/a	n/a	n/a
trinexapac-ethyl	n/a	n/a	n/a	n/a
vinclozolin	n/a	n/a	7.4 E −07	3.6 E −07
ziram	4.5 E −08	3.4 E −08	3.3 E −07	2.5 E −07

Table C.7.: Human health impacts in EU25 in 2003 expressed in DALY per country, distinguished (a) according to direct residues in food crops and fractions lost via air (wind drift) and soil (run off, leaching), and (b) according to cancer (canc) and non-cancer (nonc) effects.

country	$\text{IS}_{\text{residue,canc}}$	$\text{IS}_{\text{residue,nonc}}$	$\text{IS}_{\text{loss,canc,air}}$	$\text{IS}_{\text{loss,canc,soil}}$	$\text{IS}_{\text{loss,nonc,air}}$	$\text{IS}_{\text{loss,nonc,soil}}$
AT	5.3 E −01	1.1 E +01	6.7 E −04	3.0 E −07	5.8 E −02	7.0 E −05
BE	1.4 E +00	2.4 E +01	6.3 E −03	9.5 E −05	2.7 E −01	1.2 E −02
CY	1.4 E −01	2.7 E +00	2.0 E −05	1.2 E −06	1.3 E −02	2.4 E −04
CZ	1.2 E −01	2.2 E +00	6.5 E −03	3.5 E −05	9.2 E −02	1.3 E −04
DE	3.0 E +00	2.1 E +01	1.1 E −03	1.5 E −06	2.7 E −01	4.3 E −04
DK	1.6 E −02	9.4 E −01	5.6 E −04	2.8 E −07	5.4 E −02	8.8 E −05
EE	1.0 E −02	3.7 E −02	1.3 E −04	1.4 E −08	2.0 E −03	7.6 E −07
ES	7.6 E +01	4.1 E +02	2.4 E −02	8.3 E −04	3.2 E +00	1.4 E −01
FI	5.7 E −01	3.3 E +00	3.2 E −03	1.1 E −05	5.7 E −02	8.1 E −05
FR	2.9 E +01	3.4 E +02	1.9 E −02	1.0 E −04	8.8 E −01	1.7 E −02
GB	1.0 E +00	3.8 E +01	1.3 E −02	2.2 E −04	5.4 E −01	4.3 E −02
GR	3.0 E +01	6.2 E +01	9.1 E −03	9.8 E −05	2.2 E −01	1.3 E −02
HU	3.6 E −01	1.6 E +01	2.4 E −02	1.3 E −04	9.4 E −02	2.3 E −04
IE	1.4 E −01	5.0 E −01	5.9 E −04	1.2 E −06	3.0 E −02	2.7 E −05
IT	6.8 E +01	3.7 E +02	1.7 E −02	6.8 E −04	2.2 E +00	9.2 E −02
LT	5.5 E −03	1.6 E −01	6.9 E −05	7.6 E −09	3.9 E −03	2.9 E −06
LV	1.1 E −02	5.5 E −01	1.2 E −04	1.4 E −08	6.8 E −03	3.0 E −06
NL	3.8 E +00	2.3 E +00	3.4 E −03	4.8 E −06	1.5 E −01	1.4 E −04
PL	2.2 E −01	7.6 E +01	1.2 E −02	6.6 E −05	5.5 E −01	7.5 E −04
PT	4.4 E −01	5.5 E +01	9.9 E −03	6.8 E −05	7.8 E −02	2.3 E −03
SE	3.1 E −03	3.2 E −01	4.3 E −05	2.1 E −08	1.1 E −01	1.1 E −04
SI	6.9 E −02	1.0 E +01	3.5 E −05	3.3 E −08	4.5 E −03	1.4 E −05
SK	1.4 E −01	4.9 E +00	4.3 E −03	2.2 E −05	7.8 E −02	1.1 E −04

Table C.8.: Contribution of direct residues in food crops and fractions lost via air (wind drift) and soil (run off, leaching), as well as of cancer (canc) and non-cancer (nonc) effects to human health impacts in EU25 in 2003.

country	$\theta_{\text{residue,canc}}$	$\theta_{\text{residue,nonc}}$	$\theta_{\text{loss,canc,air}}$	$\theta_{\text{loss,canc,soil}}$	$\theta_{\text{loss,nonc,air}}$	$\theta_{\text{loss,nonc,soil}}$
AT	4.46%	95.04%	0.01%	2.5 E −06%	0.49%	5.8 E −04%
BE	5.38%	93.49%	0.02%	3.7 E −04%	1.06%	4.7 E −02%
CY	4.89%	94.66%	7.2 E −04%	4.4 E −05%	0.44%	8.3 E −03%
CZ	4.97%	90.89%	0.27%	1.4 E −03%	3.86%	5.6 E −03%
DE	12.48%	86.40%	4.7 E −03%	6.2 E −06%	1.12%	1.8 E −03%
DK	1.55%	93.06%	0.05%	2.7 E −05%	5.33%	8.6 E −03%
EE	20.96%	74.82%	0.27%	2.9 E −05%	3.96%	1.5 E −03%
ES	15.72%	83.59%	4.9 E −03%	1.7 E −04%	0.66%	2.9 E −02%
FI	14.41%	84.06%	0.08%	2.7 E −04%	1.45%	2.0 E −03%
FR	7.77%	91.99%	0.01%	2.8 E −05%	0.24%	4.6 E −03%

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Table C.8 (continued)

country	$\theta_{\text{residue,canc}}$	$\theta_{\text{residue,nonc}}$	$\theta_{\text{loss,canc,air}}$	$\theta_{\text{loss,canc,soil}}$	$\theta_{\text{loss,nonc,air}}$	$\theta_{\text{loss,nonc,soil}}$
GB	2.66%	95.81%	0.03%	5.7 E −04%	1.38%	1.1 E −01%
GR	32.93%	66.80%	0.01%	1.1 E −04%	0.24%	1.4 E −02%
HU	2.17%	97.12%	0.14%	8.1 E −04%	0.56%	1.4 E −03%
IE	20.80%	74.57%	0.09%	1.9 E −04%	4.53%	4.0 E −03%
IT	15.45%	84.02%	3.9 E −03%	1.5 E −04%	0.50%	2.1 E −02%
LT	3.17%	94.51%	0.04%	4.4 E −06%	2.28%	1.7 E −03%
LV	1.86%	96.92%	0.02%	2.5 E −06%	1.20%	5.3 E −04%
NL	60.93%	36.70%	0.05%	7.5 E −05%	2.31%	2.3 E −03%
PL	0.28%	98.99%	0.02%	8.5 E −05%	0.71%	9.7 E −04%
PT	0.80%	99.04%	0.02%	1.2 E −04%	0.14%	4.3 E −03%
SE	0.72%	74.75%	0.01%	4.9 E −06%	24.49%	2.5 E −02%
SI	0.67%	99.28%	3.4 E −04%	3.3 E −07%	0.04%	1.4 E −04%
SK	2.69%	95.69%	0.08%	4.3 E −04%	1.53%	2.2 E −03%

Table C.9.: Human health damage costs in EU25 in 2003 expressed in million Euro per country, distinguished (a) according to residues in food crops and fractions lost via air (wind drift) and soil (run off, leaching), and (b) according to cancer (canc) and non-cancer (nonc) effects.

country	$EC_{residue,canc}$	$EC_{residue,nonc}$	$EC_{loss,canc,air}$	$EC_{loss,canc,soil}$	$EC_{loss,nonc,air}$	$EC_{loss,nonc,soil}$
AT	2.1 E −02	4.5 E −01	2.7 E −05	1.2 E −08	2.3 E −03	2.8 E −06
BE	5.5 E −02	9.6 E −01	2.5 E −04	3.8 E −06	1.1 E −02	4.9 E −04
CY	5.6 E −03	1.1 E −01	8.2 E −07	5.0 E −08	5.0 E −04	9.4 E −06
CZ	4.8 E −03	8.7 E −02	2.6 E −04	1.4 E −06	3.7 E −03	5.3 E −06
DE	1.2 E −01	8.3 E −01	4.5 E −05	6.0 E −08	1.1 E −02	1.7 E −05
DK	6.3 E −04	3.8 E −02	2.2 E −05	1.1 E −08	2.2 E −03	3.5 E −06
EE	4.1 E −04	1.5 E −03	5.2 E −06	5.7 E −10	7.8 E −05	3.0 E −08
ES	3.0 E +00	1.6 E +01	9.6 E −04	3.3 E −05	1.3 E −01	5.7 E −03
FI	2.3 E −02	1.3 E −01	1.3 E −04	4.3 E −07	2.3 E −03	3.2 E −06
FR	1.1 E +00	1.4 E +01	7.7 E −04	4.1 E −06	3.5 E −02	6.7 E −04
GB	4.2 E −02	1.5 E +00	5.2 E −04	8.9 E −06	2.2 E −02	1.7 E −03
GR	1.2 E +00	2.5 E +00	3.6 E −04	3.9 E −06	8.9 E −03	5.3 E −04
HU	1.4 E −02	6.5 E −01	9.5 E −04	5.4 E −06	3.8 E −03	9.0 E −06
IE	5.6 E −03	2.0 E −02	2.4 E −05	5.0 E −08	1.2 E −03	1.1 E −06
IT	2.7 E +00	1.5 E +01	6.9 E −04	2.7 E −05	8.8 E −02	3.7 E −03
LT	2.2 E −04	6.5 E −03	2.8 E −06	3.0 E −10	1.6 E −04	1.2 E −07
LV	4.2 E −04	2.2 E −02	4.9 E −06	5.6 E −10	2.7 E −04	1.2 E −07
NL	1.5 E −01	9.3 E −02	1.3 E −04	1.9 E −07	5.8 E −03	5.7 E −06
PL	8.8 E −03	3.1 E +00	5.0 E −04	2.6 E −06	2.2 E −02	3.0 E −05
PT	1.8 E −02	2.2 E +00	3.9 E −04	2.7 E −06	3.1 E −03	9.4 E −05
SE	1.3 E −04	1.3 E −02	1.7 E −06	8.6 E −10	4.3 E −03	4.3 E −06
SI	2.7 E −03	4.0 E −01	1.4 E −06	1.3 E −09	1.8 E −04	5.6 E −07
SK	5.5 E −03	2.0 E −01	1.7 E −04	8.9 E −07	3.1 E −03	4.6 E −06

Table C.10.: Crop- and substance-specific human health damage costs for cancer effects caused by direct residues in food crops in EU25 in 2003 expressed in million Euro per country.

	AT	BE	CY	CZ	DE	DK	EE	ES	FI	FR	GB	GR	HU	IE	IT	LT	LV	NL	PL	PT	SE	SI	SK
cereals																							
chlorothalonil														2.3E-04									
prochloraz									1.8E-02						2.7E-02								
trifluralin											1.8E-02						3.8E-04						
maize																							
atrazine		2.9E-03		3.3E-03				6.6E-03				2.6E-03	1.2E-02						6.2E-03	5.3E-03			2.1E-03
oil seeds																							
prochloraz														2.0E-03									
propyzamide		1.3E-04				5.4E-04					3.9E-03			8.4E-05							4.2E-05		
trifluralin	1.4E-03	8.9E-05		1.5E-03			4.1E-04		1.4E-03	3.1E-02	5.1E-03		2.6E-03			2.2E-04			2.6E-03			3.0E-05	1.3E-03
potato																							
chlorothalonil				1.6E-07														1.3E-06	1.5E-06				1.4E-07
folpet										3.7E-07													
fosetyl								4.9E-09															
1,3-dichloropropene								2.3E-03			5.9E-03	1.3E-03								2.5E-04			
sugar beet																							
1,3-dichloropropene												2.0E-04											
grapes/vines																							
chlorothalonil	9.5E-04																						
folpet	1.9E-02				1.2E-01			3.6E-02		6.9E-01												2.6E-03	2.2E-03
fosetyl										3.4E-02												1.3E-04	
amitrole												1.2E+00											
1,3-dichloropropene								5.5E-01															
fruit trees																							
captan										1.9E-03								6.1E-04					
ziram															9.9E-03								
amitrole																		1.5E-01					
methidathion													6.9E-07										
1,3-dichloropropene		1.5E-02																					
vegetables																							
chlorothalonil											8.6E-03	1.2E-03					3.8E-05	1.9E-03					
fosetyl						8.4E-05						4.0E-04									8.4E-05		
trifluralin									3.2E-03					3.2E-03	5.4E-01								
1,3-dichloropropene		3.7E-02	5.6E-03					2.5E+00		3.9E-01		4.9E-02			2.2E+00					1.2E-02			
total	2.1E-02	5.5E-02	5.6E-03	4.8E-03	1.2E-01	6.3E-04	4.1E-04	3.0E+00	2.3E-02	1.1E+00	4.2E-02	1.2E+00	1.4E-02	5.6E-03	2.7E+00	2.2E-04	4.2E-04	1.5E-01	8.8E-03	1.8E-02	1.3E-04	2.7E-03	5.5E-03

Table C.11.: Crop- and substance-specific human health damage costs for non-cancer effects caused by direct residues in food crops in EU25 in 2003 expressed in million Euro per country.

	AT	BE	CY	CZ	DE	DK	EE	ES	FI	FR	GB	GR	HU	IE	IT	LT	LV	NL	PL	PT	SE	SI	SK
cereals																							
carbendazim																							1.9E-04
chlorothalonil														1.6E-03									
fenpropidin																						2.2E-04	
fenpropimorph						1.2E-06								9.5E-07				8.2E-07					
prochloraz									8.0E-03						1.2E-02								
propiconazole							3.6E-07									2.9E-06						7.2E-07	5.0E-06
2,4-d	7.5E-04			2.9E-03			2.0E-05	7.4E-03				2.8E-04	2.6E-03		3.9E-03	2.4E-04	1.2E-04						3.6E-04
chlorotoluron																						8.7E-04	
dicamba							1.0E-07									2.4E-07	4.0E-08						
dichlorprop	1.2E-05																						
dichlorprop-p									3.8E-08				8.2E-08								1.5E-07		
glyphosate				4.1E-05	1.9E-04	1.7E-04	1.4E-06	1.1E-04	3.6E-05	2.8E-04	2.7E-04	4.0E-06	2.6E-05	3.8E-05	5.7E-05	3.4E-06	3.7E-06	7.3E-05		6.9E-06	8.5E-05	5.7E-07	5.2E-06
imazamethabenz												6.6E-06											
isoproturon	2.0E-06	2.0E-05		9.1E-06	2.0E-04			2.3E-05		2.2E-04	1.6E-04				2.5E-06			1.6E-05	8.5E-05	3.0E-06	1.2E-05	3.1E-07	
linuron																	1.9E-02						
mcpa	3.9E-06	4.8E-06		1.6E-05	9.9E-05	1.9E-05		4.5E-05	1.9E-05	1.5E-04			1.4E-05	7.0E-06	3.0E-05			5.0E-05	1.9E-04	3.6E-06	4.5E-05		1.6E-05
mecoprop	4.6E-04	1.4E-04						7.6E-04				3.1E-04											
mecoprop-p					2.4E-04									7.8E-05				8.0E-05			3.5E-05		
molinate																				1.3E-04			
pendimethalin						3.5E-05					3.1E-04												
propanil																				5.6E-04			
prosulfocarb		8.8E-05				1.2E-03																	
trifluralin											4.2E-02						8.9E-04						
chlormequat		3.8E-05		1.7E-04	7.8E-04				2.1E-05	1.1E-03	1.1E-03								5.6E-05				
maize																							
thiram					7.2E-05																		
2,4-d													1.2E-03										
acetochlor				3.0E-12				2.7E-12		1.0E-11			5.8E-12						1.0E-12				3.4E-12
alachlor								2.8E-05		7.8E-05		7.2E-06			2.7E-05					8.9E-06			
atrazine		7.8E-04		8.9E-04				1.8E-03				7.0E-04	3.2E-03						1.7E-03	1.5E-03			5.7E-04
bentazone		2.0E-05											4.3E-05							8.7E-06			
bromoxynil												5.4E-16											
chloridazon																		9.3E-04					
dicamba																						6.0E-08	
dimethenamid	5.1E-06	2.9E-05																					
dimethenamid-p																		3.8E-04					
eptc																				4.2E-06			
glyphosate					2.6E-05					2.1E-04									2.3E-05				

Table C.11 (continued)

	AT	BE	CY	CZ	DE	DK	EE	ES	FI	FR	GB	GR	HU	IE	IT	LT	LV	NL	PL	PT	SE	SI	SK
metolachlor								1.5E-09				4.6E-10			1.2E-09								
pendimethalin	4.9E-06														3.2E-05				4.0E-06				
pyridate	1.2E-20																	1.5E-20					
s-metolachlor	5.2E-07				5.1E-06								8.2E-07		3.5E-06				1.6E-07	1.6E-07		3.0E-07	
sulcotrione		7.3E-04										1.6E-04						6.2E-04					
terbuthylazine	3.1E-03				3.0E-02										3.6E-02			3.7E-03				1.8E-03	
methiocarb					7.1E-13																		
oil seeds																							
carbendazim											4.9E-04								2.7E-04				
iprodione														2.0E-06									
prochloraz														8.9E-04									
tebuconazole					5.4E-05	3.5E-07													7.0E-06				
acetochlor													1.2E-12										2.5E-13
aclonifen										1.2E-04					3.8E-06								
bentazone	2.2E-06														1.6E-05								
clomazone						2.0E-04																	
clopyralid						5.2E-06			3.5E-06							1.4E-06	8.7E-07				5.2E-06		
cycloxydim															5.6E-22								
dimethachlor					2.1E-05											1.1E-07	6.8E-08						
dimethenamid													2.4E-05										
fluazifop-p-butyl									1.8E-16													1.8E-16	
glyphosate											1.3E-05												
haloxyfop						1.6E-05																	
metazachlor	7.1E-05	1.5E-05		2.2E-04	1.7E-03				9.8E-06	1.1E-03	4.2E-04			7.3E-06				3.2E-05	1.9E-04		4.4E-05		8.8E-05
napropamide										1.2E-03													
oxyfluorfen															1.6E-02								
pendimethalin	3.3E-07														4.9E-06								
prometryn																							2.6E-05
propyzamide		1.2E-05				5.3E-05					3.8E-04			8.2E-06							4.1E-06		
quinmerac	2.2E-10				1.1E-08																		
trifluralin	3.3E-03	2.0E-04		3.4E-03			9.5E-04		3.1E-03	7.3E-02	1.2E-02		6.1E-03			5.0E-04			6.0E-03			6.8E-05	2.9E-03
beta-cyfluthrin																					7.0E-09		
chlorfenvinphos														6.9E-06									
chlorpyrifos				7.1E-06															8.7E-06				2.6E-06
imidacloprid																					1.1E-05		
lambda-cyhalothrin																						5.0E-09	
thiamethoxam									4.6E-06														
chlormequat																		1.6E-05					
trinexapac-ethyl																						2.3E-29	

Table C.11 (continued)

	AT	BE	CY	CZ	DE	DK	EE	ES	FI	FR	GB	GR	HU	IE	IT	LT	LV	NL	PL	PT	SE	SI	SK
potato																							
chlorothalonil				1.1E-06														9.0E-06	1.1E-05				9.6E-07
cymoxanil	1.7E-06							1.2E-05			5.6E-05					3.4E-07	4.2E-07			8.4E-06			
fluazinam		1.7E-06			5.0E-06	8.3E-07	5.5E-08		2.8E-07					4.4E-07				6.0E-06			1.5E-06		
folpet										3.0E-07													
fosetyl								6.7E-10															
mancozeb	3.7E-07	5.5E-06		6.9E-07	4.4E-06	1.9E-06	3.1E-08	1.4E-06	5.0E-07	1.1E-05	8.6E-06	4.2E-07	1.3E-07	1.6E-06	4.9E-07	2.1E-07	8.4E-08	4.3E-06	2.2E-06	1.0E-06	1.7E-07	4.4E-08	2.6E-07
metalaxyl-m																	1.5E-06				2.5E-05		
metiram		2.6E-10			1.3E-09													3.8E-09					
propamocarb				3.6E-05	2.5E-04				1.1E-05										1.5E-04		3.8E-05	2.7E-06	2.7E-05
propineb																				4.9E-07			
aclonifen						5.0E-07																	
bentazone	2.0E-06																						
diquat		2.9E-04				7.7E-05															9.7E-05		
eptc																				6.0E-06			
linuron									2.8E-05										3.3E-04				
metribuzin				3.8E-06																			3.1E-06
paraquat												9.7E-09		3.5E-09									
pendimethalin															2.4E-07								
prometryn													2.7E-06									2.5E-07	
prosulfocarb		2.1E-05			4.8E-05	2.2E-06				4.6E-05								1.7E-05					
s-metolachlor													1.6E-06										
terbutryn																							4.8E-05
chlorpyrifos	8.1E-06			4.6E-06																		5.1E-07	
cypermethrin	4.2E-08																						
ethoprophos												1.6E-03											
1,3-dichloropropene								8.8E-04			2.3E-03	5.1E-04								9.8E-05			
sugar beet																							
dinocap																				5.1E-08			
fenpropidin					6.1E-06															2.3E-07			
flusilazole														1.4E-06									
hymexazol						7.6E-06																	
mancozeb												2.0E-07											
chloridazon	1.4E-06	1.5E-05		1.1E-05	3.2E-05					3.3E-05	1.1E-05		1.2E-05	2.1E-07	1.8E-05			1.2E-05	2.3E-05		2.3E-06		5.2E-06
clopyralid									4.2E-06					4.2E-06		1.7E-06	1.1E-06						
desmedipham	2.0E-07			2.8E-06				1.4E-06	2.0E-07										7.1E-06				6.1E-07
dicamba																						8.1E-08	
ethofumesate	5.6E-06			8.2E-06	6.8E-05	3.0E-06		9.3E-06	6.5E-06	4.3E-05					1.7E-05			9.6E-06	2.8E-05	1.9E-06			3.0E-06
glyphosate					3.2E-08	2.3E-09	2.1E-10			3.3E-08	1.6E-08			1.9E-09	1.8E-08	2.1E-10	2.1E-10				2.3E-09		
haloxyfop							1.3E-04										1.3E-04						
lenacil								2.7E-06						1.0E-06									

Table C.11 (continued)

	AT	BE	CY	CZ	DE	DK	EE	ES	FI	FR	GB	GR	HU	IE	IT	LT	LV	NL	PL	PT	SE	SI	SK
metamitron				1.7E-06								5.5E-07			3.8E-06			7.3E-06					
metolachlor												4.2E-06											
phenmedipham	7.3E-07			2.5E-06	8.9E-06	1.6E-06		1.5E-06	2.1E-06	7.7E-06	3.8E-06				2.3E-06			2.5E-06	6.6E-06	1.5E-07	2.5E-06		7.3E-07
s-metolachlor																						3.1E-06	
terbuthylazine																						7.0E-04	
aldicarb		1.2E-08																					
chlorpyrifos																							4.1E-06
oxamyl											1.8E-05												
1,3-dichloropropene												7.7E-05											
grapes/vines																							
chlorothalonil	6.7E-03																						
dinocap																						6.0E-03	
folpet	1.5E-02				9.8E-02			3.0E-02		5.7E-01												2.1E-03	1.8E-03
fosetyl										4.6E-03												1.7E-05	
mancozeb			7.0E-02	2.0E-02				1.3E+00		5.2E+00		2.1E-01	3.6E-01		1.2E+01					9.0E-01		3.4E-01	3.1E-02
metiram				4.4E-03	3.4E-01					7.7E-01			4.0E-02										7.0E-03
propineb												7.2E-02								6.3E-01			
amitrole												3.7E-01											
glyphosate	7.4E-03		4.9E-04	2.5E-03				1.7E-01				2.7E-02	4.6E-02		1.8E-01					1.1E-01			
chlorpyrifos			3.2E-03																				
dimethoate													3.0E-02										
1,3-dichloropropene								2.1E-01															
captan										4.6E-03								1.5E-03					
cyprodinil																2.6E-06						1.3E-05	
difenoconazole																	2.8E-06						
dinocap											5.5E-04												
dithianon	1.8E-05					3.6E-05					2.7E-04								9.1E-04				
dodine				5.6E-06															7.2E-05				
fenhexamid						2.3E-07																	
iprodione										4.5E-04											2.4E-05		
kresoxim-methyl														8.5E-09									
mancozeb	4.2E-02	6.2E-02		9.7E-03	1.7E-01	2.7E-02		1.2E-01		3.0E-01			8.7E-02			2.7E-03	4.1E-04		1.6E-01	5.0E-02			6.5E-03
metiram					8.7E-03										9.0E-02								5.8E-04
myclobutanil											2.5E-05												
pyrimethanil	9.9E-08																						
thiram															1.2E-02			1.7E-03	1.8E-03	1.1E-03			
tolylfluanid		3.2E-03			4.6E-03	4.6E-04			3.1E-04									3.1E-03	9.8E-03		7.6E-04		
ziram															1.7E-02								
amitrole																		4.8E-02					
glufosinate-ammonium									4.2E-03														
glyphosate				2.1E-03	5.3E-03			2.5E-02				7.4E-03	4.8E-03							1.1E-02		7.1E-04	3.5E-04

Table C.11 (continued)

	AT	BE	CY	CZ	DE	DK	EE	ES	FI	FR	GB	GR	HU	IE	IT	LT	LV	NL	PL	PT	SE	SI	SK
terbuthylazine																						1.8E-02	
chlorpyrifos											3.3E-05	9.1E-05											
chlorpyrifos-methyl	7.4E-03			1.8E-03																			9.2E-04
diazinon																						8.2E-04	
dimethoate													2.6E-03										
fenthion												2.9E-03											
methidathion													1.6E-07										
methiocarb									1.1E-06														
parathion-methyl												1.2E+00											
thiamethoxam																5.5E-05	2.7E-05						
1,3-dichloropropene		5.8E-03																					
vegetables																							
chlorothalonil											6.1E-02	8.5E-03					2.7E-04	1.3E-02					
fosetyl						1.1E-05						5.4E-05									1.1E-05		
iprodione																		1.4E-02					
mancozeb	3.5E-02	4.0E-01	3.1E-02	2.7E-02	1.2E-01			2.1E+00		4.5E-01		3.2E-01	5.9E-02		6.1E-01				1.2E+00	4.2E-01		1.2E-02	2.0E-02
metiram				2.6E-03	2.6E-02															1.1E-02			
propamocarb																		1.8E-03				9.5E-05	
propineb												1.7E-01								4.1E-02			
aclonifen									2.6E-04														
bentazone	3.6E-03	5.2E-03			1.6E-02	6.0E-03			8.0E-04	6.6E-02	2.1E-02										2.4E-03		
clopyralid																1.7E-03	1.3E-03				4.3E-03		
linuron									1.1E-01										1.5E+00				
mcpa						4.9E-04																	
mcpb	3.6E-03			8.4E-03							5.4E-02												
pendimethalin	5.5E-04			6.9E-04	1.2E-02	2.1E-03		1.1E-02		2.2E-02					1.6E-02			2.8E-03			4.1E-04		5.5E-04
prometryn							3.7E-04									1.5E-04	2.2E-04					3.7E-04	1.5E-03
propachlor											1.1E-01			6.4E-03					7.2E-02				
simazine											1.2E+00												
s-metolachlor													3.1E-04										
trifluralin									7.5E-03					7.5E-03	1.2E+00								
carbofuran						1.7E-04																	
chlorpyrifos																			4.6E-03				
dazomet	3.3E-01	4.7E-01								6.0E+00													
diazinon																						2.4E-02	1.2E-01
dimethoate														3.5E-03					2.9E-02		4.7E-03		
methiocarb									4.8E-05														
methomyl								1.1E+01															
pirimiphos-methyl																1.1E-03							
1,3-dichloropropene		1.4E-02	2.2E-03					9.5E-01		1.5E-01		1.9E-02			8.4E-01					4.6E-03			
total	4.5E-01	9.6E-01	1.1E-01	8.7E-02	8.3E-01	3.8E-02	1.5E-03	1.6E+01	1.3E-01	1.4E+01	1.5E+00	2.5E+00	6.5E-01	2.0E-02	1.5E+01	6.5E-03	2.2E-02	9.3E-02	3.1E+00	2.2E+00	1.3E-02	4.0E-01	2.0E-01