SR 862

Pesticide use and freshwater ecotoxic impacts in biofuel feedstock production: a comparison between maize, rapeseed, *Salix*, soybean, sugarcane and wheat

Maria K. Nordborg

May 2013

Pesticide use and freshwater ecotoxic impacts in biofuel feedstock production: a comparison between maize, rapeseed, *Salix*, soybean, sugarcane and wheat

Maria K. Nordborg

SR 862
ISBN: 978-91-7290-326-5
v. 1.1

Cover picture: Pesticide application with boom sprayer in a soybean field in Goiás, Brazil. Photo: Christel Cederberg, 2011.

Foreword

This is a 30 credits Master of Science Thesis in Industrial Ecology at Chalmers University of Technology. The Thesis was conducted at the division of Physical Resource Theory at the Department of Energy and Environment at Chalmers and at SIK, the Swedish Institute for Food and Biotechnology, under the supervision of Christel Cederberg (SIK). Göran Berndes (Chalmers) was examiner of the Thesis.

Abstract

Background

Biofuel production is expected to increase significantly over the coming decades. Given that climate change mitigation is a major rationale for biofuel promotion, greenhouse gas savings have so far been a main concern, but there is a need to consider other environmental impact categories as well; for example ecotoxicity due to pesticide use in biofuel feedstock production. Ecotoxicity is an impact category that has often been omitted from agricultural Life Cycle Assessments in the past due to high complexity and lack of consensus regarding characterisation.

Aim and scope

The aim of this thesis is to evaluate the environmental performance of a selection of biofuel feedstocks in terms of pesticide use in cultivation and associated freshwater ecotoxic impacts. The feedstocks included are: maize (USA: two cases – with and without insecticide), rapeseed (Europe), *Salix* (Sweden), soybean (Brazil: GM and non-GM), sugarcane (Brazil) and wheat (Europe).

Method

Pesticide use was investigated and typical field application scenarios were constructed. PestLCI 2.0 was used as an emission inventory model to determine emissions to air and surface water and USEtox 1.01 was used as a characterisation model to determine the potential freshwater ecotoxic impacts expressed in Comparative Toxic Units ecotoxicity (CTUe). Additional pesticides, soil and climate profiles were added to PestLCI and additional characterisation factors (CFs) were calculated in USEtox. Pesticide use and ecotoxic impact scores were allocated to biofuels and associated co-products through partitioning based on energy content (no co-products were assumed for *Salix* and sugarcane).

Results

Sugarcane, conventional soybean and maize all require almost the same amount (18−19 g) of pesticide active substance (AS) for production of 1 GJ biofuel energy while rapeseed and wheat require 40% and 80% more respectively. *Salix* has by far the lowest pesticide AS application rate, both per hectare and year and per energy unit of biofuel output. Concerning freshwater ecotoxic impacts per hectare and year, *Salix* and rapeseed have the lowest scores (1 and 2 CTUe/ha/yr respectively) and sugarcane the highest: 89 CTUe/ha/yr - which is more than three times that of any other feedstock. The high score of sugarcane is associated with the use of the herbicides atrazine, 2,4-D and ametryn. In relation to biofuel energy output, the impact score of sugarcane is improved in relation to the other crops, due to high energy output. Production of 1 TJ biofuel energy from rapeseed causes an ecotoxic impact score of 31 CTUe, while production of 1 TJ biofuel energy from wheat, maize (insecticide case), GM soybean and sugarcane give rise to ecotoxic impact scores 4, 10, 13 and 22 times larger, respectively. The European cases have lower ecotoxicity scores in general compared to the North and South American cases; probably an effect of stricter pesticide legislation in Europe. The top-three AS with highest ecotoxic impact scores are atrazine (sugarcane, 56.8 CTUe/ha/yr), 2,4-D (sugarcane, 17.8 CTUe/ha/yr) and chlorpyrifos (maize, 16.1 CTUe/ha/yr) – all three of which are known to be problematic pesticides.

Conclusions

There is a large variation in freshwater ecotoxic impacts of the assessed alternatives, both when compared to hectare and year and biofuel energy output. In addition, allocation influence the results significantly. There is no correlation between amount of pesticides used and ecotoxic impact caused, but location and timing are highly significant for emissions to various environmental compartments and hence ecotoxic impact scores. The largest challenges were encountered in relation to the dynamic character of pesticide use and in dealing with ecotoxicological effect data in calculation of new CFs. The models used are still immature and further research is needed to develop and make models fully compatible. Due to the limitations of the study, especially in relation to inventory of pesticide use, the ecotoxic impacts cannot be interpreted as fully representative for the crops in general. However, *Salix* has the lowest (most favourable) score in all environmental performance indicators and it is likely that a future biofuel from *Salix* would be associated with lower pesticide use and associated freshwater ecotoxic impacts compared to the other alternatives.

Key words

Freshwater ecotoxicity, biofuel, pesticides, USEtox, PestLCI, maize, rapeseed, *Salix*, soybean, sugarcane, wheat.

Sammanfattning

Bakgrund

Framställning av biodrivmedel förväntas öka väsentligt inom en snar framtid. Givet att biodrivmedel premieras som ett led i att reducera klimatpåverkan är det naturligt att diskussionen kring biodrivmedels miljöaspekter hittills mest handlat om potentiella utsläppsbesparingar av växthusgaser, men det finns ett tydligt behov av att beakta även andra miljöpåverkanskategorier; till exempel ekotoxicitet på grund av användningen av bekämpnings-medel i odlingen av biodrivmedelsgrödor. Ekotoxicitet är en miljöpåverkanskategori som tidigare ofta uteslutits från livscykelsanalyser av jordbruksprodukter på grund av hög komplexitet och brist på konsensus med avseende på miljöpåverkansbedömning.

Syfte och omfattning

Syftet med denna studie är att utvärdera miljöprestanda hos ett urval av biodrivmedelsgrödor med avseende på bekämpningsmedelsanvändning och potentiell sötvattensekotoxicitet orsakad därav. De grödor som ingår i studien är: majs (USA: två fall – med och utan insekticid), raps (Europa), *Salix* (Sverige), soja (Brasilien: GM och icke-GM), sockerrör (Brasilien) och vete (Europa).

Metod

Bekämpningsmedelsanvändningen undersöktes och typiska applikationsscenarier upprättades för varje gröda. PestLCI 2.0 användes för att beräkna utsläppen till luft och ytvatten och USEtox 1.01 användes för att bedöma sötvattensekotoxiciteten uttryckt i Comparative Toxic Units ecotoxicity (CTUe). Nya pesticider samt jord- och klimatprofiler lades till i PestLCI vid behov och ytterligare karakteriseringsfaktorer beräknades i USEtox. Bekämpningsmedelsanvändning och ekotoxicitetstal allokerades till biodrivmedel och biprodukter, baserat på energiinnehåll (inga biprodukter antogs för *Salix* och sockerrör).

Resultat

Produktion av 1 GJ biodrivmedelsenergi från sockerrör, konventionell soja och majs kräver i stort sett lika stor mängd aktiv substans (AS) pesticid (18−19 g), medan raps och vete kräver 40% respektive 80% mer. *Salix* har den överlägset lägsta bekämpningsmedelsanvändningen, både i relation till hektar och år och i relation till energiavkastning. I fråga om sötvattensekotoxicitet, har *Salix* och raps lägst ekotoxicitetstal per hektar och år (1 respektive 2 CTUe/ha/år) och sockerrör högst: 89 CTUe/ha/år, vilket är mer än tre gånger så högt som för någon annan gröda. Sockerrörs höga ekotoxicitetstal beror på användningen av de tre herbiciderna atrazin, 2,4-D och ametryn. I relation till energiavkastning är dock sockerrörs ekotoxicitetstal förbättrat i jämförelse med de andra grödorna, på grund av hög energiavkastning. Produktion av 1 TJ biodrivmedelsenergi från raps ger upphov till ett ekotoxicitetstal på 31 CTUe, medan produktion av 1 TJ biodrivmedelsenergi från vete, majs (insekticid-fallet), GM soja och sockerrör ger upphov till ekotoxicitetstal som är 4, 10, 13 respektive 22 gånger större. Grödorna som odlas i Europa har generellt lägre ekotoxicitetstal jämfört med grödorna som odlas i Nord- och Sydamerika; troligen ett resultat av striktare pesticidlagstiftning i EU. De tre AS med störst ekotoxicitetstal är atrazin (sockerrör, 56.8 CTUe/ha/år), 2,4-D (sockerrör, 17.8 CTUe/ha/år) and klorpyrifos (majs, 16.1 CTUe/ha/år) – all tre kända för att vara problematiska pesticider.

Slutsatser

Det finns en stor variation i sötvattensekotoxicitet mellan de jämförda alternativen, både i relation till hektar och år och energiavkastningsenhet. Allokering har en stor påverkan på resultaten. Det finns inget samband mellan mängd använda pesticider och ekotoxicitet, däremot är plats och tidpunkt av central betydelse för utsläppen till luft och ytvatten och därmed även ekotoxicitet. De största utmaningarna var att handskas med bekämpningsmedels-användningens dynamiska karaktär och ekotoxikologisk effektdata vid beräkning av nya karakteriseringsfaktorer. Modellerna som användes är än så länge relativt nya och mer arbete behövs för att utveckla och göra dem kompatibla. På grund av studiens begränsning, speciellt gällande inventering av bekämpningsmedels-användningen, bör ekotoxicitetstalen inte ses som representativa för grödorna generellt utan snarare som resultat av dessa specifika fall. Dock kan det slås fast att *Salix* har lägst (fördelaktigast) resultat i samtliga indikatorer och det är troligt att ett framtida biodrivmedel från *Salix* skulle ge upphov till lägre bekämpningsmedelsanvändning och sötvattensekotoxicitet än övriga jämförda alternativ.

Acknowledgements

I would like to extend sincere gratitude and appreciation towards everyone involved in this project, especially my supervisor Christel Cederberg, agronomist and adjunct professor at the Swedish Institute for Food and Biotechnology (SIK) and my examiner Göran Berndes, associate professor at Physical Resource Theory, Chalmers. Thank you, Christel, for sharing your large engagement, interest and knowledge about pesticide related issues and for always taking time for this project, even when time was scarce. Thank you, Göran, for valuable comments during the course of the project and for always being positive and supportive.

I would also like to extend a special thanks to everyone at the department of Sustainable Food Production (Miljö och Uthållig produktion) at SIK. Thank you for providing me with the ideal working environment to do my Master's Thesis in and for positive and constructive critique following my presentation. A special thanks to Magdalena Wallman for always being helpful, answering day-to-day questions and discussing difficulties.

I would also like to thank everyone that contributed with their expertise in this project – without your knowledge and experience this project would not have been possible. Thanks to David Ertl, Erik Gerlach, Daniel Meyer, Nils Yngvesson and Per Åsheim for providing valuable crop specific information. Thanks to Peter Fantke, Mark Huijbregts and Teunis Dijkman for providing support in relation to models. A special thanks to Teunis for your extensive help with adjusting PestLCI and always being fast – and answering many questions!

I would also like to thank everyone that read through earlier drafts of this report, scanning for errors and contributing towards increased quality of the text. This includes Andreas Emanuelsson and Magdalena Wallman at SIK and opponents Filip Buric, Lina Hammarstrand and Andreas Särnberger at Chalmers.

List of abbreviations

2,4-D	2,4-dichlorophenoxy acetic acid
AMI	Assessment of the Mean Impact: assessment method in ecotoxicology
AS	Active substance. The biologically active part of a pesticide formulation.
Bt	*Bacillus thuringiensis*. Referring to type of genetic modification in which crops have integrated ability to produce insecticidal bacterial toxins from the Bt-bacterium.
CAS	Chemical Abstracts Service: numerical identification system of chemicals.
CF(s)	Characterisation factor(s)
CTUe	Comparative Toxic Units ecotoxicity
DDGS	Dried Distillers Grains with Solubles. Co-product from the ethanol production process used as protein fodder for livestock.
DDT	Dichlorodiphenyltrichloroethane, an organochlorine insecticide.
DTU	Technical University of Denmark
EPA	Environmental Protection Agency
EU	European Union
F	Fungicide(s)
FAME	Fatty Acidy Methyl Esters (biodiesel)
FAO	Food and Agricultural Organisation of the United Nations
GM	Genetically modified
H	Herbicide(s)
Ha	Hectare (1 ha = 10 000 m^2)
I	Insecticide(s)
IEA	International Energy Agency
ILCD	International Reference Life Cycle Data System
J	Joule
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
n.a	not available
n.d	no date
PAF	Potentially Affected Fraction
PGR	Plant Growth Regulators: a type of pesticide
RR	Roundup Ready
SIK	Swedish Institute for Food and Biotechnology
SMILES	Simplified Molecular Input Line Entry System. A chemical notation system used to represent a molecular structure by a linear string of symbols.
SRWC	Short Rotations Woody Coppice
USDA	United States Department of Agriculture
Yr	Year

Prefixes used

K	(kilo - thousand)	10^3
M	(mega - million)	10^6
G	(giga)	10^9
T	(tera)	10^{12}
E	(exa)	10^{18}

List of tables

List of figures

CONTENTS

1. INTRODUCTION

Humanity is facing an urgent need to reduce global greenhouse gas (GHG) emissions substantially to avoid irreversible negative effects on the climate system (IPCC, 2007). The transport sector is a significant contributor, responsible for approximately 13% of global GHG emissions. Current transportation technologies rely essentially on finite fossil energy sources – petroleum supplied 95% of the total energy used in the global transport sector in 2004. Transportation is expected to grow significantly over the coming decades with an annual energy growth rate of 2% in the sector (Barker et al. 2007).

In order to address climate change, the transport sector is facing the challenge of shifting from fossil fuels to more sustainable fuels and biofuels have been identified as one important contributor towards this end. Biofuels currently supply around 3% of the global road transport fuel demand (IPCC, 2011). However, this share is expected to rise significantly over the coming decades as a result of national policies and plans aimed at reducing GHG emissions, increase energy security and support domestic agriculture (Pires and Schechtman, 2010). A scenario developed by the International Energy Agency (IEA) suggests that by 2050 biofuels might supply 27% of the world transport fuel (IEA, 2011).

Agricultural systems of today are dependent on synthetic inputs such as fertilizers and pesticides. Pesticides are chemicals designed to kill target organisms but pose a potential threat not only to target organisms but also human health (Hallenbeck and Cunningham-Burns, 1985) and the environment at various scales (Thompson, 1996). Over the past decades, the worldwide production and use of pesticides has increased (FAO, 1999) and it is likely that the future large-scale deployment of biofuels will lead to increased dependence on agrochemicals as the world population is growing along with its demands on food, fibre and fuel from agricultural land.

Conventional biofuels of today are mainly produced from food crops in intense agricultural systems, and are commonly assumed to have a better environmental performance than the fuels they replace. However, this perception deserves to be questioned and the projected large-scale deployment of biofuels carefully investigated to ensure that the transition towards reduced fossil fuel dependency in transportation is achieved in a sustainable manner without unacceptable risks. Policy makers as well as industry need guidance to encourage investment in biofuels with low environmental impacts and avoid technology lock-in in biofuel production systems with high environmental impacts. Up to now, focus has been mainly on potential GHG saving from biofuels, demonstrated in for example the EU Renewable Energy Directive (EC, 2009a) and the US Renewable Fuel Standard (USEPA, 2007), but there is a need to consider all relevant environmental impacts associated with the entire life cycle of biofuels; from cultivation through production and use. Not least the environmental impacts from intensive pesticide, most important ecotoxicity.

Life cycle assessment (LCA) is an environmental system analysis tool that can be used to map the impacts of products along their life cycle and characterise the impacts in various categories. Ecotoxicity is an impact category that has often been omitted from agricultural LCAs in the past (Rosenbaum et al. 2008) due to high complexity and lack of consensus regarding characterisation. However, consensus among key researchers in ecotoxicity was reached in 2008 with the launch of the “scientific consensus” model USEtox (Rosenbaum et al. 2008).

At the department of Sustainable Food Production (Miljö och Uthållig produktion) at the Swedish Institute for Food and Biotechnology (SIK) numerous agricultural LCAs have been conducted over the years, but ecotoxicity has seldom been included as an impact category due to lack of knowledge about available characterisation methods. However, there is an ambition at SIK to include ecotoxicity in future LCAs (Cederberg, pers. com. 2013). A previous SIK Master’s Thesis (Bennet, 2012) concluded that USEtox is the most suitable model for LCA practitioners at SIK - marking a first important step towards integrating ecotoxicity. The thesis is a further step towards this goal.

It is clearly urgent to take a closer look on pesticide use in a biofuel context and compare various biofuel feedstocks in terms of ecotoxic impact potential. There is also a need at SIK to learn more about available ecotoxicity characterisation methods - this study combines these two objectives.

This thesis is the first of its kind, using a state-of-the-art pesticide inventory model, PestLCI 2.0 (Dijkman et al. 2012), and the best available model for characterisation of freshwater ecotoxicity (Hauschild et al. 2013); USEtox (Rosenbaum et al. 2008) for studying the potential freshwater ecotoxicity caused by pesticide use in a selection of biofuel crops.

2. AIM, SCOPE AND DELIMITATIONS

Aim

The aim of this thesis is to

(a) compare a selection of biofuel feedstock production systems in terms of pesticide use and associated potential freshwater ecotoxic impact, in order to
(b) evaluate the environmental performance of the different biofuel feedstock production systems, and by doing so,
(c) contribute to methodology development within the ecotoxic impact category in Life Cycle Assessment at the Swedish Institute for Food and Biotechnology (SIK).

Scope and delimitations

The comparison and evaluation includes six biofuel feedstock production systems, listed in table 2.1 together with key characteristics and the defined regions of the studies.

Table 2.1 Selected biofuel cropping systems for this study, key characteristics and defined regions of the studies.

Crop / biofuel feedstock	Type of biofuel	Character of cropping system	Conventional / advanced	Defined region
Maize	ethanol	annual	conventional	USA
Rapeseed	biodiesel	annual	conventional	Northern Europe
Salix	ethanol	perennial	advanced	Sweden
Soybean	biodiesel	annual	conventional	Brazil
Sugarcane	ethanol	perennial	conventional	Brazil
Wheat	ethanol	annual	conventional	Northern Europe

Table 2.1 shows that the scope includes five conventional biofuel feedstocks, of which three ethanol feedstocks and two biodiesel feedstocks. The various crops represent four annual and two perennial cropping systems. This scope include some of the most prominent biofuel feedstocks currently available and one example of an advanced ethanol feedstock[1].

The thesis is limited to evaluate freshwater ecotoxicity, as a result of pesticide emissions to air and surface water, following direct pesticide field application. Accidental spills and emissions that originate from handling and storage of pesticides are not included and neither are emissions that originate from other stages in the life cycle of pesticides.
Emissions to other environmental compartments such as soil and ground water are not included. Terrestrial and marine ecotoxicity as well as human toxicity are beyond the scope of this thesis.

[1] An introduction to biofuels including conventional and advanced biofuel feedstocks is provided in chapter 3.1.

Only the active substances (AS) in herbicides (H), fungicides (F) and insecticides (I) are included. Other types of pesticides, such as nematicides and seed disinfectants, as well as other pesticide product ingredients, such as solvents and surfactants, are not included[2].

Toxicity of pesticide metabolites, as well as cocktail effects, are beyond the scope of this thesis.

[2] An introduction to pesticides is provided in chapter 3.2.

3. BACKGROUND

Chapter 3 present background information of relevance for thesis and can be omitted by the well-versed reader. The information has been complied through literature review.

Chapter 3.1 provides an introduction to biofuels and biofuel feedstocks with focus on the current situation from a global perspective. The most important conventional biofuel feedstocks are listed and major future developments within the sector are projected. The scope of this thesis is motivated in this chapter.

Chapter 3.2 provides an introduction to pesticides. The chapter reviews and discusses advantages and disadvantages of pesticides, various pesticide classification systems, pesticide indicators found in the literature and in statistics and ends with a discussion on pesticide resistance and genetically modified (GM) crops. Special sections are devoted to glyphosate and alternatives to chemical management.

Chapter 3.3 provides an introduction to Life Cycle Assessment (LCA) since key methodology in this thesis is derived from LCA. The various steps of LCA are outlined with particular focus on Life Cycle Impact Assessment (LCIA).

Chapter 3.4 provides an introduction to toxicity in LCIA. The basic theory for toxicity assessment in LCA is outlined and key concepts such as fate, exposure and effect reviewed. The chapter ends with a section on ecotoxic effect assessment in LCA and models for toxicity in LCIA.

3.1 Biofuels and biofuel feedstocks

Bioenergy is energy derived from biomass and is classified as renewable. The global demand and use of bioenergy has increased during the past 40 years and accounted for 10.2% of global primary energy supply in 2008, or 50.3 EJ. 60% of the biomass feedstock consisted of traditional biomass, in the form of fuel wood used for cooking and heating in primarily developing countries (IPCC, 2011).

Biofuel is one type of bioenergy, that may be defined as liquid and gaseous fuels of organic origin (IEA, 2011), typically used in the transport sector in the form of ethanol, biodiesel and biogas. Biofuels supplied around 2% of the global road transport fuel demand in 2008, and close to 3% in 2009 (IPCC, 2011), but this share is expected to rise significantly over the coming decades. A scenario recently developed by International Energy Agency (IEA), aimed at cutting global greenhouse gas (GHG) emissions by half until 2050, suggests that biofuels may contribute significantly towards this goal by supplying up to 27% of the world transport fuel in 2050 (IEA, 2011).

The global biofuel production has grown at remarkable rates during the past decade: between 2000 and 2008, the yearly production of ethanol increased by 18% per year while biodiesel increased with 37% per year (Pires and Schechtman, 2010).

The growth of the biofuel sector is policy driven by mainly USA, Brazil and EU, with the objectives to increase energy security, support domestic agriculture and reduce GHG emissions (Pires and Schechtman, 2010). It has been estimated by IEA Bioenergy (2009) that the future production growth rate of biofuels will be 6 − 8% yearly.

Many countries have policies and plans aimed at increasing the biofuel share in transport for example in the form of blend regulations. The USA's Renewable Fuel Standard dictates how much biofuel that shall be used in the transport sector in absolute terms (USEPA, 2007); the European Union's Renewable Energy Directive bids that 10% of the total energy consumption in the transport sector shall come from renewable sources in 2020 (EC, 2009a) and in Sweden there is an ambitious goal of a fossil free vehicle fleet by 2030 (Government Offices, 2008).

Conventional biofuels

Biofuel feedstocks may be transformed on various conversion routes, depending on the physical and chemical nature of the feedstock, to different types of energy carriers being either liquid or gaseous. Biofuels are commonly separated into different classes depending on their level of maturity and the feedstocks they use. Conventional biofuels, or first generation of biofuels, refer to mature fuel technologies that are already widely commercialised and include bioethanol, referred to as ethanol hereafter, from sugar and starch crops, biodiesel from oil crops, renewable diesel from waste oils and biomethane from agricultural or municipal waste (IEA Bioenergy, 2009). This thesis deals with feedstocks of agricultural origin.

Conventional ethanol is made by biologically fermenting the sugar in sugar or starch crops to ethanol. Starch crops have to go through a hydrolysis process prior to fermentation which requires additional energy compared to fermentation of sugar crops. Ethanol is used as a gasoline substitute in gasoline engines, sometimes mixed with petroleum gasoline in different blends depending on engine specifications. So called flexi-fuel vehicles can run on any blend of ethanol and petroleum gasoline (IEA Bioenergy, 2009).

Conventional biodiesel from oil crops are made by transesterification of vegetable oils with alcohol into fatty acid esters. Methanol is most commonly used, producing fatty acid methyl ester, FAME. Ethanol can also be used, producing fatty acid ethyl esters, FAEE. Biodiesels are used a substitute to petroleum diesel, and conventional diesel engines allow blending with up to 20% (IEA, 2011). Conventional renewable diesel is made from residual oils and fats, such as tallow and grease, through a hydrogenation process, although still only deployed small scale (IEA Bioenergy, 2009).

The global production of liquid biofuels reached 93 billion litres in 2009, of which 82% was ethanol and 18% biodiesel (IPCC, 2011). USA, Brazil and EU dominate the global biofuel production, with over 85% of the total production, followed by China and Canada (IEA Bioenergy, 2009).

USA and Brazil produce mainly ethanol (over 90%) while EU produce mainly biodiesel (approximately 80% biodiesel and 20% ethanol) with Germany and France as the largest producing countries. China and Canada produce mainly ethanol. More than 85% of all biodiesel is produced in the EU (IEA Bioenergy, 2009). European ethanol contributed 7% to global ethanol production in 2008 (F.O. Licht, 2009 cited in SJV, 2011).

Agricultural biofuel feedstocks can be classified into either of four categories based on their chemical make-up: oil, starch, sugar or lignocellulosa. Examples of feedstocks within each category are presented in table 3.1.

Table 3.1 Examples of biofuel feedstocks, both conventional and advanced, in the categories of oil, starch, sugar and lignocellulosa.

Category	Biofuel type	Examples of feedstocks	
Oil	biodiesel	rapeseed / canola oil palm soybean	sunflower jatropha cotton
Starch	ethanol	wheat maize rice	cassava potato barley
Sugar	ethanol	sugar cane sugar beet	sweet sorghum fruits
Lignocellulosa (herbaceous and woody)	ethanol	*Salix* spp. *Eucalyptus* spp.	switchgrass *Miscanthus*

Table 3.2 gives the shares of selected major biofuel feedstocks devoted to biofuel in 2000, 2005 and 2009 and shows that the shares for all feedstocks are increasing.

Table 3.2 Share of global production of selected biofuel feedstocks devoted to biofuel, 2000, 2005 and 2009[3] (LMC International, 2010).

Feedstock	Biofuel type	2000	2005	2009
Sugarcane	ethanol	12%	17%	22.5%
Maize	ethanol	2.5%	6%	13%
Rapeseed oil	biodiesel	3.5%	10%	33%
Soy oil	biodiesel	1%	2.5%	14%

Conventional ethanol feedstocks

In 2008 starch crops made up 55% of the feedstock into global ethanol production while sugar crops, mainly sugarcane, made up 42% of the feedstock. The remaining 3% consisted of other non-agricultural feedstocks such as forest residues or fossil fuels. 90% of the starch consisted of maize (F.O. Licht, cited in SJV, 2011), making maize the largest single feedstock into global ethanol production, accounting for close to 50%, followed by sugarcane.

The third largest feedstock into global ethanol production is wheat, of which approximately 9 million tonnes were used in 2010 (compared to approximately 135 million tonnes of maize) (IGC, cited in SJV, 2011). Other cereal feedstocks of regional importance include sorghum, barley and rye.

The share of total global production of cereals used in ethanol production has risen from 3 – 4% in 2005/2006 to 8 – 9% in 2010/2011 (IGC cited in SJV, 2011). Table 3.2 shows that 13% of all maize and 22.5% of all sugarcane produced globally was devoted to fuel ethanol in 2009.

The prime feedstocks to ethanol production in USA and Brazil are maize and sugarcane respectively. (IEA Bioenergy, 2009) The prime feedstock to ethanol production in Europe is wheat, followed by maize and smaller quantities of barley and rye (SJV, 2011).

[3] Figures have been visually read from a diagram in the cited source, therefore representing approximate values.

Conventional biodiesel feedstocks

Conventional biodiesel is primarily made from vegetable oils from oil crops and to a smaller degree from animal fats and waste cooking oil. (IEA, 2011) The share of total global production of vegetable oils used in biodiesel has risen steadily from a value close to 1% in 2000 to 12% in 2009, with a particularly strong increase after 2005. (LMC International, 2010) The top three vegetable oil produced globally is palm oil (42 million tonnes), soybean oil (37 million tonnes) and rapeseed oil (20 million tonnes)[4] (FAOSTAT, 2012).

Besides being produced in largest quantities, oil palm has the highest yield; up to 3-8 times more oil per hectare than all other oil crops. However, palm oil still only account for a minor contribution to global biodiesel production, around 1%, but indications point towards increased utilisation of palm oil in the future (Sheil et al. 2009 and Alkabbashi et al. 2009).

Rapeseed oil is the largest feedstock to biodiesel production today, globally and in the EU. The second largest feedstock in EU is imported palm oil. The prime feedstock to biodiesel production in North and South America is soybean oil. (SJV, 2011) 33% of all rapeseed oil and 14% of all soybean oil was devoted to biodiesel production in 2009 according to table 3.2.

Advanced biofuels

Advanced, or second generation, of biofuels, refer to a range of transport fuels that are produced through conversion technologies still at the demonstration and/or research stage, for example ethanol from lignocellulosic biomass and Fischer-Tropsch diesel (IEA Bioenergy, 2009).

Today, almost all biofuels are derived from crops grown on land that could be used for cultivation of food or feed. The strongest arguments in favour of advanced biofuels are that they have a higher energy efficiency, lower GHG emissions, provide a wider range of possible end-products and can in higher degree be derived from feedstocks grown on marginal land and from a wider set of possible feedstocks (Carlson and Antonson, 2011).

Examples of advanced ethanol feedstocks include woody and herbaceous lignocellulosa such as *Salix*, *Eucalyptus*, *Miscanthus* and switchgrass. Lignocellulosic biomass contains lignin, cellulose and hemicellulose. Cellulose and hemicellulose can be fermented to ethanol after being broken down into sugars in an enzymatic hydrolysis process, while the lignin remains as an unfermentable byproduct. The enzymatic hydrolysis process is more complex than breaking down starch and currently at the demonstration stage. It is expected that fuel ethanol from lignocellulose will begin to commercialise before 2020 (IEA Bioenergy, 2009 and 2012).

Examples of advanced biodiesel feedstocks include vegetable oils from non-edible oil crops such as Jatropha. Advanced biodiesel can also be made from gasification of biomass to syngas and further conversion through Fischer-Tropsch synthesis into synthetic diesels, bio-kerosene and various liquids. Example of technologies that are still

[4] Numbers refer to average yearly production quantities between 2006 and 2010.

at the research stage is conversion of sugars to synthetic diesel by help of yeast and algae as an oil feedstock – sometimes referred to as third generation of biofuel (IEA, 2011).

3.2 Pesticides

The term pesticide is defined by FAO (2003) as "*any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies*."

Pesticides are not only used in agriculture, but also in for example industry (wood preservatives, anti-fouling preparations etc.), horticulture, silviculture, animal-keeping (medicine etc.) and in household (insect repellents, sanitation etc.).

Pesticide formulations are sold under different trade names, for example Roundup, Cougar or Mavrik. Large pesticide manufacturers include for example Monsanto Company, Syngenta, Dow, Bayer CropScience and DuPont. Pesticide manufacturers and authorities sometimes prefer to use the term plant or crop protection products instead of pesticide.

Pesticide products often include several ingredients other than the active substance(s) (AS), for example: wetting agents, diluents, solvers, extenders, adhesives, buffers, preservatives and emulsifiers (FAO, 1996). Surfactants, adjuvants and fillers are other key ingredients that can increase the biological efficiency by up to a factor ten by modifying spray droplet size and increase crop uptake of the AS (Van Zelm et al. 2012).

The term pesticide also includes biocides, defoliants, fumigants, seed disinfectants (dressing agents/seed protection) and plant growth regulators (PGR). Biocides are pesticides with other purposes than plant protection usually found in industry, for example wood impregnators. Non-chemical biopesticides are also present on the market, referring to products based on naturally occurring plant toxins or micro-organisms with predatory or parasitic effects (FAO, 2007).

3.2.1 Advantages and disadvantages of pesticides

The application of pesticides in agriculture aims to keep impacts from pests on commodities on an economically acceptable level. By chemically managing weeds, pests and diseases increased yields and reduced operation costs can be achieved as agriculture becomes more rational, predictable and less labour intensive. Increased yields mean less land is needed to produce a certain amount of output. Chemical management also reduces the risk of lodged stands, development of fungal toxins, bad taste, misshaped crops, low fertility of seeds and problematic harvest (SJV and KemI, 2002).

Besides these advantages of pesticides, numerous disadvantages exist. For example, while pesticides are designed to kill target organisms they also pose a threat to the human health (Hallenbeck and Cunningham-Burns, 1985) and the environment at various scales (Thompson, 1996). While many man-made chemicals escape into the environment unintentionally during production or use, agriculture is one of the few areas in which chemicals are intentionally released into the environment to kill certain unwanted organisms (FAO, 1996).

Excessive or inappropriate use of pesticides may lead to plant poisoning, contamination of soil, disrupted soil ecology, increase in secondary pests and diseases, development of pesticide resistance, pesticide residues in food, ground water contamination and negative consequences for pollinators. (FAO, 2007) In the ecosystem level pesticides may cause disrupted predator-prey systems, reduced soil fertility and loss of biodiversity in various types of ecosystems (FAO, 1996).

The types of risks associated with pesticides have changed over time, as the type of pesticides in use has changed. The shift has been from highly toxic, unspecific, persistent and bioaccumulative pesticides (such as DDT) to modern chemically engineered compounds designed to be target-specific, biodegradable (FAO, 1999) and effective in much smaller doses. The main disadvantage of modern pesticides are their higher price, making them less available for poor farmers, and higher probability to lead to pesticide resistance (FAO, 2007).

Farmers in developing countries still to a large degree rely on old, cheaper pesticides with a less favourable environmental profile. These farmers currently face the largest challenges and risks associated with pesticide management (FAO, 1996 and 2007). While developing countries consume only 20% of global agro-chemicals, they suffer 70% of the intoxication cases (Lehtonen, 2009).

3.2.2 Classification systems

There are many ways to classify pesticides. To start with, pesticides can be classified based on target organisms, for example herbicides (weeds), insecticides (insects), fungicides (fungi or fungal spores), molluscicides (slugs and snails), acaricides (mites and ticks), rodenticides (rodents, e.g. rats) and nematicides (nematodes).

Most AS can be classified according to their chemical properties into chemical classes. Appendix I lists all pesticide AS covered in this thesis as well as the chemical classes they belong to.

A third way to classify pesticides is based on their biological mechanism function, also called mode of action. Herbicides often act by disrupting different functions related to photosynthesis, plant respiration, growth, cell and nucleus division or synthesis of proteins. Insecticides primarily act by disrupting the nervous system in different ways, for example by inhibiting the membrane transport of different minerals or inhibiting enzyme activities. Fungicides may act for example by inhibiting enzymes involved in the respiratory process or disturbing the glucose metabolism (Åkerblom, 2004).

The classification based on mode of action partially overlap with the classification based on chemical classes. Prominent groups of herbicide modes of action and how they work are: ACCase inhibitors - block an enzyme called ACCase[5], ALS inhibitors - block an enzyme called ALS or AHAS[6], dinitroanilines - inhibit the root cell division, triazines -

[5] ACCase: Acetyl coenzyme A carboxylase
[6] ALS: Acetolactate synthase. AHAS: acetohydroxyacid synthase.

inhibit photosynthesis, ureas - inhibit photosynthesis, bipyridyliums - disrupt cell membrane, synthetic auxins - disrupt plant cell growth and protein synthesis and glycines - inhibit amino-acid synthesis (Heap, 2013)

A fourth way of classifying pesticides is based on hazard and exemplified by the system developed by the World Health Organisation (WHO) that has gained widespread acceptance since its introduction 1975. The hazard referred to is acute risk to human health following exposure during a relatively short period of time and determined from assessments of oral and dermal LD50[7]-values on test animals. The WHO system comprises five classes: Ia - extremely hazardous, Ib –highly hazardous, II –moderately hazardous, III –slightly hazardous and U –unlikely to present acute hazard (WHO, 2010).

Glyphosate

Glyphosate is one of the most widely used herbicide AS today globally and deserves a special note due to its frequent appearance in this study. Glyphosate belongs to the glycines family and is a water soluble, broad spectrum, non-selective, systemic herbicide that works by inhibiting the enzyme EPSP[8] present in all plants, fungi and bacteria and essential for building proteins. Since the enzyme is not present in humans and animals it is claimed that glyphosate is a relatively harmless product when handled according to the safety instructions. (Greenpeace and GM Freeze, 2011) However, Lee et al. (2009) reports that glyphosate in combination with other common pesticide formulation ingredients can cause considerable health problems and death to swine and have caused death of humans upon ingestion. Cocktail effects are further discussed in chapter 7.4.

The first formulation containing glyphosate was introduced by the Monsanto Company in 1974 and today the company's glyphosate products are registered for use in over 130 countries, on more than 100 crops, which is more than that of any other herbicide. The most popular formulation containing glyphosate is sold under the brand name Roundup. (Monsanto Company, 2005) Monsanto Company's patent on glyphosate ran out in 2000, and since then, other companies also offer glyphosate formulations.

3.2.3 Statistics and pesticide indicators

Pesticide statistics are usually available in some form in developed countries, while for developing countries statistics are only occasionally available. Pesticide statistics can be divided into two broad categories: sales statistics and usage statistics (Eurostat, 2008).

Sales statistics are fairly simple to collect, but contain no information about which crops are treated, share of treated land, application intensity or variations between regions or crops. Sales statistics can be reported in terms of monetary value of sales or amount of sales, and are very crude indicators of trends. Eurostat conclude that (2008): "*sales statistics alone are virtually useless*".

Usage statistics cover all statistics concerning quantities of applied pesticides, gathered from farmers and growers by interviews or questionnaires. (Eurostat, 2008) Usage statistics in combination with sales statistics and information about crop acreages can produce a number of statistical measures, indicators, specified on aggregate level

[7] LD50: Lethal Dose 50 - the dose required to kill 50% of the test organisms.
[8] EPSP: 5-enolpyruvylshikimate-3-phosphate

(nationwide, for all of agriculture and all types of pesticides) or on a more detailed level (regional, crop specific and for different pesticides).

There is a general lack of harmonisation in the area of pesticide statistics, both in terms of which substances are included (for example if to include PGR in herbicides or not) and when and how data are collected and reported, which makes analysis across countries difficult. Harmonisation efforts in the EU are ongoing (Eurostat, 2008).

The closest available to official global pesticide statistics are the statistics compiled and reported by the Statistics Division of the United Nations Food and Agriculture Organisation (FAOSTAT) on pesticide trade by economic value and consumption by weight of AS, available for every FAO member country, for different chemical classes of pesticides, however not specified down to the level of different crops (FAOSTAT, 2012).

Due to the lack of global statistics, there exist no official figure on global pesticide use, but the latest estimate by the US EPA arrived at 1 590 000 tonnes AS in 2007, 60% of which was herbicides (including PGR), 25% insecticides and 15% fungicides. If other types of pesticides other than the above mentioned are included the total figure increases to 2 360 000 tonnes AS. The USA used an estimated 22% of world total in 2007. Globally the world spent more than 39.4 billion dollars on pesticides (all types) in 2007, of which USA spent 32%. Around 40% of the total expenditures were spent on herbicides, followed by insecticides and fungicides (USEPA, 2011).

In EU25 213 000 tonnes of herbicides, fungicides and insecticides AS were used in 2003, of which 50% were fungicides, 39% herbicides and 11% insecticides. The very large share of fungicides is because EU classify inorganic sulphur as fungicides. Inorganic sulphur is used primarily in wine yards and make up over a quarter of the total amount of pesticide AS used (European Commission, 2007).

In Sweden 2 400 tonnes of herbicides, fungicides and insecticides AS were sold in 2011, of which 90% were herbicides, 9% fungicides and 1% insecticides (KemI, 2012).

None of the statistical measures currently in use is fully satisfactory in relation to assessing trends related to pesticide dependency, intensity, risks and toxicological effects due to lack of correlation between applied amounts and toxicity. For example; a decrease in pesticide use per hectare and year does not by certainty mean reduced pest control and lower impacts on human health and the environment (Wivstad, 2010).

It is of great importance to measure, monitor and report the global use of pesticides in order to be able to keep track of trends, assess risks for humans and the environment and manage future use, but there is a need for more sophisticated indicators for pesticide use to be able to interpret the statistics in a meaningful way, better correlate and understand relationships between applied amounts and effectiveness, dependency, risks and toxicological effects.

Denmark is currently advancing in the area of pesticide statistics. Recently, efforts have been taken by the Danish Ministry of Environment (Miljøministeriet) to evaluate pesticides based on toxicity in order to be able to introduce a differentiated pesticide tax intended to create incentives for more environmentally benign and sound pesticides (Miljøministeriet, 2012). In preparation for the introduction of the tax, two new indicators have been developed to assist in pesticide evaluation and these will be included in the future yearly pesticide statistics.

These, and some other examples of indicators that can be encountered in the literature or in statistics, are described below.

Hectare Dose

This indicator has been developed by Statistics Sweden (Statistiska Centralbyrån, SCB) and is used in SCB's yearly pesticide statistic. It is calculated at the national level for herbicides, fungicides and insecticides separately as the quotient between sold[9] amount and recommended dose per hectare, summed over all pesticides. The recommended dose per hectare is taken from manufacturer specification if available or else from the Swedish Board of Agriculture. (SCB and KemI, 2012) Assuming the number of pesticide formulations sold is P, the formula can be expressed as in equation 3.1.

$$Hectare\ doses\ [ha] = \sum_{p=1}^{P} \frac{sold\ amount\ (p)\ [kg]}{recommended\ dose\ per\ ha\ (p)\ [\frac{kg}{ha}]}$$

Equation 3.1

This indicator can be interpreted as the number of hectares that has been treated with the recommended dose one time during one year. SCB also calculates and provides statistics over crop specific hectare doses.

Figure 3.1 present two indicators for Swedish agriculture between 1982 and 2010 and show that the indicator kg AS per hectare has declined steadily during the past 30 years, in part due to increased reliance on low-dose formulations, while the indicator hectare doses has fluctuated more over time but remained at more or less the same level. This shows that the indicator hectare dose is a better measurement of pesticide dependence than applied amounts.

[9] The statistics are collected from manufacturers on basis of sales volumes, but is interpreted in the statistics as used amounts.

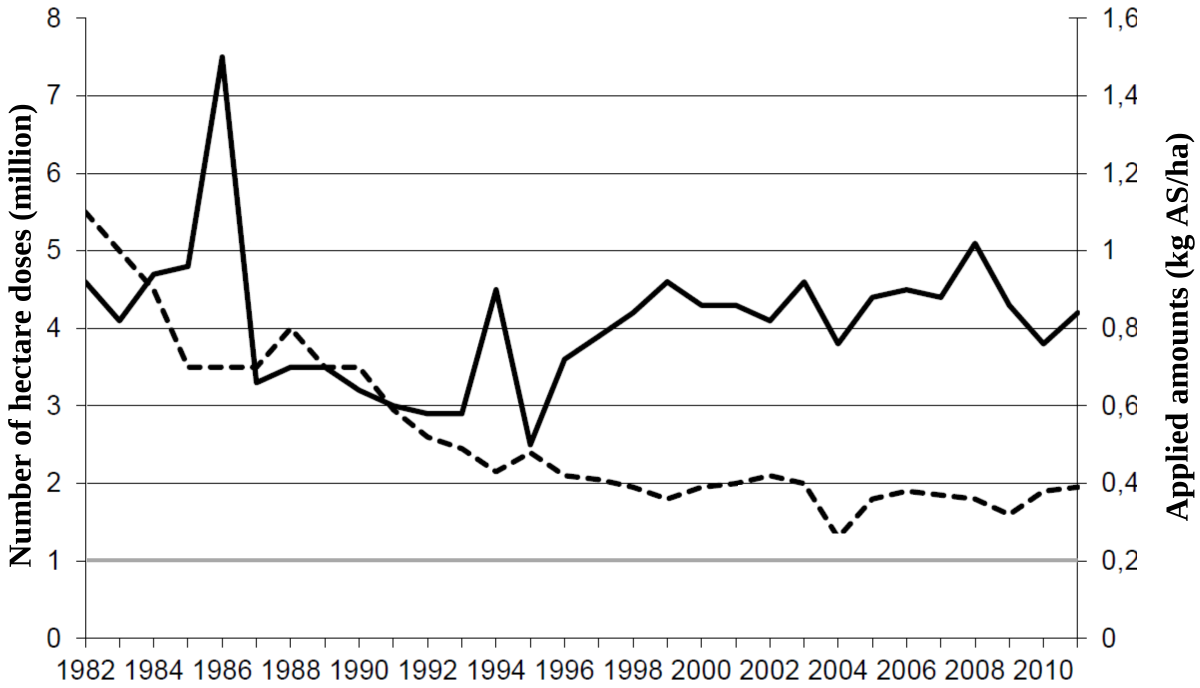


Figure 3.1 Applied pesticides in kg active substance per hectare (dashed line) and total number of hectare doses (full line) in Swedish agriculture 1982 – 2010 (Graph adopted and modified from KemI, 2012 and reproduced with permission).

Behandlingshyppighed / Hectare doses per hectare

The hectare dose indicator divided with acreage produces an indicator of the type hectare doses per hectare, which can be interpreted as the number of times one hectare can be treated one time during one growing season, assuming the recommended dose is applied. This indicator can be calculated for the total conventional agricultural area, or for areas occupied by specific crops. An indicator of this type, called *behandlingshyppighed*, has been used in Danish statistics for over 20 years (Miljøministeriet, 2012). SCB also uses this type of indicator in their yearly statistics, although without having given it a specific name (SCB and KemI, 2012).

While the number of hectare doses has remained at more or less the same level since 1982, the indicator hectare doses per hectare has increased, as around 400 000 hectares have been converted to organic farming since 1982 (Cederberg, pers. com. 2013).

Standardised treatment index (STI)

The STI indicator was developed in context of the Network for the Evaluation of The Pesticide Use in different Natural areas of Germany (NEPTUN)- project. The STI is calculated for each crop as a sum over all applications multiplying the number of AS in each application with application rate and share of treated land (Sattler et al. 2006). Assuming the total number of applications in a specified crop is denoted N, the STI can be expressed as in equation 3.2.

$$STI\ [-] = \sum_{n=1}^{N} number\ of\ AS's\ (n) \cdot \frac{applied\ dose\ (n) \left[\frac{g\ AS}{ha}\right]}{recommended\ dose\ (n)\ \left[\frac{g\ AS}{ha}\right]} \cdot \frac{treated\ area\ (n)[ha]}{total\ area\ [ha]}$$

Equation 3.2

Dose area indicator

The dose area indicator, freely translated from the Swedish *dosyteindex*, was developed by researchers at the Swedish Agricultural University (Sveriges Lantbruksuniversitet, SLU). It is calculated for a specific crop as a sum over all pesticide applications N multiplying the application rate and share of treated land (Nilsson, 2001), as in equation 3.3.

$$Dose\ area\ indicator\ [-] = \sum_{n=1}^{N} \frac{applied\ dose\ (n)\ \left[\frac{g\ AS}{ha}\right]}{recommended\ dose\ \left[\frac{g\ AS}{ha}\right]} \cdot \frac{treated\ area\ (n)\ [ha]}{total\ area\ [ha]}$$

Equation 3.3

Note that STI and dose area indicator only differ in terms of number of AS in each application.

Pesticide Load Indicator

The pesticide load indicator, freely translated from the Danish *PesticidBelastningsIndikatoren* (PBI) is the first of the two new indicators developed by the Danish Ministry of Environment and intended to assist in evaluation of pesticide environmental and health performance needed for designing the pesticide tax. It is a composite indicator, presented in table 3.3, consisting of three main indicators: health, environmental behaviour (related to fate) and environmental impact. The main indicators environmental behaviours and impact in turn consists of subindicators.

The load is calculated in different ways for the different subindicators. For example, the load in the main indicator human health is calculated based on a score point system and the hazard classifications labels associated with the different pesticides, while the load in the subindicator bees is based on acute LD50-values. The result for each indicator is an index that can be summed across the indicators to produce the total load (Miljøministeriet, 2012).

Table 3.3 Main and subindicators of the Danish pesticide load indicator (Miljøministeriet, 2012).

Main indicator	Subindicators	Unit
Human health	-	Load per kg formulation
Environmental behaviour	Persistence Bioaccumulation Mobility / leaching	Load per kg AS
Environmental impact	Mammals Birds Earthworms Aquatic environment Daphnia Aquatic plants Bees Fish Algae	Load per kg AS

Pesticide Load per area Indicator

The pesticide load per area indicator, freely translated from the Danish *FladeBelastning*, is the second of the two indicators developed by the Danish Ministry of Environment. It takes the result from the Pesticide Load Indicator and divides by acreage to produce an indicator with the unit load per area, usually hectare (Miljøministeriet, 2012).

3.2.4 Pesticide resistance and genetically modified crops

In recent years advancements in biotechnology and molecular biology have made genetic modification (GM) of crops possible. Ever since the mid-1990s GM crops developed by companies such as Monsanto Company, Syngenta, Bayer CropScience and BASF have been commercially available on the market in some countries, whereas legislation has restricted their use in others. The top GM crops on the market today include soybean, maize, cotton and rice. Traits that have been developed and integrated are for example herbicide tolerance, insect resistance, amino acid composition, modified colours and delayed ripening. (CERA, 2012) Glyphosate tolerance is one of the most popular and widespread modifications, or in the words of Syngenta (2009); "*the most quickly adopted technology in the history of agriculture*".

GM glyphosate tolerant crops, for example Monsanto Company's Roundup Ready (RR) crops, are today primarily grown in North and South America, while no GM glyphosate tolerant crops have been approved for commercial cultivation in the EU so far. For example, 90% of the soybean grown in the USA in 2009 was GM RR (Greenpeace and GM Freeze, 2011) and 98% of Syngenta's soybean seed is glyphosate tolerant (Syngenta, 2009).

The introduction of glyphosate tolerant crops has changed agricultural practices profoundly. Previously glyphosate was used before planting to clear the soil from weeds. Today glyphosate tolerant crops allow glyphosate to be sprayed on top of developing crops without harming them while eliminating weeds. This has paved the way for a shift towards reduced till or low-till practices, which is claimed to protect the soil structure and microorganisms, reduce erosion and save farmers fuel, time and money (Monsanto Company, 2005 and PIC, 2012).

In addition Monsanto Company claims that their RR system reduces the overall amount of herbicides used (Monsanto Company, n.d) while critics, such as Greenpeace and GM Freeze as well as independent researchers, claim that RR systems in fact have increased the overall use of herbicides due to large use of glyphosate. Studies have shown that the use of glyphosate on a selection of crops in the USA has increased following the adoption of GM RR crops; 39% for maize (1996 − 2005), almost 200% for cotton (1996 − 2007) and almost 100% for soybean (1996 − 2006) (Benbrook, 2001, 2004 and 2009, cited in Greenpeace and GM Freeze, 2011) A recent SIK study on pesticide use in Brazil following the adoption of GM RR soy show that pesticide use in Brazil has increased simultaneously with the nation-wide adoption of GM RR soy; herbicides with 50% (2003 − 2008) and fungicides and insecticides with 70% (2004 − 2008) (Meyer and Cederberg, 2010).

There are also mounting evidence that the heavy reliance on glyphosate over large areas in combination with abandonment of other alternative, traditional, weed management methods have led to increasing problems with herbicide resistant weeds, although the problem with pesticide resistance is by no means limited only to GM RR crops.

Due to natural genetic variability in every population of plants, insects or fungi, there is always a small share of individuals that are less susceptible to pesticides. In a test population of insects never exposed to insecticides, the share is usually less than 1‰ (Ekbom, 2002). After an insecticide treatment the less-susceptible share increases and the more frequent the treatments, the faster the selection of resistant individuals. The same pattern of development applies for weed and fungi.

Today, at least 500 insect species globally have developed resistance against at least one type of insecticide (Ekbom, 2002) and 210 weed species have developed resistance against at least one type of herbicides; the ten most important being: rigid ryegrass (*Lolium rigidum*), wild oats (*Avena fatua*), redroot pigweed (*Amaranthus retroflexus*), common lambsquarters (*Chenopodium album*), green foxtail (*Setaria viridis*), barnyard grass (*Echinochloa crus-galli*), goosegrass (*Eleusine indica*), kochia (*Kochia scoparia*), horseweed (*Conyza canadensis*) and smooth pigweed (*Amaranthus hybridus*). The top three modes of action with the highest number of resistant biotypes are ALS-inhibitors, triazines and ACCase inhibitors (Heap, 2013).

Integrated pest management – alternatives to chemical management

To slow the development of resistant populations it is important to take on an integrated pest management approach combining chemical treatment with other, more traditional management methods, of mechanical, biological and cultural nature. Examples include:

- till (turn over) the soil between cultivation periods to prevent weeds from growing and seeds from germinating (mechanical)
- hoe between rows with specialised equipment during crop development to remove weeds (mechanical)
- select varieties with natural resistance to diseases and pests (cultural)
- apply crop rotation schemes, where different crops follow each other in a specific manner from year to year in order to optimise the use of soil nutrients and the control of weeds, pests and diseases (cultural)
- vary between pesticides with different modes of action (chemical)
- promote the existence of, or deliberately introduce, natural enemies (biological)

- leave to soil to rest in periods of fallow with a cover crop that nurtures the soil and prevents soil erosion and invasion of noxious weeds (cultural)

3.3 Life Cycle Assessment

Life Cycle Assessment (LCA) is one of the most prominent and widely used environmental system analysis tool, designed for characterisation of the environmental impacts associated with a product or service, throughout its life cycle, "*from cradle to grave*". The LCA methodology has been standardised by the International Organisation for Standardisation (ISO). The compulsory steps of every LCA include:

- Goal and scope definition
- Life Cycle Inventory (LCI)
- Life Cycle Impact Assessment (LCIA)

Goal and scope definition

In the goal and scope definition the system boundaries of the LCA are clearly defined, and a functional unit, to which all impacts are related, is decided upon. This unit should represent the function of the system. A flow chart of the system is constructed.

For the life cycles of most industrial products the system boundaries between the technosphere and the ecosphere are rather easy to define in the sense that it is clear where emissions enter the environment, for example as emissions from an industry chimney or from the exhaust pipe of truck. In agricultural LCAs on the other hand the system boundaries are not as clear cut, and the international research community has not yet decided if pesticides that are applied to agricultural fields are to be regarded as emitted to the environment or not (Van Zelm et al. 2012).

Life cycle inventory

In the life cycle inventory (LCI), data are collected regarding all inputs (energy, raw material) and outputs (emissions, by- or co-products) from the studied system and related to the functional unit. LCI should account for intermediate (short-term) fate of environmental emissions on a local or regional scale. Inventory analysis of pesticides in agricultural LCAs has up to now often been dealt with using crude assumptions, such as that the entire pesticide dose is emitted to soil, or that 85% is emitted to soil, 5% to crops and 10% to air. Other times, LCA practitioners have applied a global scale model in the LCI stage (Van Zelm et al. 2012).

Life Cycle Impact Assessment

The life cycle impact assessment (LCIA) consists of classification and characterisation. Classification refers to sorting inventory data into different categories according to the environmental impacts they contribute to. Characterisation refers to the conversion of the inventory data into environmental impacts according to selected impact models by determining how much every emission contributes to every impact category. In practice, characterisation consists of weighting inventory data with so called characterisation factors (CFs). CFs indicate how much every emission or unit of energy or resource use contribute, relative to each other, to various impacts.

Examples of environmental impact categories are global warming, resource use, land use, eutrophication, acidification, ozone depletion, photo-oxidant formation and toxicity. Indicators of environmental impacts can be chosen anywhere along the chain linking emissions to impacts and are sometimes referred to as midpoints, as opposed to endpoints, or areas of protection. EU International Life Cycle Data System (ILCD) recognises three areas of protection: human health, natural environment and natural resources. For example, radiative forcing is a midpoint indicator of the impact category global warming, affecting the ends human health and natural environment (EU-JRC, 2010).

In the context of pesticide emissions in agriculture, certain boundaries can be identified in time and space, as emissions tend to disperse over time from their original source: while the inventory should account for intermediate fate of pesticide emissions on a local or regional scale, LCIA should account for the final fate and ecotoxicological impacts of pesticides on a global scale (Van Zelm et al. 2012).

Allocation

Allocation in the context of LCA refers to the situation in which several products, only one of which is included in the LCA, share the same production process. An example is the cultivation of soybean for production of biodiesel, a process in which high-protein soymeal is also produced. The allocation problem consists of how to deal with resource inputs and emissions from the production process (e.g. cultivation) with regard to different production outputs (Baumann and Tillman, 2004).

Allocation can be dealt with in LCA through system expansion or through partitioning. System expansion is often done in LCAs in which two or more alternative life cycles are compared, and refers to the inclusion of surrounding processes affected by the change. Allocation can also be dealt with through partitioning, which refers to the division of inputs and emissions between different process outputs. Partitioning can be done for example on basis of weight, monetary value or energy content of products (Baumann and Tillman, 2004).

3.4 Toxicity in Life Cycle Impact Assessment

Toxicity is defined by FAO (1996) as "*a physical or biological property which determines the capacity of a chemical to do harm or produce injury to a living organism by other than mechanical means*".

Toxicity is one of the most complicated and difficult impact categories in Life Cycle Impact Assessment (LCIA) (Baumann and Tillman, 2004) for which reason it is often omitted from LCAs (Rosenbaum et al. 2008) – even agricultural LCAs despite the obvious and high relevance. Toxicity is complicated due to a huge amount of substances that need to be included and provided with characterisation factors; a lack of knowledge about fate, expose and effect mechanisms of substances and the objective side of effect ranking. For example, there is no scientific answer on how to rank between neurological and carcinogenic effects, or effects on algae compared to effects on fish.

Although interlinked, it is common to separate between ecological toxicity (ecotoxicity) and human toxicity. Ecotoxicity can in turn be divided into aquatic and terrestrial toxicity and aquatic toxicity can further be divided into freshwater and marine ecotoxicity. (Baumann and Tillman, 2004)

Generally in toxicology; emissions (inventory data) are linked to impacts through three steps: fate, exposure and effects. (Rosenbaum et al. 2008) Before moving on to ecotoxic effect assessment in LCIA, the important concepts fate, exposure and effect are introduced.

Fate

When pesticides are applied onto an agricultural field only a fraction of the dose reaches the target (the crop or the weed). Even pesticides that reach the target may be dispersed into the environment later on. Fate refers to the distribution between different environmental compartments, such as air, water and soil, due to various transport, distribution and degradation mechanisms.

Fate is strongly time-dependent, for which reason it is common to separate between intermediate and final fate. For example, wind-drift to the atmosphere takes place in parallel to application and continues for a limited amount of time (hours) after application, while emissions to surface water may be most intense during a rainfall and take place several weeks after application.

To understand the science behind transport, distribution and degradation mechanisms of pesticides in the environment is important not only for model developers to be able to construct pesticide environmental fate models such as the ones used in this thesis, but also for farmers to be able to decide on ideal application conditions and reduce unwanted distribution of pesticides. For example, it is seldom advisable to apply pesticides if heavy rainfall is expected, as much will be lost through run-off and potentially cause harm in near-by ecosystems.

Consider an agricultural field where pesticides are applied, such as the system depicted in figure 3.2. Various transfer and degradation processes contribute towards the intermediate and final fate of the pesticides. Transport and distribution processes include for example wind drift during spraying, evaporation and volatilisation from crops and soil, absorption into crops, adsorption and infiltration into the soil, leaching through the soil and surface runoff from the field (Van Zelm et al. 2012).

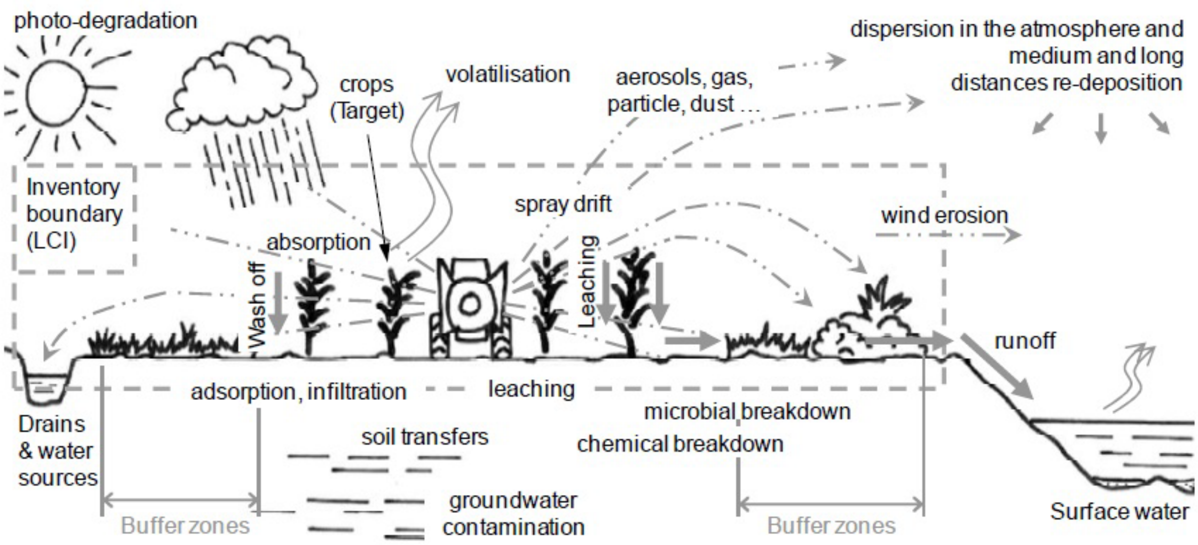


Figure 3.2 Pesticide environmental transfer mechanisms and degradation processes. (Source: Van Zelm et al. 2012. Reproduced with kind permission from Rosalie Van Zelm, pers. com. 2013)

Degradation processes are biotic or abiotic. Biotic processes include metabolism and microbial degradation. Abiotic degradation includes hydrolysis, photolysis and oxidation. (FAO, 1996) Metabolites, or degradation products, formed upon degradation may be more or less toxic than the parent compounds.

Fate also depends on various pedo-climatic factors (for example wind speed, rainfall frequency and intensity, solar irradiation and soil composition), the pesticide's physical-chemical properties, the crop's development stage, technology (spraying equipment, spraying pressure, nozzle distance etc.) and human behaviour (timing, accidental spills etc.). (Dijkman et al. 2012 and Van Zelm et al. 2012) Physical-chemical properties of significance for fate are presented in table 3.4 together with thresholds, if available.

Table 3.4 Physical-chemical parameters of significance for environmental fate. (Information from AGRITOX, 2012 and PPDB, 2009)

Parameter	Interpretation	Thresholds if available
Henry's Law constant	Indicator of a substance's preference of air relative to water and its ability to volatilise. The thresholds are valid for Henry's Law constant expressed in Pa·m^3/mole.	> 100 = Volatile 0.1 - 100 = Moderately volatile < 0.1 = Non-volatile
Vapour pressure	Indicator of a substance's ability to vapourise. The thresholds are specified for vapour pressure expressed in mPa at 25°C.	< 1 = Non-volatile 1 – 1 x 10^4= Intermediate state > 1 x 10^4 = Volatile
Log P/Log Kow	Log of octanol-water partition coefficient. Indicator of a substance's lipid solubility and its tendency to bioaccumulate.	< 2.7 = Low bioaccumulation 2.7 – 3 = Moderate > 3.0 = High
Soil degradation / half-life in soil	Expressed in days and an indicator of the persistence. Also available for other environmental compartments such as air and water. Depends on soil temperature, pH, soil moisture and microbial population.	< 30 = Non-persistent 30 - 100 = Moderately persistent 100 - 365 = Persistent > 365 = Very persistent
Solubility in water	Indicator of a substance's ability to dissolve in water. The greater the solubility the greater the bioavailability. The thresholds are valid for solubilities expressed as mg/l.	<= 50 = Low 50 - 500 = Moderate > 500 = High
Dissociation constant, pKa	Defined as the negative logarithm of the acidity constant Ka and indicates the strength of an acid and the potential for form ions in water.	The lower the pKa the stronger the acid.
Organic-carbon water partition coefficient, Koc	Also called organic-carbon sorption constant or soil adsorption coefficient. Indicator of the substance's ability to attach to soil particles and hence mobility.	The higher the Koc the greater the potential for soil-particle bound transport.

The parameters presented in table 3.4 can be used as stand-alone indicators, or combined for complex indicators. For example, degradation rate in soil combined with organic-carbon water partition coefficient can be used as a measure for leachability (PPDB, 2009).

A transfer process and at the same time fate, not accounted for figure 3.2, is accumulation and movement in biota. Some persistent pesticides, such as DDT, accumulate in the tissue of living organisms and can move large distances in space and in food chains as they bioconcentrate and cause damage especially to top predators (FAO, 2007).

Exposure

Exposure to humans may be direct or indirect. Direct exposure include dermal contact, inhalation and ingestion while indirect contact include exposure due to residues in food and contaminated ground water (FAO, 2007). Field workers are at particular risk of being directly exposed while the population at large is exposed mainly through residues in food.

Exposure to the natural environment depends on fate, bioavailability and degradation rates of pesticides. Generally, the environment and living organisms, at some scale, become exposed to every emission of pesticide leaving the agricultural field.

Effect

Effects refer to various impacts in the environment, on living organisms and on human health, specified at midpoint or endpoint level and of acute or chronic character. Effect following a single exposure, typically high doses, are called acute, while effect following exposure over longer time and several instances, generally in lower doses, are called chronic (FAO, 2007). Effects depend on a range of factors related to the species that are exposed and their development stage and level of sensitivity, the chemicals involved, exposure duration time, doses, background concentrations and cocktail effects.

Acute effects include for example death, nausea, headache, vomiting, bleeding and hypersensitivity (Lehtonen, 2009). It has been estimated by WHO that at least three million people become acutely pesticide poisoned each year, of which around 20 000 suffer lethal consequences, due to neurological or respiratory failure (WHO, 1990 cited in FAO, 1999).

Chronic effects include for example cancer, neurological damage, mutation, disruption of hormonal systems, immune systems and reproductive systems, cellular and DNA-damage and physical deformities (FAO, 1996).

Pesticide effect evaluation is a highly complex and difficult subject. The knowledge related to effects of pesticides on ecosystem, various species and human health is a patchwork of numerous separate, field and laboratory studies, often focusing on specific species and pesticide types.

Ecotoxic effect assessment in LCIA

As mentioned previously, emissions (inventory data) are generally linked to impacts through three steps: fate, exposure and effects. Assessing the toxicological impacts of chemicals consists of following these cause-effect chains. (Rosenbaum et al. 2008) CFs are generally the product of a fate factor, an exposure factor and an effect factor (Payet, 2004), the relative shares of which is determined in each specific case depending on the chemical’s properties.

Effect factors in ecotoxicology can be based on several measures based on either experimental data from laboratory tests with various species, or derived through calculation. Some of the most common measures in ecotoxicology are (Payet, 2004):

- LDX – Lethal Dose X: - the dose required to kill X% of the test organisms, commonly 50%.
- PNEC – Predicted No Effect Concentration, e.g. based on the Most Sensitive Species.
- NOEC – No Observed Effect Concentration
- LOEC – Lowest Observed Effect Concentration
- ECX – Effective Concentration to X% of the test organisms: the concentration at which X% of organisms display a predetermined effect over a predetermined test duration.

NOEC, LOEC and EC50 are perhaps the measures most commonly used in ecotoxicity in LCIA (Payet, 2004). The effects referred to can be of various types, for example intoxication, mobility, mortality, generation time, biomass growth and weight (USEPA, 2013). This thesis uses an ecotoxic characterisation method, USEtox, that use experimental EC50 data as a base for calculation of effect-factors. All ecotoxicological effect data collected and used in this thesis are available in Appendix V.

There are limitations with ecotoxicological effect measures. Laboratory tests can be inexact and depending on how tests are constructed different values can be reached. Effect tests typically involve one substance at a time in an otherwise clean environment while in nature organisms are exposed to a mix of substances and background concentrations. Only a limited number of tests have been performed for each chemical, often on a limited set of typical test species, such as *Daphnia Magna* and *Lemna Gibba* for freshwater, while those species might not be representative of the freshwater organisms in all areas.

Depending on the exposure duration, laboratory tests are classified as acute or chronic. In order to qualify as chronic, test duration times generally need to be in the same order of magnitude as the generation time of the test species, but can be shorter if organisms are tested during a sensitive life stage. There is however no scientific consensus regarding the differentiation between acute and chronic tests and different testing institutes usually have their own standards. (Payet, 2004) Most tests that have been performed within the area of ecotoxicological effect assessment are acute while chronic tests are sometimes more relevant, for example in the LCA context, for which reason to acute-to-chronic extrapolation factors can be used (Payet, 2004).

Ecotoxic effect, or impact, assessment in LCIA is generally calculated as the product of emissions to various compartments and corresponding CFs summed over all compartments and all chemicals, as in equation 3.4 where N denoted the number of chemicals assessed, C the number of compartments included, e the compartment specific emission and CF the chemical-and compartment-specific characterisation factor.

$$Ecotoxic\ impact = \sum_{n=1}^{N} \sum_{c=1}^{C} e_{c,n} \cdot CF_{c,n}$$

Equation 3.4

Models for toxicity in LCIA

Many characterisation models for toxicity have been developed under the LCIA umbrella during the years, such as CalTOX (McKone and Enoch, 2002), IMPACT 2002+ (Jolliet et al. 2003), USES-LCA 2.0 (Van Zelm et al. 2009), ReCiPe (Goedkoop et al. 2009), EDIP-97 (Wenzel et al. 1997) and Eco-indicator99 (Goedkoop and Spriensma, 2000). They differ in scope, modelling principles regarding fate, exposure and effect, number of substances and compartments included and not least in terms of the relative toxic weight assigned to different substances in the form of CFs (Baumann and Tillman, 2004 and Hauschild et al. 2011).

Traditionally, LCIA is site-generic, i.e. does not take into account where emissions take place. However, over the past decade it has become clear that for some impact categories, such as toxicity, differences in spatial conditions play a key roles for the fate, exposure and effect of pesticide. GLOBOX (Wegener Sleeswijk, 2006) is a model developed for calculations of spatially differentiated CFs for human toxicity and ecotoxicity. Research is currently on-going to incorporate spatial differentiation into toxicity characterisation models, see for example Sala et al. (2011).

Tests in GLOBOX have shown that there are significant differences between regions in terms of toxic impacts due to differences in rain rates, distributions of lakes and rivers and temperatures for ecotoxicity and human population density and food consumption patterns for human toxicity (Wegener Sleeswijk, 2006).

The fact that different models produce different results have been a source of criticism against the models and against the LCA methodology in large, but also a source of incentive for further research and developments to produce more sophisticated characterisation models and achieve scientific consensus. USEtox (Rosenbaum et al. 2008) is one of the most recent LCIA toxicity characterisation models, launched in 2008, and the result of a scientific consensus process aimed at merging several of the existing characterisation models. USEtox is the model used in this thesis; introduced in detail in chapter 4.

4. METHOD AND MATERIALS

The aim of this thesis has been accomplished through a procedure of inventory (chapter 5), calculation of environmental performance indicators (chapter 6) and interpretation of the results (chapter 6 and 7). This chapter explains the various steps of the method in detail, starting with introduction of the software models used (chapter 4.1), followed by inventory (chapter 4.2) and calculation routes (chapter 4.3).

4.1 Software models

Three software models have been used throughout this thesis;

- PestLCI 2.0 as an emission inventory and intermediate fate analysis tool (chapter 4.1.1),
- USEtox 1.01 as a final fate analysis and ecotoxic impact characterisation tool (chapter 4.1.2) and
- EPISuite 4.11 as an estimation model of physical-chemical data (chapter 4.1.3).

4.1.1 PestLCI 2.0

PestLCI v.2.0 (Dijkman et al. 2012) is an emission inventory model developed for use in agricultural Life Cycle Inventory (LCI) by a development team at the Technical University of Denmark (DTU). Version 2.0, released in 2012, replaced the previous version 1.0 from 2006 (Birkved and Hauschild, 2006) and is modelled in Analytica 4.2.

PestLCI is one of the most advanced pesticide emission inventory models presently available for use in agricultural LCI. (Van Zelm et al. 2012) It is also one under active development with an already established link to the Swedish Institute for Food and Biotechnology (SIK).

PestLCI[10] estimates emissions to three environmental compartments; air, surface water and ground water, by modelling primary and secondary distribution processes following field application. Primary distribution processes refer to the initial distribution that follow pesticide application and give the fractions deposited on plant leaves, soil and emitted to the air by wind drift. Secondary distribution processes refer to three processes that take place on leaves: volatilisation, degradation and uptake; and seven processes that take place in the soil: top soil degradation, sub soil degradation, top soil run-off, drainage system, macrospore flow, ground water leaching and top soil volatilisation (Dijkman et al. 2012).

PestLCI regards agricultural fields as part of the technosphere and only estimates the fraction of pesticides that crosses the technosphere-environment border, where the technosphere-field box is defined as a box with a bottom area equal to the field and a height extending 1 meter down in the soil column and 100 meter up into the air column. (Dijkman et al. 2012) Therefore emissions to soil are not accounted for in PestLCI. The rationale for this modelling option is explained in Birkved and Hauschild (2006).

---

[10] PestLCI 2.0 can be downloaded free of charge from http://www.dtu.dk/centre/MAN-QSA/Forskning/PhD%20projekter/PestLCI.aspx (Accessed 2013-02-07). Analytica needs to be installed on the computer in order to run the model.

PestLCI is site dependent under the assumption that local climate and soil characteristics strongly influence the specific fate distribution between different environmental compartments. While PestLCI 1.0 was limited to Danish conditions PestLCI 2.0 has been extended to cover seven soil profiles and 16 different climate zones typical to Europe and range from alpine and wet maritime to Mediterranean. (Dijkman et al. 2012) The possibility to add new pesticides and soil and climate profiles as present in PestLCI 1.0 does not exist in version 2.0 without an Analytica-license.

So far, PestLCI 1.0 has been used in 42 studies, 31 of which are ISI-journal[11] publications and PestLCI 2.0 in one study, while at least four are under preparation (Dijkman, pers. com. 2013). The model is likely to become the standardised emission inventory model for use in agricultural LCAs at SIK whenever ecotoxicity is included as an impact category in the future (Wallman, pers. com. 2013).

4.1.2 USEtox 1.01

USEtox v.1.01 (Rosenbaum et al. 2008) is a model for characterisation of human toxicity and aquatic freshwater ecotoxicity for use in comparative assessment of chemicals and their toxic effects of humans and ecosystems in Life Cycle Impact Assessment (LCIA). The model is a result of a comprehensive comparison and scientific consensus process that began in 2005, initiated by the United Nations Environment Program (UNEP) – Society for Environmental Toxicology and Chemistry (SETAC) Life Cycle Initiative, aimed at comparing seven existing toxicity characterisation models, identify the most influential model parameters and develop a scientific consensus model. The models compared were: CalTOX, IMPACT 2002, USES-LCA, BETR, EDIP, WATSON and EcoSense (Rosenbaum et al. 2008).

USEtox[12] was first launched in 2008 with updated characterisation factors (CFs) in 2010. The modelling platform is Excel, and since 2010 the model is also available in a SimaPro[13] incorporated version. The USEtox model consists of an Excel program for calculation of CFs "USEtox", a database with background data (physical-chemical, exposure and effect data) "Database_organics", and a database with CFs for more than 3000 substances "USEtox_results_organics". Corresponding databases for inorganics (21 metals) are also available but not used in this thesis.

USEtox 1.01 models the fate, exposure and effect of chemicals at midpoint level (Rosenbaum et al. 2008 and Hauschild et al. 2013) for emissions to various sub-compartments of air, water and soil.

The characterisation model for ecotoxicity consists of a fate part, an exposure part and an effect part. The fate model consists of a continental scale with six environmental compartments (urban air, rural air, freshwater, coastal marine water, natural soil and agricultural soil) nested inside a global scale with the same compartments except urban air. The continental and global scales make it possible to differentiate between chemicals

---

[11] ISI-journals refer to academic journals with so-called impact factors – a measure of the importance of various scientific journals based on average number of citations.
[12] USEtox 1.01 model, manuals and databases can be downloaded free of charge from the USEtox webpage: http://www.usetox.org/ (Accessed 2013-02-07)
[13] SimaPro is an LCA software, for example used at SIK.

that are widely dispersed and chemicals that stay closer to their origin (Fantke, pers. com. 2013).

Ecotoxicological fate factors are calculated as the mass increase (kg) in a given medium due to an emission flow (kg/day) based on the chemical's physical-chemical properties and have the dimension day while ecotoxicological exposure factors equal the dissolved fraction of a chemical (dimensionless) and represent the bioavailable share (Rosenbaum et al. 2008).

The ecotoxicological effect assessment approach adopted by USEtox is based on the Assessment of the Mean Impact (AMI)-method, presented in Payet (2004). Ecotoxicological effect factors in according to the AMI-method are based on the geometric mean[14] of EC50[15] data for species at different trophic levels in the ecosystem. The method assumes a log-normal distribution of EC50 data and linearity between concentration and response. Compared to methods based on other ecotoxicological measures such as Most Sensitive Species and NOEC, the AMI-method has the advantages that it can use both acute and chronic effect data, does not require the calculation of a Species Sensitivity Distribution (SDD)-curve, (as do many other methods), allows the calculation of confidence intervals on effect factors and has comparatively high statistical robustness and low sensitivity to species addition according to Payet (2004). Effect factors in USEtox have the dimension potentially affected fraction of species (PAF) in m^3 per kg emitted chemical (Rosenbaum et al. 2008).

Ecotoxic CFs for emissions to various environmental compartments are calculated as the product of the fate factor, the exposure factor and the effect-factor, integrated over time and volume per unit mass of an emitted chemical, summed over the global and continental scales. The unit of ecotoxicological CFs are PAF days·m^3/kg. This unit has been given the specific notation CTUe, Comparative Toxic Units, ecotoxicity (CTUe). (Rosenbaum et al. 2008)

CFs are labelled as recommended or interim. Interim denote that there is of lack of data or large uncertainties or theory gaps in the modelling of fate, exposure and/or effect. The USEtox model is primarily designed and valid for non-polar, non-ionic organic substances, while metals, organometallics, dissociating substances, amphiphilics (e.g. detergents) and organic substances with effect data covering less than three different trophic levels, are all classified as interim. (Rosenbaum et al. 2008) The use of interim CFs is encouraged although extra care should be taken in interpretation.

The landscape data (various parameters for example land areas, temperatures, wind speed, rain rates and soil erosion) modelled in USEtox represent an average default continent with average continental conditions, and is not intended to resemble any particular real continent such as North America or Europe. Hence, the model is site-generic and CFs to be interpreted as average and site-independent (Hauschild et al. 2013, Fantke, pers. com.

[14] The geometric mean of a collection of numbers $x_1 \dots x_n$ is defined as: $\sqrt[n]{\prod_i^n x_i}$.

[15] EC50 data refer the effective chemical concentration measured in mg/l at which 50% of test organisms display a pre-determined effect (various possible) during a defined test-period. More on ecotoxicological measures in chapter 3.4.

2013). However, the opportunity exists to manually modify landscape data to increase accuracy and produce regional CFs.

USEtox does not have a ground water compartment (as has PestLCI) since the science behind ground water toxicity characterisation is not too advanced yet and rather fragmented (Fantke, pers. com. 2013). The freshwater compartment in USEtox corresponds to the surface water compartment in PestLCI (Fantke and Huijbregts, pers. com. 2013).

USEtox has recently been appointed the best among existing characterisation model for freshwater ecotoxicity and human toxicity, by the EU International Life Cycle Data system (ILCD) (Hauschild et al. 2013).

4.1.3 EPISuite 4.11

The Estimation Program Interface Suite™ (EPISuite) for Windows v. 4.11 (USEPA, 2012) is a "toolbox" of thirteen different estimation programs for various physical and chemical properties, developed by the US Environmental Protection Agency's (EPA) office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC). EPISuite[16] was used in this thesis as the default database of physical-chemical data required by USEtox, as suggested by the USEtox team (Rosenbaum et al. 2008).

In addition to estimation models, several of the programs have built-in databases with experimental data and references. The only input required by EPISuite is SMILES[17]-notation, entered manually or searched for through CAS[18] number on the main page, "Welcome screen", of the interface.

All thirteen programs were either run in rapid succession by entering SMILES on the main screen, selecting "Full" under "Output" and pressing the calculate button. Or, programs were run one at a time, referred to hereafter as single program mode, by selecting the desired program from the left-hand menu on the EPISuite main screen and enter SMILES.

The single-program mode was found to have the advantage of always giving experimental data if available. Experimental data, whenever available, were always favoured over estimated, according to the recommendation in Huijbregts et al. (2010b). Experimental data were also presented under the "All results" tab in the Results window but not always under the respective program tabs in the Results window.

Results, i.e. estimated data, of all programs, appeared under separate program tabs in the Result window as well as under the "All results" tab, from where they were collected. The results were also displayed at the bottom of the main screen of the EPISuite interface under separate program tabs. The following seven EPISuite programs were used in this thesis. Further details how these programs were used are given in chapter 4.3.

[16] EPISuite needs to be installed on the computer. It can be downloaded free of charge from http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm (Accessed 2013-02-19)

[17] Simplified Molecular Input Line Entry System is a chemical notation system in which molecular structure are represented by a linear string of symbols.

[18] Chemical Abstracts Service is a numerical identification system of chemicals.

AOPWIN - the Atmospheric Oxidation Program estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals using methods based on structure-activity relationships (USEPA, 2012). Used in this thesis to retrieve hydroxyl radical rate constants, K_{OH}.

BIOWIN – estimates the probability of rapid aerobic and anaerobic biodegradation of an organic compound in the presence of mixed populations of environmental microorganisms through seven separate models (USEPA, 2012). Biowin3, "expert survey ultimate biodegradation model", is recommended by the USEtox team (Huijbregts et al. 2010a) and was used throughout this thesis for derivation of biodegradation rates in water, soil and sediment.

HENRYWIN - estimates the Henry's Law Constant of organic compounds at 25°C and contains an experimental database (USEPA, 2012).

KOCWIN - estimates the soil adsorption coefficient (Koc) of organic compounds. Koc can be defined as (USEPA, 2012): "*the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium*". The program has two estimation methods for Koc (Molecular Connectivity Index (MCI) and Log Kow estimation method) as well as an experimental database. The MCI method is recommended by the USEtox team (Huijbregts et al. 2010a) and was used throughout this thesis.

KOWWIN - estimates the logarithmic octanol-water partition coefficient (low Kow) of organic compounds and contains an experimental database (USEPA, 2012).

MPBPVP - estimates melting point, boiling point, and vapour pressure. Used in this thesis for retrieval of vapour pressure at 25°C. Contains an experimental database and three estimation methods for vapour pressure: the Antoine, the modified Grain and the Mackay method (USEPA, 2012). The physical state of a chemical determines which method is best suited (Huijbregts et al. 2010a).

WSKOWWIN - estimates the water solubility of organic compounds using the log octanol-water partition coefficient (low Kow) and contains an experimental database (USEPA, 2012).

4.2 Inventory

In the inventory, data of both qualitative and quantitative nature were collected to provide material for the calculation of various environmental performance indicators.

4.2.1 Typical field pesticide application scenarios

It was decided to collect and construct typical field pesticide application scenarios, that should represent realistic farm application practices. This decision was based partially on the field based design of the emission inventory model, PestLCI, and partially on the feasibility of the task. First priority was given to data from experienced experts and second priority to national or regional statistics or case studies. Attempting to construct application scenarios representative for northern Europe, for example, would include hundreds of pesticides and such an application is unrealistic for any real field and data collection and processing would be beyond the scope of this thesis. In addition, national or regional statistics are not available for every country.

The typical field pesticide application scenarios were required to contain the following information, based on the requirements by PestLCI:

- field length and width (m)
- field soil
- field climate
- annual irrigation (mm)
- fraction of field drained (%)
- type of tillage
- field slope (%)
- applied pesticides specified by active substance name
- application rate (dose) (kg/ha)
- method of application
- month of application
- crop type and crop development stage at time of application

In addition, frequencies of application (1/yr) were collected in order to consider major year-to-year fluctuations and even out the pesticide application and the freshwater ecotoxic impact over the years. The frequency factor indicates how often, on average, the pesticide is applied in a year to a given field.

Agricultural management of crops was also investigated in terms of weeds, pests and diseases, in order to provide background for pesticide application as well as assist in construction of typical field pesticide application scenarios and make relevant assumptions. This inventory, of a more qualitative nature, is presented in the inventory chapters 5.1.2 – 5.6.2 labelled "Agricultural management". The typical field pesticide application scenarios are presented in the inventory chapters 5.1.3 – 5.6.3 with supporting information in Appendix II.

4.2.2 Gross energy yields

It was decided to measure impacts in relation to gross energy output, as opposed to net. Gross energy was selected in order to avoid implicit assumptions regarding for example technologies and utilisation degrees. Fuel yields in litre per hectare were converted using the lower heating values of ethanol and biodiesel to get the gross energy yield expressed as GJ per hectare and year.

Lower heating values are applicable in the context of combustion engines and are traditionally favoured in Europe, over higher heating values (Boundy et al. 2011). The lower heating value of a fuel is defined as: (Boundy et al. 2011) "*the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which assumes the latent heat of vaporization of water in the reaction products is not recovered*".

Collected data on fuel and energy yields for biodiesel and ethanol feedstocks, as well as all sources used are presented in chapter 5.7.

4.3 Calculation routes

In the calculation stage, several environmental performance indicators were developed, based on the following measures:

- amount of pesticide active substance (AS) applied (g AS)
- gross energy yields (J)
- freshwater ecotoxic impact (CTUe)

These measures were then related to hectare and year to get comparable indicators. While the first two measures were calculated with the help of simple arithmetics from the data collected during inventory, the last measure, freshwater ecotoxic impact in CTUe, required a slightly more advanced calculation route. The various steps are illustrated in figure 4.1 and summarised in short as:

- Addition of missing pesticides to PestLCI
- Regionalisation of PestLCI for sites outside of Europe
- Inventory of emissions to air and surface water using PestLCI
- Collection of CFs from the USEtox database
- Calculation of CFs not included in the USEtox database
- Calculation of freshwater ecotoxic impact

Lastly, the two measures amount of pesticide AS applied (g AS) and freshwater ecotoxic impact (CTUe) were allocated through partitioning. The different steps are explained in detail in chapters 4.3.1 – 4.3.7.

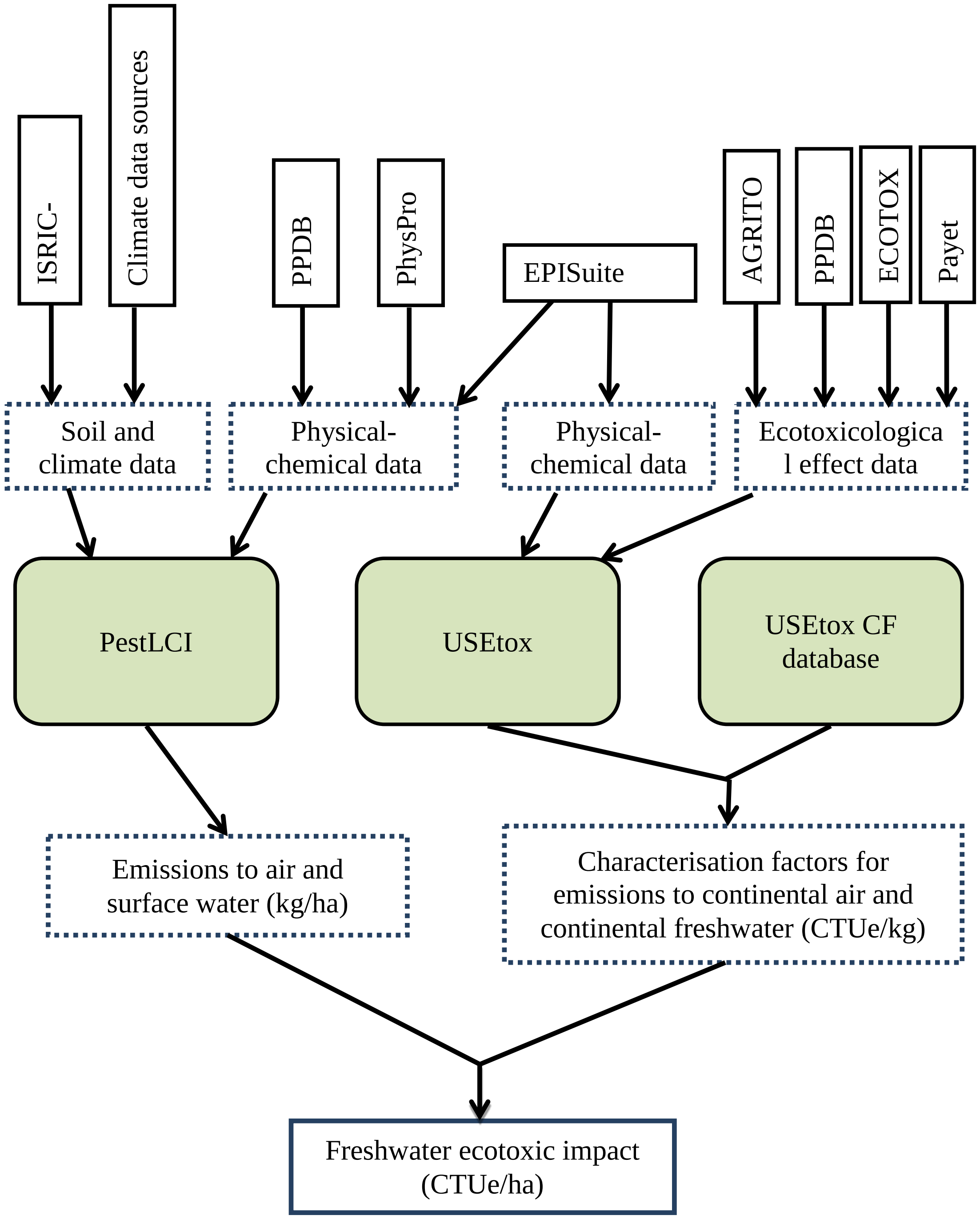


Figure 4.1 Flowchart illustrating the methodology for calculation of freshwater ecotoxic impact.

4.3.1 PestLCI pesticide addition route

For pesticides not already included in PestLCI the opportunity to manually add pesticides to the program was kindly offered by the PestLCI development team represented by Teunis Dijkman. In order to do this, a number of properties and parameters had to be collected and sent to Dijkman. Table 4.1 lists the required data as well as the sources used.

Table 4.1 PestLCI pesticide data requirements to add new pesticides to the model with notation according to Dijkman (pers. com. 2013).

PestLCI pesticide data requirement	Unit	Explanation / Comments
Type	-	Herbicide, insecticide, fungicide, etc.
CAS no.	-	Chemical Abstract Services number.
SMILES-notation	-	Simplified Molecular Input Line Entry System notation.
Molecular mass	g/mole	More commonly referred to as molecular weight.
Solubility and ref. temp.	g/l, ^{o}C	Solubility in water and reference temperature at which solubility was determined.
Vapour pressure and ref. temp.	Pa, ^{o}C	Vapour pressure and reference temperature at which vapour pressure was determined.
pKa	-	First dissociation constant, neutral to charged. Not present in EPISuite. Not applicable for non-ionizing substances.
Log Kow	-	Log of octanol-water partition coefficient. Denoted Log P in PPDB and PhysProp.
Koc	l/kg	Soil organic carbon-water partition coefficient. Denoted soil adsorption coefficient in EPISuite.
Soil $t_{½}$ and ref. temp.	days, ^{o}C	Soil biodegradation half-life and reference temperature at which degradation in soil was determined. Denoted DT50 in PPDB.
Atmospheric OH rate and ref. temp.	cm^3/ (molecule·sec)	Overall OH-radical oxidation rate constant and temperature at which it was determined or estimated.
No sprayzone width	m	Width of the zone along the edges of the field in which it is forbidden to spray the chemical.
E(a) Evaporation	kJ/mole	Activation energy for evaporation.

It was prioritised in this thesis to use the same data sources as the model developers to maintain consistency with the other pesticides already included in PestLCI. For that reason, first priority was given to the Pesticide Properties Database (PPDB, 2013) and second priority to the Physical Properties Database (SRC, 2013) according to the recommendation by Dijkman (pers. com. 2013).

Pesticide Properties Database[19] (PPDB) is an online database developed by the Agriculture and Environment Research Unit (AERU) at the University of Hertfordshire, UK. It contains an extensive set of physical-chemical data and a smaller set of ecotoxicological effect data for around 1100 pesticides and 500 metabolites including all AS used in the EU (PPDB, 2013). The database also provides information regarding formulations, environmental fate and human health information.

[19] The PPDB is available at: http://sitem.herts.ac.uk/aeru/footprint/index2.htm (Accessed 2013-02-22)

The Physical Properties Database[20] (PhysProp) is a database developed by the Syracuse Research Centre (SRC) over the past two decades. A subset of the full database is available as an online demo version containing estimated and experimental values for melting point, boiling point, water solubility, Log Kow, vapour pressure, pKa, Henry's Law constant and atmospheric OH-rate for around 25 000 compounds (SRC, 2013). Experimental data were favoured over estimated data.

Regarding soil degradation half-life times, three test-values representing different test conditions were available in PPDB labelled "Typical", "Laboratory" and "Field". For this thesis, it was decided to use the "Typical" values as recommended by Dijkman (pers. com. 2013), representing a mean of all field and laboratory studies (PPDB, 2009) and the reference temperature was assumed to be 20°C, although it was not stated.

If the required properties could not be found in neither PPDB nor PhysProp, experimental or estimated data from EPISuite were used, primarily atmospheric OH rate. It was found by entering AOPWIN in single program mode or under the "All results" tab in the Results window. If experimental data were lacking the "overall OH rate constant" estimate available under the AOPWIN "Hydroxyl Radicals Page 2" (or for some pesticides only by accessing the program in single program mode) was used.

In a few cases Koc-values were also retrieved from EPIsuite. In those cases the MCI-estimation method was used. For "No spray-zone width" it was decided to use a default value of 0 m, in accordance with the other pesticides already included in PestLCI. No data regarding activation energy for evaporation were found, for which reason a default value of 100 kJ/mole was used.

4.3.2 Regionalisation of PestLCI

In order to account for climate and soil conditions on sites outside of Europe, PestLCI had to be regionalised to local soil and climate. The opportunity to manually add new soil and climate data to the model was kindly offered by the PestLCI development team represented by Teunis Dijkman. In order to do this, soil and climate data had to be collected and sent to Dijkman. Tables 4.2 and 4.3 list the required data.

Table 4.2 PestLCI soil data requirements to create new soil profiles with notation according to Dijkman (pers. com. 2013).

PestLCI soil data requirements
Start depth for every horizon (m)
End depth for every horizon (m)
Fraction of clay (particles <2 µm) in every horizon
Fraction of silt (particles 2-50 µm) in every horizon
Fraction of sand (particles >50 µm) in every horizon
Percentage organic carbon in every horizon
pH in every horizon
Name of every horizon
Soil bulk density (not necessary to provide)
Overall soil type (sand, silt or clay)

[20] The PhysProp database is available at: http://www.srcinc.com/what-we-do/product.aspx?id=133 (Accessed 2013-05-03)

Table 4.3 PestLCI climate data requirements to create new climate profiles with notation according to Dijkman (pers. com. 2013).

PestLCI climate data requirements and sources used in this thesis	Unit
Latitude	degrees
Longitude	degrees, E+ W-
Location	-
Elevation	m
Solar irradiation, monthly average, for every month	$Wh/m^2/day$
Average air temperature, monthly average, for every month	˚C
Minimum air temperature, monthly average, for every month	˚C
Maximum air temperature, monthly average, for every month	˚C
Precipitation, monthly average, for every month	mm
Number of days with >1mm precipitation, monthly average, every month	-
Average rainfall on a rainy day, monthly average, for every month	mm
Rain frequency, monthly average, for every month	1/day
Potential evaporation, annual average[1]	mm

1) Not necessary to provide if minimum and maximum air temperature, latitude and elevation are provided.

In this thesis, a regionalised version of PestLCI was developed for Iowa, USA, in order to perform emission inventory for maize. Climate data were taken from Iowa City, Johnson County, while the soil sample was taken from a rainfed, arable culture land in Grundy County, Iowa.

In order to perform emission inventory for Brazilian crops (soybean and sugarcane) the data previously collected by Bennet (2012) for regionalisation of PestLCI 1.0 to Mato Grosso, Brazil, was used to regionalise PestLCI 2.0. The details of Mato Gross regionalisation are available in Bennet (2012).

Soil data were collected for every horizon in the soil down to depth of 1 m. All soil data were collected from the ISRIC-WISE Harmonized Global Soil Profile Dataset v 3.1 (Batjes, 2008 and 2009). The ISRIC-WISE[21] database contains harmonised soil data from over 10 000 soil profiles from all over the world, compiled by the ISRIC World Soil Information (Batjes, 2008).

A suitable soil sample was identified by its coordinates in the WISE3_SITE data sheet in ISRIC-WISE. The profile's key characteristics, such as slope, altitude and land use type were checked to make sure it was a suitable sample. Its WISE3-id number was noted and the corresponding soil data for every horizon down to a depth of 1 m collected from the WISE_3 HORIZON data sheet. All soil data collected for regionalisation to Iowa, USA, are available in Appendix VI.

Climate data were collected from various internet sources. All climate data collected for regionalisation to Iowa, USA, and the sources used, are available in Appendix VII.

[21] The ISRIC-WISE database can be freely downloaded from http://www.isric.org/data/data-download (Accessed 2013-02-20).

4.3.3 Inventory of emissions to air and surface water using PestLCI

Several input data labelled as primary inputs, secondary inputs and adjustable model parameters were needed in order to operate in PestLCI. The primary and secondary input requirements formed the basis of the inventory of pesticides application scenarios, explained in chapter 4.2. Table 4.4 lists the primary and secondary input data requirements and gives details regarding the input formats and available choices. Default values for adjustable model parameters were used in this thesis.

Table 4.4 PestLCI primary and secondary input data requirements, input formats and available choices.

Input data requirements	Input format	Specification of available choices and comments
Field size	User defined length (m) and width (m).	Spraying equipment assumed to move parallel to length.
Field soil	Several predefined choices.	Seven different soil profiles with varying compositions of sand, silt and clay intended to cover the whole of Europe.
Climate	Several predefined choices.	25 different climate sets covering 16 European climate zones, ranging from alpine, wet maritime to Mediterranean.
Annual irrigation	User defined (mm)	-
Fraction drained	User defined (0 - 1)	-
Depth of drainage system	User defined (m)	-
Tillage type	Three predefined choices	Conventional, reduced or no tillage
Field slope	Used defined (%)	-
Application method	Several predefined choices.	IMAG[22] conventional boom potato IMAG conventional boom flower bulb IMAG conventional boom sugar beet IMAG conventional boom cereals IMAG conventional boom bare soil IMAG cross flow fruit tree leafed IMAG cross flow fruit tree leafless PestLCI 1[23] field crops PestLCI 1 tall crops PestLCI 1 aircraft PestLCI 1 soil incorporation
Crop type and development stage	Several predefined choices.	-
Pesticide active substance name or CAS no	90 predefined active substances.	-
Pesticide application rate	User defined (kg/ha)	Also referred to as dose.
Month of application	January - December	-

[22] IMAG refer to a wind drift loss functions based on the IMAG Drift Calculator added to version 2.0 of the model (Dijkman et al. 2012).

[23] "PestLCI 1" in the context of application method refer to wind drift functions from version 1.0 of PestLCI.

Emission inventory was carried out, one pesticide at a time, by entering the data collected during inventory into PestLCI. Actual application doses were used rather than yearly averages.

While PestLCI 2.0 give the emissions to ground water, surface water and air, only the emissions to air and surface water (expressed as kg per hectare) were collected from PestLCI, since USEtox lacks characterisation methods for ground water.

The emissions inventory results, presented in detail in Appendix VIII, are to be interpreted as intermediate fate of the pesticides on a local or regional scale, while the final fate remains to be modelled by USEtox in the characterisation stage.

4.3.4 Collection of CFs from USEtox database

Characterisation factors (CFs), both recommended and interim, were obtained from the Excel file "*USEtox_results_organics*"[24].

Although interim CFs indicate that there is of lack of data or large uncertainties or theory gaps in the modelling, it was decided to include interim CFs, since they at least represent a best-estimate and are better than nothing. However, the classification for every CF collected was noted; and if interim, the reason for it. All CFs used in this thesis, along with the details regarding classifications are available in Appendix IX.

USEtox provide CFs for various sub-compartments of air, water and soil[25]. In this thesis the CFs denoted as "*Ecotoxicological characterization factor in CTUe, Emissions to Continental Air, Freshwater*" and "*Ecotoxicological characterization factor in CTUe, Emissions to Continental Freshwater, Freshwater*" were used[26], since they best correspond to the air and surface water compartments of PestLCI (Fantke and Huijbregts, pers. com. 2013). Hereafter, these characterisation factors are referred to as CF air and CF water in short. CFs for soil were not collected since inventory results for this compartments were not available from PestLCI.

4.3.5 Calculation of new characterisation factors in USEtox

For pesticides that were not already included in the USEtox database, new CFs had to be determined in USEtox. In order to determine a pesticide's CFs in air and water a number of physical-chemical properties and ecotoxic effect data were required, listed in table 4.5.

---

[24] CFs can also obtained from the USEtox database in SimaPro, but the LCA practitioner should remember to always use the latest available CFs since updates come regularly. A comparison in this thesis between CFs from 2008 and 2010 revealed significant differences.

[25] The LCA practitioner should be aware that USEtox Excel and USEtox SimaPro do not have the same notation and division between different environmental sub-compartments.

[26] These CFs correspond to the SimaPro CFs denoted as "water (unspecified)" and "air (stratosphere + troposphere)" according to the conversion table in Bennet (2012).

Table 4.5 Properties and parameters required by USEtox for calculation of new characterisation factors with notations as in USEtox.

Notation	Explanation	Unit	Necessary to provide as input in USEtox
MW	Molecular weight	g/mole	Yes
Kow	Partition coefficient between octanol and water	-	Yes
Koc	Partition coefficient between organic carbon and water	l/kg	No
K_H25C	Henry's law coefficient/constant	$Pa{\cdot}m^3/mole$	No
Pvap25	Vapour pressure at 25°C	Pa	Yes
Sol25	Water solubility at 25°C	mg/l	Yes
K_{DOC}	Partition coefficient between dissolved organic carbon and water	l/kg	No
$kdeg_A$	Degradation rate in air	1/s	Yes
$kdeg_W$	Degradation rate in water	1/s	Yes
$kdeg_{Sd}$	Degradation rate in sediment	1/s	Yes
$kdeg_{Sl}$	Degradation rate in soil	1/s	Yes
avlogEC50	Measure of ecotoxic effect based on acute and chronic EC50 data.	log mg/l	Yes

Physical-chemical data

EPISuite^{TM} (chapter 4.1.3) was used as the default database for derivation of the necessary physical-chemical data and experimental data were always favoured over estimated data, according to the USEtox team's recommendation in Huijbregts et al. (2010a).

Molecular weight was found under the "All results" tab in the EPISuite Results window.

Experimental data for Log Kow, also denoted Log P in EPISuite, was found under the "All results" tab in the Result window or under the KOWWIN tab. This value was raised to the power of ten to get the Kow-value[27]. In case experimental data were lacking, the KOWWIN estimate for log Kow was used.

Experimental data for Koc were found by entering the KOCWIN program in single program mode or under the "All results" tab in the Results window. Note that experimental data are not shown under the KOCWIN tab in the Results window. The Log Koc was raised to the power of ten to get the Koc value. If experimental data were lacking, the KOCWIN estimate from MCI (Molecular Connectivity Index) was used. If the MCI-estimate was lacking, the USEtox built in estimation $Koc = 1.26 \cdot Kow^{0.81}$, was used. This estimation was applied automatically if the corresponding Excel-box was left blank. (Huijbregts et al. 2010a)

Experimental data for K_H25C were found by entering the EPISuite HENRYWIN program in single program mode or under the "All results" tab in the Results window. Note that experimental data are not shown under the HENRYWIN tab in the Results window. If experimental data were not available the USEtox built-in estimation $K_H25C = MW{\cdot}Pvap25/Sol25$, was used. This estimation was applied automatically if the

[27] Note that "Exp. Log" refers to experimental log.

corresponding Excel-box was left blank. (Huijbregts et al. 2010a) EPISuite estimates for K_H25C were not used.

Experimental data for vapour pressure at 25°C were found under the MPBPVP "General" tab in the Results window or under the "All results" tab in the Results window and converted to Pa, when given in mm Hg[28]. If experimental data were lacking the Modified Grain method estimate for solids was selected, or the average of the Antoine and Modified Grain estimate for liquids and gases. The physical state of pesticides was found in PPDB (2013). The Modified Grain and Antoine method estimates were available under the MPBPVP "Vapour pressure" tab in the Results window.

Experimental database value for Sol25 was found under the Water Solubility tab in the Results window. If experimental data were lacking the EPISuite WSKOW estimate from Log Kow was used, available under the "Water Solubility" tab in the Results window.

Neither experimental nor estimated K_{DOC} values were available in EPISuite. Instead the USEtox built-in estimation $K_{DOC} = 0.08 \cdot Kow$ for chemicals with log Kow < 7.5 was used for all pesticides, applied automatically when the corresponding Excel-boxes were left blank. (Huijbregts et al. 2010a)

Experimental degradation rates in air, water, sediment and soil were not available in EPISuite. An estimate for degradation rate in air, $kdeg_A$, was made according to equation 4.1[29], where K_{OH} is the overall hydroxyl radical rate constant (in units of cm^3/molecules·sec) and [OH] is the hydroxyl radical concentration per 12 hours of daylight (in units of molecules or radicals per cm^3).

$$kdeg_A = \frac{K_{OH} \cdot [OH]}{2}$$

Equation 4.1

A default value of $[OH] = 1.5 \cdot 10^6$ was used according to Huijbregts et al. (2010a). Experimental data for K_{OH} were available by entering AOPWIN in single program mode or under the "All results" tab in the Results window. If experimental data were lacking the "overall OH rate constant" estimate available under the AOPWIN "Hydroxyl Radicals Page 2" (or for some pesticides only by accessing the program in single program mode) was used.

For degradation rate in water, $kdeg_W$, an estimation was made based on table 4.6. Table 4.6 show relationships between the Biowin 3 "Ultimate biodegradation timeframe" output, as found under the BIOWIN "General" tab in the Results window, and the biodegradation rate in water.

[28] 1 mm Hg = 133.32 Pa

[29] The division factor 2 was not mentioned in Huijbregts et al. (2010a) but used to get the same result as USEtox. This conclusion was reached after comparing CFs for a selection of chemicals already included in the USEtox database with calculated CFs. Bennet (2012) arrived at the same conclusion.

Table 4.6 Relationship between Biowin3 output, Ultimate biodegradation timeframe, as given under the "General" tab in EPISuite BIOWIN, and assumed biodegradation rate for water used for calculation of characterisation factors. Table adopted from Huijbregts et al. (2010a).

EPISuite BIOWIN Biowin3 Output	Biodegradation rate in water (1/s)
Hours	4.7E-05
Hours to Days	6.4E-06
Days	3.4E-06
Days to Weeks	9.3E-07
Weeks	5.3E-07
Weeks to Months	2.1E-07
Months	1.3E-07
Recalcitrant	4.5E-08

For degradation rates in sediment and soil, $kdeg_{Sd}$ and $kdeg_{Sl}$, equations 4.2 and 4.3 were used as estimation. (Huijbregts et al. 2010a)

$$kdeg_{Sd} = \frac{kdeg_W}{9}$$

Equation 4.2

$$kdeg_{Sl} = \frac{kdeg_W}{2}$$

Equation 4.3

Freshwater ecotoxicological effect data

The last parameter, *avlogEC50*, is a measure of the ecotoxicological effects and based on experimental EC50-data from different aquatic freshwater organisms. The *avlogEC50* parameter was calculated in the following manner (Huijbregts et al. 2010a):

- Collection of acute and chronic EC50-data expressed in mg/l from various databases (listed below).
- In case of more than one EC50-value for similar test conditions the geometric mean[30] of all values was taken.
- Conversion of acute EC50s to chronic equivalent EC50s by applying an acute-to-chronic extrapolation factor of two, according to equation 4.4.

$$Chronic\ equivalent\ EC50 = \frac{Acute\ EC50}{2}$$

Equation 4.4

Similar test conditions were interpreted as same pesticide, species and test duration time. Type of tested effects, type of test and other test characteristics were disregarded. Following these initial steps the *avlogEC50* parameter value could be attained in two equivalent manners:

1) According to the user manual in Huijbregts et al. (2010b, p. 16-17) by taking the log of all chronic equivalent EC50s and calculate the arithmetic mean of all log-values.
2) According to the method described in Payet (2004, p. 65) by calculating the geometric mean of all chronic equivalent EC50s and take the log of the geometric mean.

---

[30] The geometric mean of a collection of numbers $x_1 \ldots x_n$ is defined as: $\sqrt[n]{\prod_i^n x_i}$.

In short; if there are N chronic-equivalent EC50s, denoted x, *avlogEC50* can be calculated according to equation 4.5.

$$av_{logEC50} = \frac{\sum_{i=1}^{N} \log(x_i)}{N} = log\left(\sqrt[N]{\prod_{i=1}^{N} x_i}\right)$$

Equation 4.5

The differentiation between acute and chronic tests was made in the following manner: whenever it was indicated in a database whether a test was acute or chronic that classification was used. For cases when it was not stated, a classification based on test duration presented in table 4.7 was used. For cases when the test duration time was not stated the test was assumed to be acute.

Table 4.7 Differentiation between acute and chronic EC50-tests based on test durations (modified from Payet, 2004).

Type of organism	Acute	Chronic
Vertebrates	< 7 days	≥ 7 days
Invertebrates	< 7 days	≥ 7 days
Plants	< 7 days	≥ 7 days
Algae	< 3 days	≥ 3 days

During effect data collection the following information was noted for each EC50-value:

- the species' scientific name
- the duration of the test in days
- the database's classification of the test as acute or chronic
- the organism group of each species, separating between algae, aquatic plants, aquatic invertebrates, fish, molluscs and freshwater insects
- the source of the data

All ecotoxicological effect data collected and used in this thesis, including all supporting information, are available in Appendix V.

Databases for freshwater ecotoxicological effect data

According to Huijbregts et al. (2010a) first priority should be given to chronic data from Payet (2004); second priority to acute data from Payet (2004), applying an acute-to-chronic extrapolation factor of 2.2 and third priority to acute data from RIVM e-toxBase, applying an acute-to-chronic extrapolation factor of 2.

Access to the RIVM e-toxBase was applied for, but not granted, since the online database was about to close down shortly due to financial issues (Wintersen, pers. com. 2013). Payet (2004) only contained three of the substances required and while an updated and expanded online-version of the database in Payet (2004) was available through the company Tools4 environment[31], it was decided not to acquire the license.

[31] A demo version of Aiida is available at: http://aiida.tools4env.com/ (Accessed 2013-03-18)

In cases when Payet (2004) did not contain the pesticides of interest other sources were used, primarily PPDB, AGRITOX and ECOTOX. All databases used are presented below.

Payet (2004) - The AMI-database in the appendix of Payet[32] (2004) contains a list of already calculated geometric mean chronic equivalent EC50s for 522 substances, a large share of which are pesticides. Log was taken on these geometric means, denoted "*Chronic* $HC50_{EC50}$", to get a number corresponding to the USEtox's *avlogEC50* parameter, according to equation 4.5. Number of species was also noted from Payet (2004). Pesticides were found in Payet (2004) by searching on CAS-number since most pesticides were not denoted by their common name.

PPDB (2013) - The Pesticide Properties Database[33], is an online database developed by the Agriculture and Environment Research Unit (AERU) at the University of Hertfordshire, UK. It contains a rather small set of ecotoxicological effect data for around 1 100 pesticides, including all AS used in the EU (PPDB, 2013). Up to three EC50-test values are available for each pesticide within the three predefined categories "*Aquatic invertebrates - Acute 48 hour EC50*", "*Aquatic plants - Acute 7 day EC50, biomass*" and "*Algae - Acute 72 hour EC50, growth*".

AGRITOX (2013) - a French database[34] of plant protection substances created in 1986 by the French National Institute for Agricultural Research. The database contains, besides sections on physical-chemical data, toxicity, regulatory data and behaviour in the environment, a rather extensive section on ecotoxicity. Effect data in AGRITOX originate from published scientific articles and dossiers submitted by the industry to regulatory bodies within the EU and have been expert reviewed (AGRITOX, 2013). PPDB and AGRITOX were found to often overlap in their coverage of test-results but AGRITOX generally provided more information regarding test conditions and more exact test values than PPDB.

ECOTOX - (USEPA, 2013) is an extensive database created by the US Environmental Protection Agency, consisting of three separate toxicity databases of which one for aquatic ecosystems called AQUIRE. EC50-data in ECOTOX were found by performing an "Advanced Database Query", selecting EC50 as the test result endpoint and freshwater as exposure media. The database was rather difficult to navigate in, and only contained a few of the substances of interest for this thesis.

If effect data could not be found in any of the above mentioned databases, pesticide datasheets from the industry or from authorities, such as European Commission and USEPA, were used in a few cases. All sources used are listed in Appendix V.

4.3.6 Calculation of freshwater ecotoxic impact

In order to calculate the freshwater ecotoxic impact attributed to a given pesticide, the theory outlined in chapter 3.4 and equation 3.4 was followed with slight modification in

[32] Payet (2004) is available upon request to the author by email. See references.
[33] PPDB is available at: http://sitem.herts.ac.uk/aeru/footprint/index2.htm (Accessed 2013-03-18)
[34] AGRITOX is available at: http://www.dive.afssa.fr/agritox/index.php (in French) (Accessed 2013-03-18)

the form of multiplication factors, so called frequency factors. These were used in order to take into account frequencies of application and even out the ecotoxic impact over the years. For example, if a pesticide was applied every fourth year the yearly average ecotoxic impact was calculated as 25% of the ecotoxic impact attributed to the actual application.

Yearly average freshwater ecotoxic impact (CTUe/ha/yr) attributed to the application of a pesticide P was calculated according to equation 4.6, where f_P denote pesticide P's frequency factor (1/yr), $e_{air,P}$ and $e_{water,P}$ denote emissions of pesticide P to the environmental compartments of air and water (kg/ha) and $CF_{air,P}$ and $CF_{water,P}$ denote freshwater characterisation factors for emissions to air and freshwater respectively (CTUe/kg).

$$Freshwater\ ecotoxic\ impact\ (P) = \left(e_{air,P} \cdot CF_{air,P} + e_{water,P} \cdot CF_{water,P}\right) \cdot f_P$$

Equation 4.6

The yearly average freshwater ecotoxic impact for a given cropping system was then calculated as the sum over all pesticides.

4.3.7 Allocation of results

Several of the crops included in the study are associated with co-products in the production of biofuel. It was therefore decided to allocate the results through partitioning in order to take into account other production system outputs besides biofuel. It was decided to partition on the basis of energy content according to the EU Renewable Energy Directive (EC, 2009a) and the EU Fuel Quality Directive (EC, 2009b).

Allocation factors, presented in table 4.8, were retrieved from the BioGrace GHG calculation tool[35] (2011). These allocation factors have been calculated on the basis of energy content of main product (biofuel) and co-products, in typical production systems.

Ethanol from *Salix* is not handled by the Renewable Energy Directive (EC, 2009a) and is not included in BioGrace GHG calculation tool and was not allocated. It should be noted that the allocation factor of sugarcane is 100% to ethanol[36] according to BioGrace (2011).

---

[35] The BioGrace Excel greenhouse gas emission calculation tool is available for download from the BioGrace homepage: www.biograce.net (Accessed 2013-03-20).

[36] It can be claimed that allocating 100% to ethanol in the sugarcane-case is not fair since most modern sugarcane ethanol production plants use the co-product bagasse as a feedstock to produce local CHP and in addition often sell excessive electricity to the grid. However, it was decided in this thesis to use the allocation factors available in BioGrace (2011).

Table 4.8 Allocation factors based on energy content and co-products of biofuel production process (Source: BioGrace, 2011)

Crop	Allocation factor of main product	Main product	Co-product
Maize	54.6%	Ethanol	DDGS (10% moisture)
Rapeseed	58.7%	FAME from rapeseed oil	Rapeseed cake and refined glycerol.
Soybean	32.9%	FAME from soy oil	Soy cake and refined glycerol.
Sugarcane	100%	Ethanol	-
Wheat	59.5%	Ethanol	DDGS

Allocation factors were applied on yearly average pesticide amounts and ecotoxic impact scores. Results are presented in chapter 6 in allocated as well as unallocated formats.

5. INVENTORY AND CROP INTRODUCTION

A qualitative and quantitative inventory was performed for each of the selected feedstocks and is presented here accordingly. Chapters 5.1 – 5.6 deal with each of the selected crops and chapter 5.7 deals with the gross energy yields of the different biofuel production systems. Chapter 5.1 - 5.6 are divided into three subchapters: “introduction”, “agricultural management” and “typical field pesticide application scenarios”.

The introductions contain a short, general overview of each of the different crops for the purpose of orientation and background information.

The sections “agricultural management” contain a description of cultivation practices. Common and important weeds, insect pests and diseases for each crop are listed as well as how they are managed, to provide a background for pesticide application. This information acts both as an orientation for the reader, as well as a source of information that during the thesis assisted in construction of typical pesticide application scenarios and the choice of relevant assumptions. Scientific names of weeds, insect pests and plant diseases have been taken from various Internet sources, such as the American Phytopathological Society (APS, 2013).

The sections “typical field pesticide application scenarios” outlines the essentials of the application scenarios used in this thesis. Supporting information regarding all pesticides included in the scenarios, doses, application times and methods, crop development stages at times of application and frequencies of application are available in Appendix II.

5.1 Maize

5.1.1 Introduction

Maize (*Zea mays*), figure 5.1, also called corn, belongs to the true grasses, *Poaceae*, family and is by definition a cereal. The plant, originally a tropical grass, has been cultivated for thousands of years in Central America and is a staple food crop for millions of people today, especially in Central and South America and Africa. The plant has high water requirements and is sensitive to drought. Under optimal conditions, maize yields more than any other cereal crop. (Bayer CropScience, 2012)

While a large proportion of maize grown in developing countries goes to human consumption, a majority of maize grown in developed countries is used as fodder to cattle, pigs and poultry and as a feedstock for production of starch, high fructose corn syrup and ethanol. (Bayer CropScience, 2012) Today, maize is the largest feedstock to global ethanol production accounting for close to 50%. (SJV, 2011). USA was the largest maize producer in 2010, producing 37% of world total, followed by China and Brazil (FAOSTAT, 2012). Key figures on maize production in the USA are presented in table 5.1.

The share of US maize going to fuel ethanol has increased by a factor of 5 during the past 10 years, reaching 39.5% in 2011 (a third of which becomes production residues in the form of DDGS and ultimately ends up in the feed sector) (NCGA, 2012). Per hectare yields in the USA has more than doubled between the first half of the 1960s and today, shown in table 5.1. Iowa is the state with the largest maize production (USDA NASS, 2012) and is taken as a point of reference in the following discussion.

Figure 5.1 Maize plant with ear. (Photo: danellesheree. Source: Flickr, 2013)

Table 5.1 Key figures for maize production in the USA, representing yearly averages (FAOSTAT, 2012).

	USA 1961-1965	USA 2006-2010
Area harvested for maize (average) (thousand hectares)	22 900	32 100
Production of maize[1] (average) (thousand tonnes)	95 600	311 000
Yield per hectare (average) (tonnes/hectare) *calculated*	4.17	9.68

1) Production of maize refer to clean, dry weight of grain (12-14% moisture) in the form usually marketed (FAOSTAT, 2012).

5.1.2 Agricultural management

I Iowa, maize is typically planted in April and harvested in September to October (ISUST, 2009) on 20 – 50 hectare fields (Ertl, pers. com. 2013). Early and effective weed control is of great importance for maize since it is sown with rather large row distances,, develops slowly and is sensitive to competition from weeds over water and soil nutrients. In practice it often means complete removal of weeds prior to planting, achieved by chemical means (Everest et al. 2012).

Recently, genetically modified (GM) varieties of maize have been developed and incorporated with traits such as glyphosate tolerance (e.g. Monsanto's Round-up Ready (RR) maize) and ability to produce insecticidal bacterial toxins from the bacterium *Bacillus thuringiensis*, so called Bt-maize. Such biologically engineered varieties are already widely adopted by US farmers: in 2011 49% of US maize had more than one GM-trait, 23% had a single GM-trait in the form of herbicide tolerance and 16% had a single GM-trait in the form of insect resistance (Bt) while only 12% was non-GM (NCGA, 2012).

The most recent statistics, provided by the US Department of Agriculture's National Statistics Service (NASS), show that herbicides were applied to 98% of all acreage grown with maize in 2010. The top three herbicide AS (used in largest amounts) were glyphosate, atrazine and acetochlor. 62% of the acreage planted with maize was under no-till or minimum-till practice in 2010 (USDA NASS, 2011) and 16% was irrigated in 2007 (USDA NASS, 2012).

Glyphosate tolerant maize has to a large extent led to replacement of traditional inter-row hoeing in favour of intensive use of, and reliance on, glyphosate in growing crops to control weeds (Everest et al. 2012). Glyphosate is often complemented with other herbicides, such as atrazine (Ertl and Gerlach, pers. com. 2013), to achieve a broader protection and tackle the increasing problem of glyphosate resistant weeds. Difficult grass weeds in maize include crabgrasses (*Digitaria* spp.), goosegrass (*Eleusine indica*), crowfoot grass (*Dactyloctenium aegyptium*), Johnson grass (*Sorghum halepense*) (Everest et al. 2012) as well as Barnyard grass (*Echinochloa crus-galli*) and foxtails (*Setaria spp.*) (PIC, 2012).

Johnson grass, a perennial grass that propagates both by seeds and through rhizomes, is perhaps the most troublesome weed, since it competes aggressively over soil nutrients, acts as a vector for virus borne disease (Everest et al. 2012) and quickly develops herbicide resistance. Between 1991 and 2010 Johnson grass developed resistance against ACCase inhibitors, ALS inhibitors and glycines on at least 18 sites all over USA. Multiple documented cases of resistance against atrazine have been confirmed on maize fields all over USA. Examples from Iowa include giant foxtail (*Setari faberi*) and lambsquaters (*Chenopodium album*) (Heap, 2013).

The warm and dry climate where maize is usually grown does not favour fungal disease development and fungal disease in maize is hence a comparatively small problem. If good agricultural practices are maintained, such as proper crop rotation (with non-grass crops), tillage and selection of resistant varieties, diseases are usually effectively controlled, and even when local outbreaks do occur, fungicide application is rarely economically motivated. (Everest et al. 2012) Statistics from USDA show that fungicides were applied to only 8% of US maize fields in 2010 although this figure may vary from year to year. The top three fungicides were pyraclostrobin, propiconazole and azoxystrobin (USDA NASS, 2012).

However, some of the most problematic fungal diseases to maize in the USA are different rusts (*Puccinia sorghi, P. polysora* and *Physopella pallescens*), ear rots (for example *Diplodia* spp. and *Aspergillus* spp.), storage rots (for example *Aspergillus* spp. and *Penicillium* spp.) and stalk rots (several species). Among the rusts Southern rust (*Puccinia polysora*) is the most destructive. In addition, common smut (*Ustilago maydis*), southern corn leaf blight (*Bipolaris maydis*), crazy top downy mildew (*Sclerophthora macrospora*) and maize dwarf mosaic virus are also of concern locally and occasionally. (Everest et al. 2012) Fungicides, when used, are typically applied by aircraft at fully grown crops (Ertl, pers. com. 2013).

There are over 20 common insect pests that are able to cause severe damage to maize by feeding on various parts of the plant, such as the ears, silks, tassels or leaves or attacking the roots or stalks (Everest et al. 2012). The two most damaging insects in the USA are two rootworm species: western and northern corn rootworm (*Diabrotica virgifera virgifera* and *D. barberi*). Rootworms refer to the larva state of a beetle. Yield losses are due both to young larvae feeding off the roots and adult beetles feeding off the flowers and kernels. Rootworms can be controlled by crop rotation, selection of resistant varieties and insecticides. There is also Bt-maize available with protection against rootworms. (Gassmann and Weber, 2012)

Other insects of significant importance include the European corn borer (*Ostrinia nubilalis*), black cutworm (*Agrotis ipsilon*), fall armyworm (*Spodoptera frugiperda*) and corn earworm (*Helicoverpa zea*) (Gassmann and Weber, 2012).

Statistics from USDA show that insecticides were applied to 12% of US maize fields in 2010, although this figure may vary significantly from year to year, with the top three insecticides being chlorpyrifos, tefluthrin and tebupirimphos. (USDA NASS, 2012) Insecticides are typically applied either by the planter in conjunction with planting (soil insecticides) or later during tassling by aircraft, against rootworm beetles, while farmers that grown Bt-maize typically do not use insecticides (Ertl, pers. com. 2013). However, recent reports on insects developing resistance against Bt-maize (such as the European corn borer) (UM Extension, 2008) suggest that the use of insecticides on Bt-maize might increase in the near future.

5.1.3 Typical field pesticide application scenarios and cases

The assumed maize field is located in the state of Iowa, USA, sown in April and harvested in September - October. The field has the following characteristics:
Size: 35 ha (500×700 m^2)
Climate: Iowa City, Iowa, USA
Soil: Grundy County, Iowa, USA
Irrigation: 0 mm
Drainage: 25% of the field
Tillage: reduced tillage
Slope: 1%

Two cases have been considered:

1. GM glyphosate tolerant maize with integrated insect resistance (Bt-maize) for which case no insecticide is applied (referred to as “Maize, no I”)
2. GM glyphosate tolerant maize without integrated insect resistance for which case one insecticide (chlorpyrifos) is applied (referred to as “Maize, I”)

The two cases only differ with regard to the insecticide chlorpyrifos. Two herbicides (glyphosate and atrazine) are applied in both cases. These herbicides represent the top two herbicide active substances (AS) used on maize in the USA in 2010 (USDA NASS, 2012). The atrazine dose is taken from a suggested scenario created by Erik Gerlach (pers. com. 2013) and the glyphosate dose is calculated, assuming a total herbicide dose of 2 558 g AS per hectare and year. This herbicide dose represent the average dose applied to the share of herbicide treated US maize fields in 2010 (USDA NASS, 2012).

Atrazine is applied pre-plant in March and glyphosate on top of growing crops when plants are approximately 50 cm tall, in June. The IMAG conventional boom sugar beet is chosen as application method since the wind drift curve for this application method has been derived for sugar beet crops at an average height of 50 cm (Dijkman, pers. com. 2013).

In the insecticide case it is assumed that one dose of chlorpyrifos at 187 g AS per hectare is applied at tasseling time when the plants are fully grown, by aircraft. This insecticide dose represent the average dose applied to the share of insecticide treated US maize fields in 2010 (USDA NASS, 2012). No fungicides are applied.

Supporting information is available in Appendix II. This application scenario has been constructed with the assistance of David Ertl and Erik Gerlach (pers. com. 2013) as well as information from USDA NASS (2012) and NCGA (2012).

5.2 Rapeseed

5.2.1 Introduction

Rapeseed (*Brassica napus*), figure 5.2, also called oilseed rape, is an annual plant within the *Brassicaceae*, cabbage, family that has been cultivated for thousands of years, originally for use in non-food applications such as lamps, soap and lubricants. (Fediol, n.d) Technical applications are still of major importance, with around a third of the global rapeseed oil in 2009 going to biodiesel production, making rapeseed oil the largest feedstock into present biodiesel production (LMC International, 2010). In EU, the share is even larger; estimated to 60% of the rapeseed grown in the EU to be used in biodiesel production (IEA Bioenergy, 2009).

Figure 5.2 Flowering rapeseed plant. (Photo: Nick Saltmarsh. Source: Flickr, 2013)

Rapeseed produce seeds with 33-48% oil content. The residue meal that remains after crushing the seeds is a valuable co-product as high-protein fodder for cattle and pigs. Rapeseed is sown during either spring (summer varieties) or autumn (winter varieties). Winter rape dominates in Europe and has higher yield levels than summer rape (Fediol, n.d).

EU is the largest rapeseed oil producer in the world and rapeseed is used as a feedstock for biodiesel primarily in Europe (Fediol, n.d). Most of the rapeseed is cultivated in the northern and western regions of Europe (SJV, 2006). Table 5.2 present key figures for rapeseed and rapeseed oil production in this region. In Europe, Germany is the largest producer, followed by France and United Kingdom. In Germany the area under rapeseed cultivation has doubled during the past 20 years (FAOSTAT, 2012). Germany is taken as a point of reference in the following discussion with some examples from Sweden where cultivation practices are similar.

Table 5.2 Key figures for rapeseed and rapeseed oil production in northern and western Europe[1], representing yearly averages. (FAOSTAT, 2012)

	Northern and western Europe 1961-1965	Northern and western Europe 2006-2010
Area harvested for rapeseed (average) (thousand ha)	376	4 360
Production of rapeseed (average) (thousand tonnes)	704	14 300
Production of rapeseed oil (average) (thousand tonnes)	211	6 240
Yield per hectare of rapeseed (average) (tonnes/ha) *calculated*	1.88	3.28
Yield per hectare of rapeseed oil (average) (tonnes/ha) *estimated*[2]	0.56	1.43

1) Northern and western Europe include: Austria, Belgium, Denmark, Estonia, Finland, France, Germany, Ireland, Latvia, Lithuania, Luxembourg, Netherlands, Norway, Sweden, Switzerland and United Kingdom.
2) Calculated by dividing the production of rapeseed oil over the acreage grown with rapeseed. This corresponds to 44% oil content and 100% extraction rate.

5.2.2 Agricultural management

Winter rapeseed is sown in the autumn and harvested in July or early August the following summer when the seeds have become dark brown and hard. In Germany, rapeseed is commonly rotated with cereals such as winter barley or maize. (GMO Safety, 2010) Rapeseed is rather weak at the early stages of development and competes poorly with many frequently found weeds for which reason it is important to effectively control weeds at the beginning of the sowing period and ensure the soil bed is as clean as possible. In later stages of development rapeseed is strong and outrivals many troublesome weeds. (Weiss, 1983)

In Germany virtually the entire area under rapeseed is treated with herbicides. It is common practice to apply herbicides once or twice, using two or three different AS, at sowing time and shortly after sowing. (GMO Safety, 2010) Chemical weed treatment is sometimes complemented with mechanical inter-row tillage (Schmidt, 2007).

Rapeseed is a dicot and so are many of the frequently found weeds; reducing the number of herbicides that can be used to a rather limited set. Many weeds commonly found in cereals are better controlled at the rapeseed stage in the crop rotation and vice versa, to avoid the problem of common sensitivity. Rapeseed can act as cleaning-brake in a crop-rotation with cereals. Common dicot weeds include chick weed (*Stellaria media*), cleavers (*Galium aparine*), field chamomile (*Anthemis arvensis*), Shepherd's purse (*Capsella bursa-pastoris*) and wild radish (*Raphanus raphanistrum*). Common monocot weeds include black grass (*Alopecurus myosuroides*), meadow grass (*Poa* spp.), wild oats (*Avena fatua*) and Italian rye-grass (*Lolium multiflorum*). (Berry et al. 2012)

Some of the most serious fungal diseases in Europe include three soil borne diseases: Sclerotinia stem rot (*Sclerotinia sclerotiorum*), Verticillium wilt (*Verticillium longisporum*) and clubroot (*Plasmodiophora brassicae*), two foliar diseases: light leaf spot (*Pyrenopeziza brassicae*) and Phoma leaf spot (*Leptosphaeria* spp.) and one seed borne disease: dark leaf and pod spot (*Alternaria* spp.). (Berry et al. 2012) Soil borne diseases have increased lately due to shortened rotations (Berry et al. 2012), however, they can often be effectively controlled by applying crop rotation of adequate length, eliminating weeds that are potential disease hosts, ploughing down crop debris left on ground and selecting resistant varieties. (Weidow, 2008)

The EU Management Strategies for European Rape Pests (MASTER) project regard the following six insect pests to be the most serious threats to winter rapeseed in Europe: pollen beetle (*Meligethes aeneus*), cabbage stem flea beetles (*Psylliodes chrysocephala*), rape stem weevils (*Ceutorhynchus napi*), cabbage seed weevils (*Ceutorhynchus assimilis*), Brassica pod midge (*Dasineura brassicae*) and Cabbage stem weevil (*Ceutorhynchus pallidactylus*) (MASTER, 20--). In addition cabbage aphids (*Brevicoryne brassicae*) can be of concern regionally and occasionally (Weiss, 1983).

Pollen beetles are widespread in all temperate climates and affect around two thirds of the European rapeseed (EPPO, 2007). The beetles overwinters as adult and are drawn towards yellow flower buds in early spring to lay eggs. Both larvae and adults feed off the pollen in the developing flower buds. (Weiss, 1983). Despite a potential to cause large damage, rapeseed plants have a recognised ability to compensate for large losses of buds. By not treating pollen beetles in winter rape yield losses have been estimated for Swedish conditions to be around 110 kg per hectare on average up to total damage in worst case (SJV and KemI, 2002).

Pollen beetles have been treated intensively and almost exclusively with pyrethroids in Europe for the past 20 years due to lack of insecticides with alternative modes-of-action. Little surprising, this has led to development of resistance and today, pollen beetles across Europe show signs of resistance against pyrethroids. This has led to significant crop losses in recent years and increasing use of insecticides. (EPPO, 2007) In Sweden local problems exist with resistance against 6 out of 7 available pyrethroid formulations (SJV, LRF and HIR, 20--). Neonicotinoids are also available against pollen beetles but have suspected negative effects on pollinators (see for example Lehrman, 2012). Rapeseed is partially self-pollinating but gain in yields from insect pollination.

5.2.3 Typical field pesticide application scenario

The assumed rapeseed field is located in Görlitz, Germany, sown in the autumn with winter rapeseed and harvested early the next summer. The field has the following characteristics:

Size: 10 ha (500×200 m^2)
Climate: continental (Görlitz, Germany)
Soil: average
Irrigation: no
Drainage: 100% of the field
Tillage: conventional
Slope: 1%

The field is ploughed prior to sowing. Glyphosate is applied on average every four years, primarily against couch grass. The glyphosate dose is based on a recommendation regarding the formulation Roundup Bio (Monsanto Company, 2008). All herbicides (metazachlor, quinmerac and cycloxydim) are applied during August – September; cycloxydim to remove voluntary cereals assuming rotation with cereals. The insecticide alpha-cypermethrin is applied in September against flea beetles, on average three years of five in three quarters of a full dose. The full dose is based on a recommendation in BASF (201-). The insecticide thiacloprid is applied against pollen beetles two years of three, in April. The fungicide boscalid is applied to on average 30% of fields every year, in May.

All pesticides are applied using a conventional boom sprayer for cereals. Supporting information is available in Appendix II. This application scenario has been constructed with the assistance of Nils Yngvesson (pers. com. 2012) and information from KemI (2013). All pesticide doses are based on information from Yngvesson and valid for northern Europe.

5.3 Salix

5.3.1 Introduction

Salix, figure 5.3, refer to a genus compromising over 400 species of deciduous trees and shrubs, known as willows, sallows and osiers, native to the Northern Hemisphere. Traditional use of *Salix* species include windbreaks and (snow)fences, basket and furniture production and ornamental planting. A recent and increasing area of application is soil remediation as *Salix* has the ability to take up and hold soil contaminants such as heavy metals (Volk et al. 2004).

Figure 5.3 *Salix* plantation. (Photo: Villeskogen. Source: Flickr, 2013)

Salix species, like all woody trees and shrubs, have an ancient history of bioenergy utilisation as burning material in household stoves and fireplaces. However, large scale cultivation of *Salix* for bioenergy production is rather new and *Salix* still only contributes a small share towards this end (Ericsson et al. 2009). *Salix* represent a perennial cropping system characterised by fast growth allowing short rotation (3-4 years), high yields, strong regrowth through coppice even after multiple harvests and a broad genetic base that allows for breeding of new varieties. This system is commonly referred to as short rotation woody coppice (SRWC). The geographical focus of this study is Sweden.

The interest for *Salix* as a bioenergy crop in Sweden started during the 1970s energy crisis (Volk et al. 2004). A breeding program initiated in 1987 has so far produced around 30 species, some with good resistance against pests and diseases, and increased average yields by around 60%. (Kolm et al. 2011) The Swedish breeding program focus primarily on *Salix viminalis* and its hybrids with *Salix schwerinii* (IEA Bioenergy, 2012). Commercial plantations have supplied the internal market since the 1990s but today a majority of *Salix* material grown in Sweden is exported to other countries in Europe. (Kolm et al. 2011)

Incineration to produce heat or combined heat and power (CHP) is the most common offset for *Salix* in Sweden today. (SalixEnergi Europa, n.d) Lignocellulosic biomass such as *Salix* can also be converted to ethanol by advanced technology, although not commercial yet.

The area grown with *Salix* in Sweden has declined over the past decade from close to 18 000 hectares to 12 000 hectares today, due to problems with diseases, yields and profitability. However, new varieties with better resistance against disease and higher yields are under development and the market for wood chips is perhaps better than ever. Therefore initiatives and effort are currently taken to reverse this trend and promote the crop (Ramstedt, pers. com. 2012 and SJV, 2012).

5.3.2 Agricultural management

A typical plantation establishment consists of field preparation in the autumn prior to planting by deep-ploughing and application of a broad-spectrum herbicide. In the spring, prior to planting, a second batch of herbicides are applied, followed by planting of *Salix* coppice. (Yngvesson, pers. com. 2012) *Salix* is often grown on land less suitable for food crops (Kolm et al. 2011). *Salix* coppice are rather poor at competing with weeds in the early stages of development, making complete removal of weeds prior to field establishment important. Field experiments have shown that biomass growth can be reduced with up to 95% the first year if weeds are not properly controlled. (SJV, 2012)

After the first year when the root system is established and the shoots have grown tall, weeds no longer constitute a problem. *Salix* is harvested during winter or early spring when the average temperature is below 4˚C, usually between October and March (SJV, 2012). The first harvest produces $20 - 25$ dry tonnes per hectare and successive harvests $30 - 35$ dry tonnes per hectare. (SalixEnergi Europa, n.d), or 10 dry tonnes per hectare and year on average throughout the plantations lifecycle, on better sites (IEA Bioenergy, 2012). A plantation can be harvested $7 - 8$ times (Volk et al. 2004) and last 20-30 years. Herbicide application can be repeated after every harvest-cycle if the weed situation demands it (Ramstedt, pers. com. 2012).

In Sweden only three pesticide formulations (all three herbicides) are “on-label” approved for use on *Salix*: Fenix, Focus Ultra and Kerb flo 400 (KemI, 2013) but “off-label” exemptions allow Cougar (containing isoproturon) and Bacara to be used as well, as recommended by SJV (2012) and SalixEnergi Europa (n.d). Farmers typically apply recommended doses, or less, "*hoping for the best*" according to the experience of Mauritz Ramstedt (pers. com. 2012).

SRWC face special challenges in disease management due to the perennial nature and the fact that plantations traditionally are single-genotype. The most serious fungal disease to *Salix* is leaf rust (*Melampsora* spp.) (IEA Bioenergy, 2012). This pathogen is highly adaptable and quickly develops fungicide resistance; it thrives on strong and healthy plants in cooler maritime climates, contrary to many other fungi, and can cause biomass production losses with up to 40%. Other fungi of secondary importance are for example *Marssonia* spp., *Fusicladium saliciperdum*, *Glomerella miyabeana* and *Cryptodiaporthe salicella* (Ramstedt, 1999).

Rust is currently managed by constantly developing new varieties with better resistance (Ramstedt, pers. com. 2012) and avoiding single-genotype plantations. The recommendation is to mix clones from six to ten different genotypes (IEA Bioenergy, 2012).

Leaf beetles are the most serious insect pest (Björkman, pers. com. 2012). Three types of leaf beetles (*Chrysomelidae* spp.) are of concern, among which *Phratora vulgatissima* is the largest problem. The other two leaf beetles are *Galerucella lineola* and *Lochmaea caprea*. (Kolm et al. 2011) The biomass yield reduction as a result of defoliation caused by leaf eating insects has been estimated to 40% in field experiments by Höglund et al. (1999) but if insect populations are moderate plants are usually good at compensating (Ramstedt, pers. com. 2012).

Leaf beetles live through one year and overwinter as adults. In the spring they move into *Salix* plantations, and other habitats, to lay their eggs. Larvae and adults feed off the leafs. A few years after harvest (undisturbed state) research has shown that there is usually a balance between leaf eating insects and predator insects; a type of well-functioning biological control (Björkman and Eklund, 2004). A *Salix* plantation may thus provide a suitable habitat for many insect species and a more diverse environment than many other annual mono-cultured cropping systems.

Despite problems, current fungal diseases and insect pests are not severe enough to economically motivate use of fungicides or insecticides and in addition there are no approved substances and pesticide application on full grown coppice is not practicable (Björkman, pers. com. 2012). To conclude: management strategies against insect pests and fungal diseases consist of development of ever better varieties, clone mixing and biological control.

5.3.3 Typical field pesticide application scenario

The assumed *Salix* plantation is located in Linköping, Sweden and has the following characteristics:
Size: 10 ha (500×200 m^2)
Climate: North European and Continental (Linköping, Sweden).
Soil: average
Irrigation: 0 mm
Drainage: 0%

Slope[37]: 2%

In the autumn prior to field establishment, the field is ploughed and glyphosate applied. The glyphosate dose is based on a recommendation regarding the formulation Roundup Bio (Monsanto Company, 2008). In April the following year, prior to planting, the herbicide Bacara (containing flurtamone and diflufenican) is applied to the field against dicot weeds. The *Salix* seedlings are planted in April – June and allowed to grow for three years without further pesticide application. After three years the field is harvested, followed by a new batch of Bacara. The same procedure, with harvest every third year, is repeated throughout the plantation life cycle, except for the last harvest, after which no herbicide is applied. This gives a total of seven applications of Bacara. The plantation life time is set to 21 years.

No other pesticides are applied and all herbicides are assumed to be applied at “bare soil” using a conventional boom sprayer. The tillage parameter is set to conventional for glyphosate and no-till for the subsequent applications. Supporting information is available in Appendix II.

This application scenario has been constructed with the assistance of Per Åsheim from SalixEnergi Europa (pers. com. 2012) and information from KemI (2013).

5.4 Soybean

5.4.1 Introduction

Soybean (*Glycine max*), figure 5.4, also called soya bean, is a legume within the *Leguminosae*, bean, family, native to Asia, where it has been cultivated for more than 3000 years. In the 19th century, soybean spread across the globe with Chinese emigrants and rapidly became one of the most important crops of the 20th century, grown particularly for its high protein content and complete combination of amino acids (Soyatech, n.d).

The beans contain up to 40% protein but are also high in oil (18-20%), render soybean being classified as an oil crop by FAO. Around 85% of soybeans are crushed and separated into protein-rich soymeal and oil. Almost all of the soymeal is fed to livestock and a large proportion of the oil goes for human consumption. The remaining share of beans are either directly consumed by humans or destined for industrial applications. Traditional food made from soybean include soy sauce, tofu, tempeh and miso. (Soyatech, n.d) One new but increasing application is biodiesel production from soy oil. Out of all soy oil produced globally in 2009, 14% went to biodiesel production (LMC International, 2010).

[37] A somewhat higher slope than for the food crops is assumed since *Salix* is sometimes grown on marginal land.

Figure 5.4 Soybean plant. (Photo: UGA College of Ag. Source: Flickr, 2013)

Global soybean production has increased by over 500% during the past 40 years (Soyatech, n.d) and three countries produce over 80% of the world total; United States, Brazil and Argentina (Soy Stats, 2012). Brazil is the geographical focus of this study. Key figures on soybean production in Brazil are presented in table 5.3.

Table 5.3 Key figures for soybean and soybean oil production in Brazil, representing yearly averages. (FAOSTAT, 2012)

	Brazil 1961-1965	Brazil 2006-2010
Area harvested for soybean (average) (thousand hectares)	337	21 800
Production of soybean[1] (average) (thousand tonnes)	354	59 300
Production of soybean oil (average) (thousand tonnes)	31.6	6 110
Yield per hectare of soybean (tonnes/ha) *calculated*	1.05	2.72
Yield per hectare of soybean oil (tonnes/ha) *estimated* [2]	0.19	0.49

1) Production data on soybean refer to weight of dry product as marketed (FAOSTAT, 2012)
2) Estimated from soybean yields and assuming 100% oil extraction rate and 18% oil content in soybeans.

Brazil produced 29% of world total in 2011 (Soy Stats, 2012), primarily in the states of Mato Grosso, Paraná and Rio Grande do Sul (Soyatech, n.d). Production reached an all-time high in 2010 with 75.5 million tonnes of soybean (Soy Stats, 2012).

5.4.2 Agricultural management

Recently, genetically modified (GM) glyphosate tolerant soybean has been developed by seed companies such as Monsanto and Syngenta and made available to the market starting in 1996 (Soyatech, n.d). In Brazil GM glyphosate tolerant soybean varieties have been grown since 2003 in Rio Grande do Sul and in the whole of Brazil since 2005. In 2009 GM glyphosate tolerant soybean covered 71% of the total soybean acreage in Brazil (Meyer and Cederberg, 2010).

Soybean cultivation in Brazil represent an intense agricultural systems with high chemical input and frequency of pesticide application. The soybean crop is responsible for around 45% of all pesticides sold in the country as reported by Meyer and Cederberg (2010). In 2008 a total of 140 500 tonnes of active substance (AS) was used on the total soybean acreage of 21.2 million hectares, resulting in an average of 6 600 g AS per hectare of which herbicides made up 64%, fungicides 8%, insecticides 15% and other types of pesticides the remaining share. (Meyer and Cederberg, 2010)

Soybeans are typically sown in Brazil between September and November and matures in around 130 days (Meyer, pers. com. 2013). Soybean can be grown in pure mono-cropping systems or in rotation with other crops such as maize and wheat. Around two-thirds of soybean farmers double-crop soybean with maize within the cycle of one year; an intense form of cultivation in which the soil the exposed to pesticides a large share of the year (Meyer and Cederberg, 2010).

Weed is a constant problem for Brazilian soybean farmers and is regarded to be able to cause larger potential yield losses than diseases or insects; up to 75% as reported by Syngenta (2009). Management of weeds is Brazil has changed fundamentally since the introduction of GM glyphosate tolerant varieties. Today, a majority of soybean farmers have more or less abandoned tillage as a means of controlling weeds in favour of increased chemical input prior to planting and on top of crops (Meyer and Cederberg, 2010).

There are indications on increasing problems with weeds in Brazil, probably linked to weeds becoming resistant to glyphosate (Meyer and Cederberg, 2010). Five weed species have been confirmed so far to have developed resistance against glycines in Brazil: horseweed (*Conyza canadensis*), hairy fleabane (*Conyza bonariensis*), Sumatran fleabane (*Conyza sumatrensis*), sourgrass (*Digitaria insularis*) and Italian ryegrass (*Lolium multiflorum*) (Heap, 2013). Johnsongrass (*Sorghum halepense*), considered one of the most troublesome weeds in agriculture due to its perennial nature and two modes of propagation, has developed resistance against glycines in the neighbouring country of Argentina and constitutes a serious threat to RR soybean in the whole of South America with current practices.

Brazil increased its herbicide use on soybean with 50% during a period of five years (2004-2008), reaching on average 4 240 g AS per hectare in 2008. Although the Brazilian statistics does not provide information down to the level of individual pesticides, research has shown that approximately 50% of herbicides used in Brazil as a whole is glyphosate making it the most popular herbicide used. (Meyer and Cederberg, 2010) Further, paraquat-based herbicides have increased by 400% during a period of four years (2005-2008) (Riesemberg and Silva, 2009, cited in Meyer and Cederberg, 2010) and due to increasing problems with glyphosate resistant weeds in Brazil, it is likely that paraquat will take market shares from glyphosate in the future.

A fungus first discovered in the state of Paraná in 2001 spread rapidly across the country and in the following season of 2001/2002 an estimated 60% share of the total acreage cultivated with soybean was affected by the disease. The disease, Asian soybean rust (*Phakopsora pachyrhizi*), a wind-born pathogen, is classified as the most important and devastating disease is soybean in Brazil today (Meyer and Cederberg, 2010). The rust make plants pre-mature, causes defoliation and fewer seeds per pod and resulting yield losses with up to 80% (Syngenta, 2009).

The second most important fungal disease is powdery mildew (*Microsphaera diffusa*) which first appeared in the late 1990s but now occurs all over the country (Meyer and Cederberg, 2010).

There are a huge number of insect pests in soybean production that are potential targets of chemical application. The most troublesome insect pests in South America today are the velvet-bean caterpillar (*Anticarsia gemmatalis*), three types of stink bugs, *Euschistus heros*, *Piezodurus guildinii* and *Nezara viridula* (Meyer and Cederberg, 2010), soybean cyst nematodes (*Heterodera glycines*) and soybean aphids (*Aphis glycines*) (Syngenta, 2009).

Brazil increased its insecticide use on soybean with 70% during a period of five years (2004-2008), reaching on average 1 kg AS per hectare in 2008. Fungicide use on soybean also increased with 70% during the same period, to an average of 0.55 kg AS per hectare in 2008. (Meyer and Cederberg, 2010)

5.4.3 Typical field pesticide application scenarios and cases

The assumed soybean field is located in Mato Grosso, Brazil, sown in October and harvested in February, after 130 days. The field has the following characteristics:
Size: 250 ha (5 000×500 m^2)
Climate: Mato Grosso, Brazil
Soil: Mato Grosso, Brazil
Irrigation: 0 mm
Fraction drained: 0%
Tillage: No tillage
Slope: 1%

Two cases have been considered:

1. GM glyphosate tolerant soybean (referred to as “GM soybean”)
2. Conventional non-GM soybean (referred to as “conventional soybean” or “non-GM soybean”)

The two cases differ in terms of the types of herbicides used, while fungicides and insecticides are the same in both cases. GM soybean is sprayed 11 times during the growing season (with 10 different AS), while conventional soybean is sprayed 12 times (with 13 different AS). The application method has been set to conventional boom cereals. It is assumed that one round of soybean is cultivated per field and year. Supporting information regarding all pesticides used, doses, times of application and crop development stages at times of application are available in Appendix II.

These application scenarios have been constructed with information gathered through an interview with the manager of a farm in Brazil, February 2013, by Daniel Meyer (pers. com. 2013). These scenarios therefore represent the actual practice at one farm in the growing season of 2012/2013, except for the two last fungicide treatments that had not been decided upon at the time of the interview. Two last fungicide treatments (F 3 and F 4, with ID number as in Appendix II) were assumed to be the same as F 1 and F 2 but in different doses.

The farm that was visited cultivated soybean at 10 400 hectare, 85% of which was conventional and 15% of which was GM glyphosate tolerant soybean. In addition to the information gathered at the farm, information regarding pesticide formulations was retrieved from SEAB (2012).

5.5 Sugarcane

5.5.1 Introduction

Sugarcane (*Saccharum officinarum),* figure 5.5, is a tropical perennial grass within the *Poaceae,* true grasses, family, native to tropical regions of South Asia where it has been grown from approximately 6000 BC. The sugarcane plant contains 75% water and 10-15% sugar. It was originally grown for the sweet juice extracted from the thick fibrous stem by chewing. The two largest application areas for sugarcane today are production of sugar for human consumption and production of ethanol. Sugar has been produced from sugarcane for at least 2000 years and today, 70% of world sugar originates from sugarcane. (Kew, n.d)

Figure 5.5 Sugarcane plant. (Photo: majorbonnet. Source: Flickr, 2013)

Sugarcane is cultivated in around 100 countries in tropical and temperate areas and is produced in larger amounts than any other food commodity; more than twice as much as the world's second largest food commodity; maize. The largest sugarcane producing countries in terms of output are Brazil, India and China in the named order. (FAOSTAT, 2012)

Sugarcane has the highest conversion efficiency from raw material to ethanol among all crops used in fuel ethanol production, since the sugar does not have to be broken down before fermentation. (SJV, 2011) Bagasse is a valuable co-product from juice extraction that is used for combined heat and power (CHP) and can be used for production of ethanol in the future when advanced conversion routes become available. (Ometto et al. 2009)

The focus of this study is Brazil; the world leader in sugarcane production and with a long history of utilisation of sugarcane ethanol as vehicle fuel. Key figures for sugarcane production in Brazil are presented in table 5.4.

Table 5.4 Key figures for sugarcane production in Brazil, representing yearly averages. (FAOSTAT, 2012)

	Brazil 1961-1965	Brazil 2006-2010
Area harvested for sugarcane (average) (thousand hectares)	1 500	7 850
Production of sugarcane[1] (average) (thousand tonnes)	65 600	616 000
Yield per hectare (average) (tonnes/hectare) *calculated*	43.3	78.5

1) Production data on sugarcane refer to the weight of the harvested crop, free of soil, plant tops and leaves (75% water content) (FAOSTAT, 2012).

Sugarcane has been grown in Brazil for almost 500 years. As early as 1903 Brazilian authorities suggested that sugarcane ethanol be used as vehicle fuel, since petroleum products were expensive and not readily available. In 1931 the government commanded at least 5% ethanol blend in gasoline to take advantage of agricultural over-production. During the energy crisis of the 1970s sugarcane ethanol production gained new force and production increased by a factor of six during only five years, stimulated by financial policy and blend regulations. The 2003 introduction of flexi-fuel cars acted as further market stimulus and the internal market for ethanol is expected to continue to grow. Today, the average blend level is 25%. In Brazil as a whole, sugarcane accounted for 16% of the national energy mix in 2007. (BNDES and CGEE, 2008)

Between 1975 and 2007 yield increases and more efficient ethanol production technology resulted in a per hectare ethanol yield increase of on average 3.1% per year, reaching around 6 300 litres per hectare in 2007, according to a recent LCA study (Ometto et al. 2009).

Sugarcane is grown all over Brazil and is the third largest crop after soybeans and maize in terms of cultivated acreages. 60% of the production is located to the state of São Paulo while new production units expand into neighbouring states such as Minas Gerais, Goiás and Mato Grosso do Sul. Four fifths of the farm land is owned directly or indirectly by the sugar and ethanol industry. During the 2006/2007 harvest 55% of the sugar content from sugarcane was used in ethanol production. (BNDES and CGEE, 2008)

5.5.2 Agricultural management

Sugarcane is a perennial that once planted may stand more than five years before cleared. The perennial nature of the crop make proper field preparation critical. If the previous crop was sugarcane, as is often the case, the old stalks are removed by either machinery (approximately one-third of fields) or by pesticides, (approximately two-thirds of fields). Pesticides are applied to the soil during soil preparation and at planting time, as well as later during the cropping cycle. (Ometto et al. 2009)

Sugarcane is planted by burying two node long cane stalk seedlings in furrows, around 25 cm deep, 1.3 – 1.4 meters apart. The cane stalks root and produce new shoots in a process referred to as stooling. One stool may produce several stems, up to five meters in height. After 12 − 14 months the canes are harvested. The harvest season coincide with the dry season and extend from April to November with a peak during May to August (Ometto et al. 2009 and Meyer, pers. com. 2013). Harvest has traditionally been facilitated by pre-burning the field to remove leaves and facilitate cutting, but current legislation restrict this practice. However, in São Paulo, burning prior to harvest is still practiced on 75% of the total acreage. (Ometto et al. 2009).

After harvest, the stools produce new shoots, known as rotoon crops. During the first 30 days sugarcane can compete with weeds with no loss in productivity. After this initial period herbicides are typically applied to remove competing weeds, commonly 30 − 60 days after harvest (Meyer pers. com. 2013). Five to six harvest cycles are completed before the field is regenerated. The trend is towards mechanised harvest without burning for environmental and labour safety reasons, although burning has helped in keeping certain weed species and insect pests down. Only a very small fraction of Brazilian sugarcane is under irrigation, on an experimental basis (UNICA, 2007).

The total use of pesticides on sugarcane has decreased over the years as a result of increased use of biological pest control, selective application and genetic improvements (UNICA, 2007 and Lehtonen, 2009). Despite this, pesticide use on sugarcane is still intense and pose a serious problem. Areas of large-scale sugarcane cultivation, such as the Corumbataí River basin, have been linked to severe water contamination and an estimated 700 cases of pesticide poisoning and 15 deaths in 1998 (Lehtonen, 2009).

Initially it was believed that leaving the straw on ground, as in no-burn harvest, would reduce, or even eliminate, the need for herbicides, but this has proven wrong. In fact, leaving straw on ground has favoured the emergence of new troublesome weeds, such as several species of *Ipomoeas,* as well as new pests (UNICA, 2007).

The 12 most important weeds in Brazil according to a 1970-inventory were: nutgrass (*Cyperus rotundus*), Bermuda grass (*Cynodon dactylon*), hairy crabgrass/large crabgrass (*Digitaria sanguinalis*), little hogweed (*Portulaca oleracea*), Indian goosegrass (*Eleusine indica*), junglegrass/junglerice (*Echinochloa colonum*), Johnson grass (*Sorghum halepense*), Guinea grass (*Panicum maximum*), itchgrass (*Rottboelia exaltata*), spiny amaranth (*Amaranthus spinosus*), billygoat weed (*Ageratum conyzoides*) and yellow nutsedge (*Cyperus esculentus*). Today, signalgrass (*Brachiaria decumbens*), Alexander grass (*Brachiaria plantaginea*), wild poinsettia (*Euphorbia heterophilla*), tropical spiderwort (*Commelina benghalensis*) and several species of *Ipomoeas* can be added to the list (UNICA, 2007).

Weed management methods in sugarcane have changed in parallel with the agro-technological development with regard to machinery and chemicals. A typical weed management scenario of today consists of four strategies: avoidance of weeds brought in with seedling (especially nutgrass), crop rotation with *Leguminosae*, mechanical working of the soil before planting and herbicides, typically broad-spectrum, long-residual formulations. Between 2000 and 2003 an average of 2 360 g active substance (AS) herbicides per hectare and year was used on sugarcane in Brazil[38] (UNICA, 2007). In a field study from the sugarcane growing region of Corumbataí River basin region of São Paulo between 2000 and 2003, it was found that five compounds together make up 71% of the herbicides used on sugarcane: glyphosate (20%), atrazine (15%), ametryn (15%), 2,4-D (11%) and metribuzin (10%) (de Armas et al. 2005). A somewhat more recent record report that ametryn, tebuthiuron, hexazinone and simazine make up 80% of all herbicides applied to sugarcane in Brazil (Lehtonen, 2009).

The two most important insect pests on sugarcane in Brazil are the sugarcane borer (*Diatraea saccharalis*), also known as the sugarcane beetle, and the sugarcane weevil (*Sphenophorus levis*). The sugarcane borer is a moth present in all of Brazil and currently subject to Brazil's largest biological control program using primarily the parasitic wasp *Cotesia flavipes*. In most cases biological control suffice; in other cases insecticides are available. The sugarcane weevil is a pest that is currently spreading rapidly due to movement of seedlings and the shift towards mechanical harvesting. The weevils harm the sprouts and the base of developing stalks, and yield losses may reach up to 23 tonnes per hectare and year in infested areas (UNICA, 2007).

Between 2000 and 2003 an average of 125 g AS insecticides per hectare and year was used on sugarcane in Brazil. (UNICA, 2007) A few of the most common insecticides are fipronil, thiamethoxam, cardofuran, imidacloprid and endosulfan (banned since 2011). Insecticides are applied as soon as an infestation is detected, i.e. at any time during the year (Meyer pers. com. 2013). If canes are too high for boom sprayer, aircraft is used (Egeskog, pers. com. 2013).

Other main pests include: Migdolus beetle (*Migdolus fryanus*), currently affecting around 100 000 hectare in São Paulo with average yield losses of 30 tonnes per hectare and year, caused by the larva stage of the beetle to the plant's root system. This pest is commonly controlled by insecticides. Spittlebugs (*Mahanarva fimbriolata*) are currently controlled primarily by biological means, specifically the fungus *Metarhizim anisopliae* but are expected to increase with the shift towards mechanical harvesting. Yield losses caused by this bug reach 15 tonnes per hectare and year on average. Five species of defoliating caterpillars are present is almost all of Brazil's sugarcane growing areas, but are in most cases controlled effectively by natural enemies. Leaf-cutting ants (*Atta spp.*) are favoured by mechanical harvesting and might increase in the future. Ants currently cause yield losses between 1.5 − 2 tonnes per hectare and year (UNICA, 2007).

Fungicide application to sugarcane in Brazil is virtually zero according to UNICA (2007). The only economically viable method of controlling diseases in sugarcane is by selecting

[38] The pesticide application data cited in UNICA (2007) has been compiled with original data from National Syndicate for the Agricultural Defensives Industry (SINDAG) and the Brazilian National Institute of Geography and Statistics and National Agricultural Supply Company (IBGE/CONAB).

resistant varieties and disease control is the main reason behind the constant development and release of new varieties, and the replacement of old. (UNICA, 2007) On average six new varieties are released each year, and more than 500 varieties are currently on the market. (BNDES and CGEE, 2008) However, there are indications that fungicide application on sugarcane has become more common during recent years, in cases when natural resistance and biological control methods fail (Egeskog, pers. com. 2013).

Some of the historically large disease epidemics on sugarcane in Brazil include the sugarcane smut epidemic of the 1980s caused by the fungus *Ustilago scitaminea* that affected the NA56 − 79 variety grown on more than 50% of the sugarcane acreage in São Paulo state, and the sugarcane yellow leaf syndrome (viral disease) that infested all of the acreage grown with the SP6163 variety in less than three years during the 1990s and lead to its quick replacement (UNICA, 2007).

Research to produce genetically modified (GM) sugarcane varieties have so far produced resistance to herbicides, smut, Mosaic virus, sugarcane yellow leaf syndrome and sugarcane borer and as of 2007, these varieties were tested in field. (UNICA, 2007) Monsanto are currently developing Roundup Ready and Bt-sugarcane with integrated insect resistance against the sugarcane borer, planned for launch in Brazil, but it is uncertain when it will be ready for market entrance. (Monsanto Company, 2013)

5.5.3 Typical field pesticide application scenarios and cases

The assumed sugarcane field is located in Mato Grosso, Brazil, prepared in January and harvested every year in August. The field has the following characteristics:
Size: 250 ha (5 000×500 m^2)
Climate: Mato Grosso, Brazil
Soil: Mato Grosso, Brazil
Irrigation: 0 mm
Fraction drained: 0%
Slope: 1%

While the vast majority of sugarcane is cultivated in the state of São Paulo and less than 3% in Mato Grosso (Meyer, pers. com. 2013), climate and soil conditions of Mato Grosso were assumed in this study to take advantage of the soil and climate data already collected by Bennet (2012) to develop a regionalised version of PestLCI to Mato Grosso.

The herbicide types and application doses were decided based on the following information:

- 2 360 g AS per hectare and year applied to sugarcane in Brazil on average between 2000 and 2003 (UNICA, 2007)[39]
- the five most commonly used herbicides, on average between 2000 and 2003, in the sugarcane growing region of Corumbataí River basin region, São Paulo, were: glyphosate (20%), atrazine (15%), ametryn (15%), 2,4-D (11%) and metribuzin (10%) (percentage of total amount of herbicides) (de Armas et al. 2005)

[39] The pesticide application data cited in UNICA (2007) has been compiled with original data from National Syndicate for the Agricultural Defensives Industry (SINDAG) and the Brazilian National Institute of Geography and Statistics and National Agricultural Supply Company (IBGE/CONAB).

The plantation is assumed to be harvested five times within the life length of five and a half years. Glyphosate is applied once during the plantation life cycle, prior to field establishment, in January. A mix of herbicides is applied every year, two months after harvest, in October, except after the last harvest when no herbicides are applied. That gives a total of four applications.

Conventional tillage is assumed for glyphosate and no tillage for all other pesticide applications. At the time of herbicide application the plants are approximately 50 cm tall. The application method is set to conventional boom cereals and the crop type to Maize I (this was considered the crop morphology in closest resemblance of sugarcane).

The insecticide types and application doses were decided based on the following information:

- 125 g AS per hectare and year applied to sugarcane in Brazil on average between 2000 and 2003 (UNICA, 2007)
- insecticides can be applied at any time of the year when needed (Meyer, pers. com. 2013)
- two of the most commonly used insecticides are fipronil and thiamethoxam (Meyer, pers. com. 2013)

Insecticides are assumed to be applied in November, by conventional boom cereals, four times during the plantation life cycle, in equal amounts. No fungicides are applied. Supporting information is available in Appendix II.

5.6 Wheat

5.6.1 Introduction

Wheat (*Triticum* spp.), figure 5.6, refer to several species within the *Triticum* genus of the true grasses, *Poaceae*, family. Wheat is one of the oldest cultivated crops on Earth and one of the most important staple crops today. The area grown for wheat is larger than that of any other crop, almost 220 million hectares worldwide producing over 640 million tonnes per year (average between 2006 and 2010), most of it in China, India, USA and Russia (FAOSTAT, 2012). In 2008 wheat made up almost 48% of the total amount of cereals produced in EU27 (Eurostat, 2010) and it is constantly taking market shares from other grains (PAN Germany, 2002).

Wheat has higher demands on climate, soil and water supply than other cereals and prefers the cooler regions of the temperate zone. Varieties are either summer or winter types; indicating sowing period. (Bayer CropScience, 2012) Wheat is grown not only for human food but also for fodder and more recently and increasingly for technical applications including ethanol production. Winter wheat (*Triticum aestivum*) is more commonly used in ethanol production due to its higher yield levels.

Figure 5.6 Wheat in a wheat field. (Photo: NDSU Ag Communication. Source: Flicker, 2013)

Wheat is the main ethanol production feedstock in Europe, and the third largest globally. On a global scale, wheat is however a rather small contributor to global ethanol production, accounting for less than 6%. Europe and Canada are the largest producers of fuel ethanol from wheat. (SJV, 2011) Co-products from ethanol production include straw and DDGS (IPCC, 2011).

An estimated share of 12-20% of Swedish wheat went to ethanol production in 2011 (SJV, 2011 and Beckman, pers. com. 2012) Key figures for wheat production in northern and western Europe are presented in table 5.5. For the sake of the following discussion, Germany is taken as a point of reference with some examples from Sweden where cultivation practices are similar.

Table 5.5 Key figures for wheat production in northern and western Europe[2], representing yearly averages. (FAOSTAT, 2012)

	Northern and western Europe 1961-1965	Northern and western Europe 2006-2010
Area harvested for wheat (average) (thousand hectares)	8 460	13 500
Production of wheat[1] (average) (thousand tonnes)	26 800	92 900
Yield per hectare of wheat (average) (tonnes/hectare) *calculated*	3.16	6.89

1) Production data on wheat refer to the weight of clean, dry grains (12-14% moisture) in the form usually marketed. (FAOSTAT, 2012)
2) Northern and western Europe include: Austria, Belgium, Denmark, Estonia, Finland, France, Germany, Ireland, Latvia, Lithuania, Luxembourg, Netherlands, Norway, Sweden, Switzerland and United Kingdom.

5.6.2 Agricultural management

The largest overall problem in European wheat cultivation is weed, but in western Europe fungal diseases are nearly as important. Insect pests are overall of less importance and more uneven from year to year (Jørgensen et al. 2008). Pesticide use is in accordance with this pattern. A majority of pesticide active substance (AS) input in European cereals is herbicides, followed by fungicides, while insecticide use is rather small (European Commission, 2007). In Germany, wheat is the crop with the second highest intensity of pesticide treatment, next to potatoes. The average wheat field is treated with pesticides 3.4 times in a year. (PAN Germany, 2002)

There are indications on increasing problems with moncot weeds in wheat. Contributing reasons could for example be that wheat is increasingly mono-cropped or in narrower rotations, increased reliance on reduced tillage and a warmer and more moist climate (see for example Wivstad, 2010, SJV and KemI, 2002 and Cederberg et al. 2007). Since wheat is also a monocot, grass weeds are harder to control in wheat than dicot weeds by chemical methods.

According to a 2011-poll among Swedish cereal farmers 47% of respondents regarded couch grass (*Agropyron repens*) as the most troublesome weed in cereal cultivation, followed by wind grass (*Apera spica-venti*), annual bluegrass (*Poa annua*) and black grass (*Alopecurus myosuroides*), all of which are monocots. (Bayer Crop Science, 201-) Evidence from European fields suggest that black grass is an increasing problem with regard to both distribution and herbicide resistance (Bayer CropScience, 2012 and Wivstad, 2010). Additional troublesome weeds are wild oats (*Avena fatua*), cleavers (*Galium aparine*), chick weed (*Stellaria media*) and brome grass (*Bromus spp*.). (PAN Germany, 2002 and Oerke et al. 1994)

The susceptibility of wheat to fungal diseases is largely dependent on crop rotation practices, soil type and weather (Cederberg et al. 2007). Generally, the climate and weather conditions of central Europe favour fungal diseases. (PAN Germany, 2002) Yield losses due to fungal diseases differ greatly between different types of diseases, but range between 200 – 1 000 kg per hectare for Swedish conditions (SJV and KemI 2002).

According to the ENDURE wheat case study septoria leaf blotch (*Septoria tritici*) is the most important disease in Europe followed by brown rust (*Puccinia triticina*). Other diseases of major concern are take-all (*Gaeumannomyces graminis*), fusarium (*Fusarium* spp.), powdery mildew (*Blumeria graminis*) and tan spot (*Drechslera tritici-repentis*) (Jørgensen et al. 2008). Two other significant rusts are yellow rust (*Puccinia striiformis*) and black rust (*Puccinia graminis*). In 2009-2010 an aggressive new strain of yellow rust emerged and caused an epidemic and enormous yield losses in primarily central Asia (ICARDA, 2011).

Yellow rust has been ranked the disease with greatest potential to cause yield losses, up to 50%, followed by, in the named order: brown rust, septoria leaf blotch, tan spot and powdery mildew (SJV, LRF and HIR, 20--).

Many fungicides that effectively control septoria leaf blotch also works well on rust. Tan spot and take-all can often efficiently be dealt with using good agricultural practices such as proper crop rotation. Fusarium ear blight is considered a growing problem in many European countries, not only because of potential yield losses but perhaps more importantly because of fungal mycotoxins production of concern for human health. (Jørgensen et al. 2008) Many wheat varieties have natural resistance against some fungal diseases, but according to PAN Germany, when choosing varieties, farmers prioritise potential yields higher than resistance against disease and often treat even resistant varieties with fungicides, to be "*on the safe side*" (PAN Germany, 2002).

Insect pests in wheat are of less significance compared to weeds, diseases and abiotic stress factors such as weather and soil conditions. Even when discovered, insect pests are sometimes left untreated since severe damage as a result of insect pests is rare. Many times non-chemical preventive measures are enough to keep insects at bait (FAO, 2002).

However, in Germany, the most problematic insects in wheat are grain aphids (*Sitobion avenae*), which appear in large numbers certain years. At extreme conditions, they can cause production losses of up to 20%. Besides feeding off the wheat crop, aphids are problematic since they are vectors of the Barley Yellow Dwarf Virus (BYDV), a serious viral disease capable of causing even greater losses. In addition, grain aphids show increasing signs of resistance against pyrethroids. (IRAG UK, 2012)

Other insect pests include yellow wheat blossom midge (*Contarinia tritici*) (Cederberg et al. 2007), cereal leaf beetles (*Oulema melanopus*), wheat bulb fly (*Delia coarctata*), saddle gall midge (*Haplodiplosis marginata*) and frit fly (*Oscinella frit*). (PAN Germany, 2002) Wheat blossom midge is commonly controlled using pyrethroid insecticides (Cederberg et al. 2007).

5.6.3 Typical field pesticide application scenario

The assumed wheat field is located in Görlitz, Germany, sown in September with winter wheat and harvested in July. The field has the following characteristics:
Size: 10 ha (500×200 m^2)
Climate: continental (Görlitz, Germany)
Soil: average
Irrigation: 0 mm
Drainage: 100% of the field
Tillage: conventional
Slope: 1%

The field is ploughed prior to sowing. Glyphosate is applied on average every four years, primarily against couch grass. The glyphosate dose is based on a recommendation regarding the formulation Roundup Bio (Monsanto Company, 2008).

Four herbicides (prosulfocarb, florasulam, fluroxypyr-meptyl and tribenuron methyl) are applied every year. Prosulfocarb is applied post-emergence in October and the other herbicides in April. Three fungicides (fenpropimorph, propiconazole and prothioconazole) are applied during May-June and one insecticide (esfenvalerate) in June. Fenpropimorph and propiconazole are applied every second year on average, against yellow rust. All pesticides are applied using a conventional boom sprayer.

This application scenario has been constructed with the assistance of Nils Yngvesson (pers. com. 2012) and information from KemI (2013). All pesticide doses are based on information from Yngvesson and valid for northern Europe. Supporting information is available in Appendix II.

5.7 Gross energy yields

Biodiesel yields, representing nominal values from 2010 for conventional biodiesel, were found in IEA (2011) and converted using the lower heating value of biodiesel, to get the gross biodiesel energy yield expressed as GJ per hectare and year. The energy yields for biodiesel feedstocks are presented in table 5.6.

Table 5.6 Gross energy yields of biodiesel feedstocks.

Biofuel feedstock	Biodiesel yield (litres/ha/yr)	Gross energy yield[1] (GJ/ha/yr)
Rapeseed	1700	57
Soybean	700	23

1) Calculated using the lower heating value of biodiesel: 33.32 MJ/litre (GREET, 2010 cited in Boundy et al. 2011).

Gross energy yields for ethanol feedstocks were calculated through a series of steps:

1. For maize, sugarcane and wheat: collection of crop yields from tables 5.1, 5.5 and 5.6. These yields represent yearly averages between 2006 and 2010 in the defined regions of study and have been collected from FAOSTAT (2012). More information is available in tables 5.1, 5.5 and 5.6.
2. For *Salix*: collection of yield from IEA Bioenergy (2012) representing dry matter on better sites.
3. Collection of information regarding ethanol production levels from different types of feedstocks.
4. Calculation of ethanol yields in litres per hectare and year as the product of crop yields and amount of ethanol produced from one tonne feedstock.
5. Calculation of gross energy yield in GJ per hectare and year as the product of ethanol yields and the lower heating value of ethanol.

The energy yields for ethanol feedstocks are presented in table 5.7. Gross energy yields in GJ per hectare and year for all biofuel feedstocks after conversion to fuel are presented in figure 5.7.

Table 5.7 Gross energy yields of ethanol feedstocks.

Biofuel feedstock	Crop yield (tonnes/ha/yr)	Ethanol produced from one tonne feedstock[1] (litres/tonne)	Ethanol yield (litres/ha/yr)	Gross energy yield[2] (GJ/ha/yr)
Sugarcane	78.5	79	6 200	132
Maize	9.68	380	3 680	78
Wheat	6.89	385	2 650	56
Salix	10	260	2 600	55

1) Source: F.O. Licht (2003) cited in SJV (2011).
2) Calculated using the lower heating value of ethanol: 21.27 MJ/litre (GREET, 2010 cited in Boundy et al. 2011).

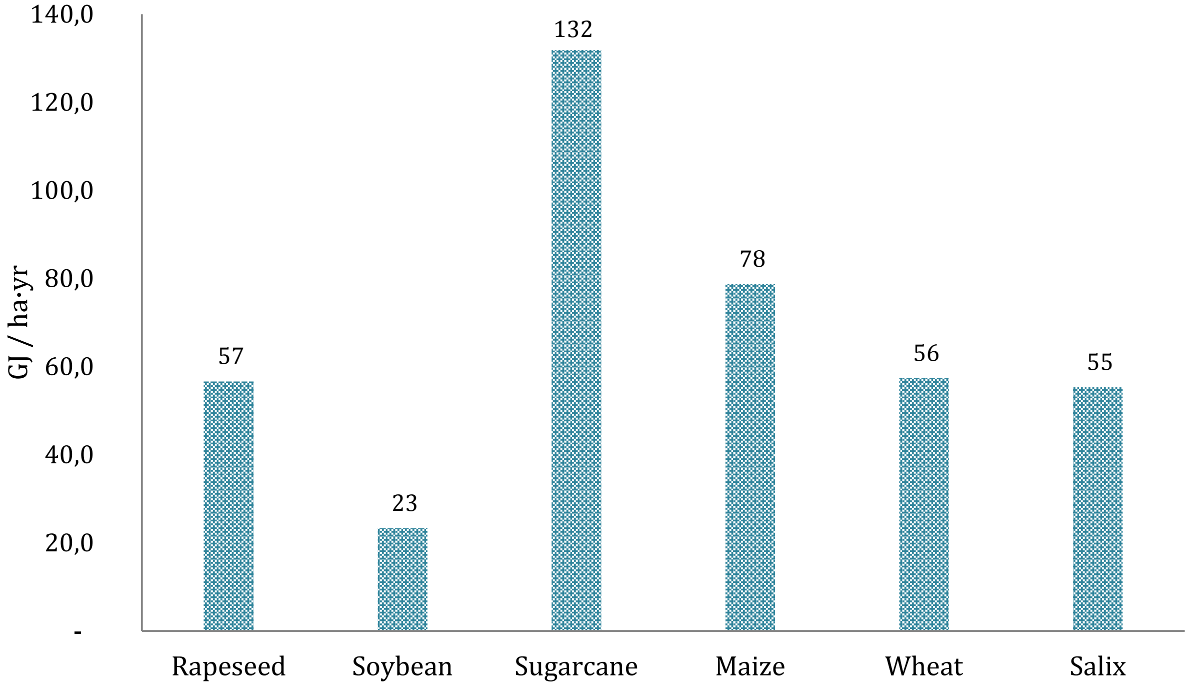


Figure 5.7 Gross energy yield in GJ per hectare and year for the selected biofuel feedstocks after conversion to fuel.

6. RESULTS AND INTERPRETATION

Chapter 6.1 show and interpret various environmental performance indicators for each of the different crops and cases. Chapter 6.2 present the top-ten active substances (AS) with largest ecotoxic impact scores. Chapter 6.3 show and interpret the contributions of individual pesticides to the total freshwater ecotoxic impacts for each of the different crops and cases. All interpretations are based on the allocated results unless stated otherwise.

6.1 Environmental performance indicators

Figure 6.1 present the yearly average pesticide application in g AS per hectare and year, in allocated and unallocated formats, based on the assumed pesticide application scenarios (Appendix II).

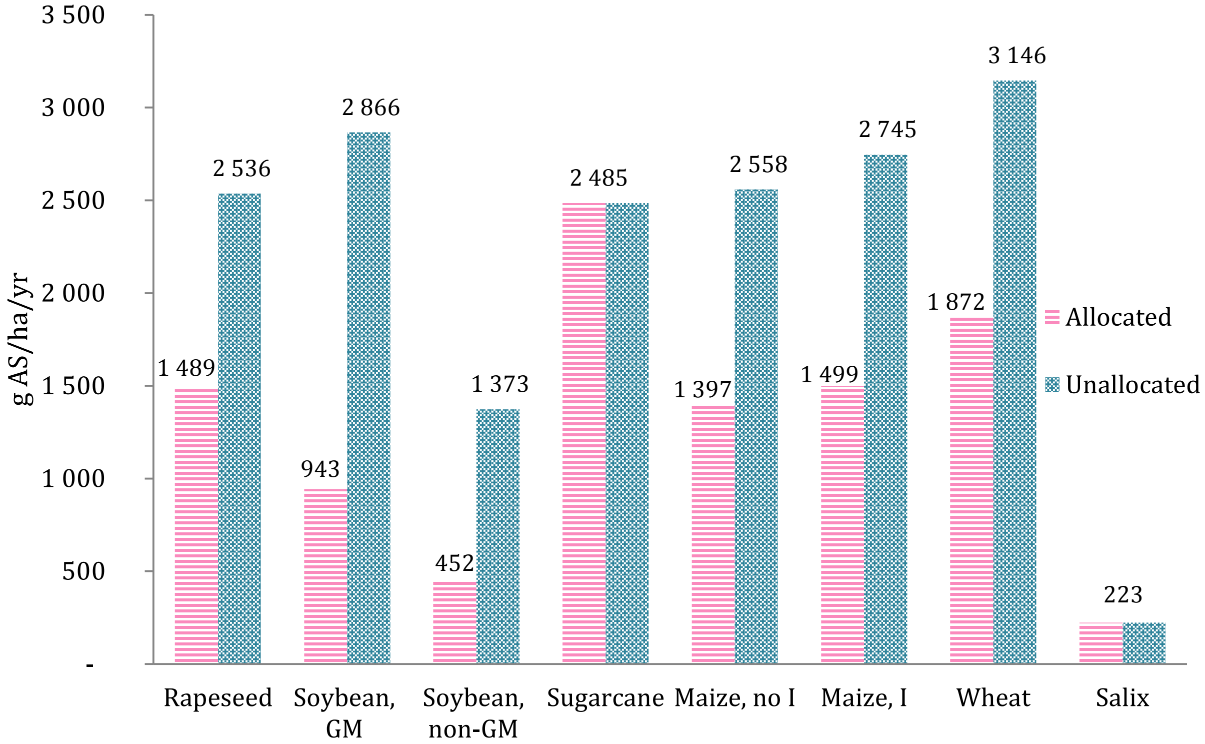


Figure 6.1 Yearly average pesticide application in g AS per hectare and year for each of the various cropping systems.

As seen in Figure 6.1, there are no major differences in application levels in the different crops (unallocated levels) - except *Salix* that require significantly less. This is partially because pesticides are applied to *Salix* only once every three years while pesticides are applied to the other crops several times every year.

The amounts presented in figure 6.1 are rather under- than overestimates and the largest uncertainties exist in the application levels of Brazilian crops; soybean and sugarcane.

Soybean data were collected through a farmer interview and represent the practice at one farm in the growing season of 2012/2013. However, it is known that farmers are not always willing to reveal the true levels of their application (Cederberg, pers. com. 2013) for which reason these levels have to be accepted with caution. In a recent SIK-study

(Meyer and Cederberg, 2010) it was found that on average 5 790 g AS (H, F and I) were applied to soybean crops in 2008 suggesting that the pesticide levels assumed in this study may be significantly underestimated.

The herbicide and insecticide doses applied to sugarcane are based on averaged national statistics for the years 2000 – 2003 (UNICA[40], 2007) and the doses of individual herbicides are decided based on conditions in the Corumbataí River basin region of São Paulo (de Armas et al. 2005). It is possible that the situation is much different today. For example, UNICA (2007) state that fungicide application on sugarcane is virtually zero, while evidence from 2013 (Egeskog, pers. com. 2013) suggest that fungicides are sometimes applied nowadays when biological measures and resistant varieties fail to control disease.

It should be noted that the pesticide amounts applied to GM soybean are well above the pesticide amounts of non-GM soybean (more than double). Although this is merely the practice of one farmer, it is worth noticing, since proponents of GM crops often claim that GM crops reduces the need of pesticides (see for example Monsanto Company, n.d).

Table 6.1 present the frequencies of application of herbicides, fungicides and insecticides, assumed in this thesis, and is an indicator of the intensity of pesticide application. Soybean and wheat have the highest intensity, with herbicides, fungicides and insecticides applied every year (soybean up to 12 times per year with H, F and I), while *Salix* has the lowest intensity with herbicides applied only once every three years.

Table 6.1 Frequencies of application of herbicides, fungicides and insecticides in all crops and cases.

	Frequency herbicides (%)	Frequency fungicides (%)	Frequency insecticides (%)
Rapeseed	100%	30%	67%
Soybean, GM	100%	100%	100%
Soybean, non-GM	100%	100%	100%
Sugarcane	73%	0%	73%
Maize, no I	100%	0%	0%
Maize, I	100%	0%	100%
Wheat	100%	100%	100%
Salix	33%	0%	0%

A relevant indicator of environmental performance in the context of biofuels, is pesticide input in relation to the energy output. This indicator is presented in figure 6.2, in allocated and unallocated formats.

[40] The pesticide application data cited in UNICA (2007) has been compiled with original data from National Syndicate for the Agricultural Defensives Industry (SINDAG) and the Brazilian National Institute of Geography and Statistics and National Agricultural Supply Company (IBGE/CONAB).

Figure 6.2 Pesticide application per energy output in g AS per GJ for each of the various cropping systems.

Dividing pesticide input by energy output favour crops with low pesticide input in relation to energy output. The high score of unallocated GM soybean is explained by the fact that it is the crop with second largest pesticide input and lowest energy output. The allocated result is however not as outstanding since only 32.9% is allocated to soybean biodiesel and the remaining share to co-products.

Figure 6.2 shows that sugarcane, soybean (conventional case) and maize (both cases) all require almost the same amount, 18−19 g AS, for production of 1 GJ biofuel energy and that rapeseed and wheat require 40% and 80% more, respectively. *Salix* require significantly less, only 4 g AS for production of 1 GJ biofuel energy.

Figure 6.3 present the freshwater ecotoxic impact per hectare and year, in allocated and unallocated formats.

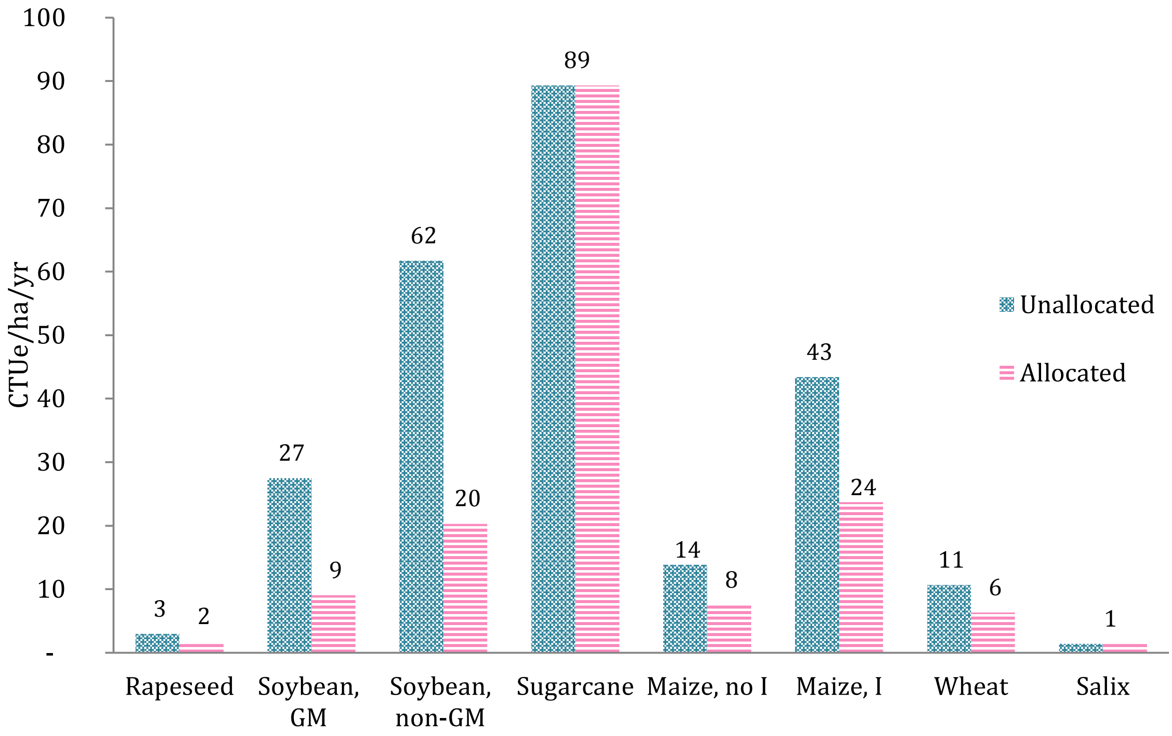


Figure 6.3 Freshwater ecotoxic impact in CTUe per hectare and year for each of the various cropping systems.

Figure 6.3 shows that *Salix* and rapeseed have the lowest ecotoxic impact per hectare and year (1.4 and 1.7 CTUe/ha/yr respectively) and sugarcane has the highest (89 CTUe/ha/yr) - more than three times larger than that of any other crop. The high score of sugarcane is the combined result of the three herbicides atrazine, 2,4-D and ametryn, further discussed in chapter 6.2. Another contributing cause is that the entire score is allocated to sugarcane ethanol while the impact scores of the other feedstocks (besides *Salix*) is partially allocated to co-product.

The ecotoxicity score of sugarcane might even be an underestimate. In this thesis it was assumed that all herbicides and insecticides were applied with conventional boom and that no fungicides were applied. However, data that were received during the finalisation of this thesis (Egeskog, pers. com. 2013) indicated that fungicides have become more common in recent years, that nematicides (beyond the scope of this thesis) are almost always applied to sugarcane and that insecticides are commonly applied with aircraft. Sensitivity test 3, presented in Appendix X, confirm that aircraft as application method dramatically increases emissions to air. Adding these factors to the application scenario of sugarcane would have led to even higher ecotoxicity score.

There is a considerable difference between the two maize cases. The difference is in total due to the addition of one insecticide; chlorpyrifos, in the insecticide-case (non-Bt maize). The characterisation factors (CFs) of chlorpyrifos have been calculated based on *avlogEC50* from Payet (2004), but the number of trophic levels is not known from Payet (2004) (see Appendix IX) for which reason it is not possible to classify the CFs as recommended or interim.

There is also a considerable difference between the two soybean cases, which in total is due to the herbicide lactofen, in the case of conventional soybean. The CFs of lactofen have been calculated but ecotoxicological effect data were only found for two freshwater species at two trophic levels which means the CFs can be classified as interim. This make the result for GM soybean somewhat uncertain and it is excluded from comparisons in the following discussion.

Figure 6.3 also shows that the European cases (wheat, rapeseed and *Salix*) have lower ecotoxicity scores than the crops grown in North and South America. This is likely to be an effect of rather strict pesticide legislation in Europe where several measures have been taken during the past 20 years aimed at reducing negative effects of pesticide use, involving for example: revised pesticide registration criteria, the ban on several problematic AS, education of farmers, testing of application apparatus, optimal application guidelines, taxes on pesticides and limitations on aerial spraying (FAO, 1996).

A relevant measure in the context of biofuels is freshwater ecotoxicity in relation to energy output, presented in figure 6.4, in allocated and unallocated formats.

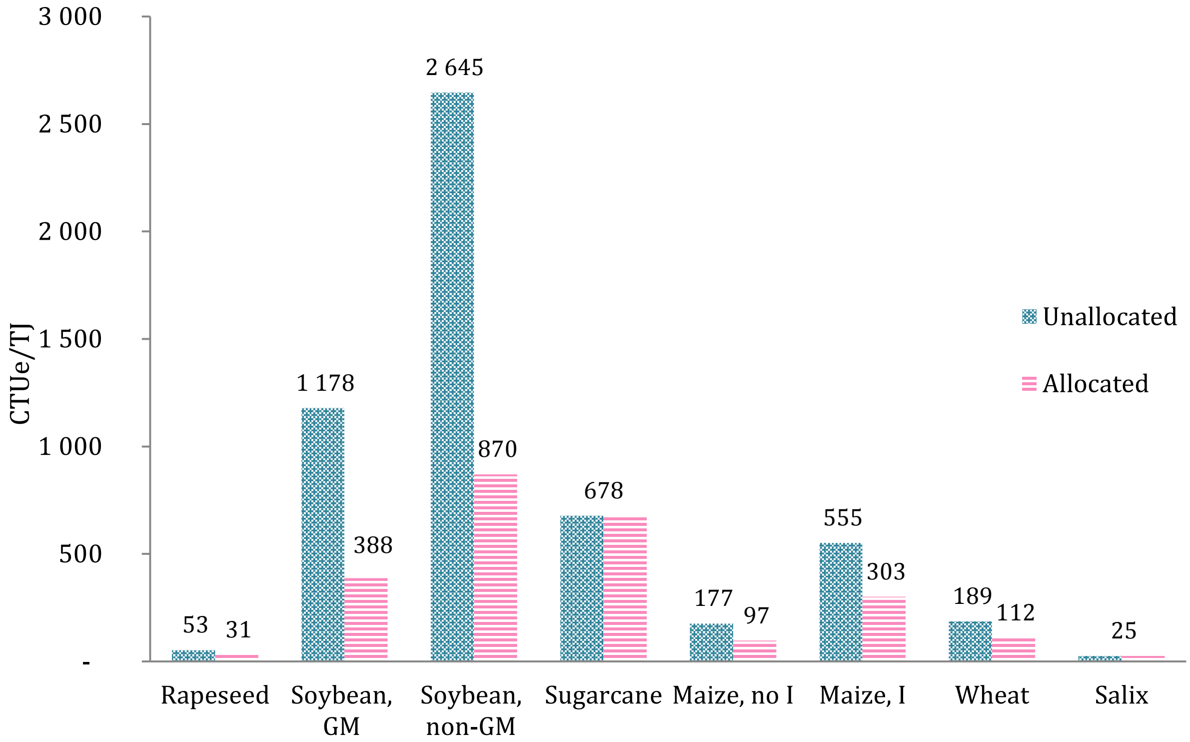


Figure 6.4 Freshwater ecotoxic impact per energy output in CTUe per TJ for each of the various cropping systems.

Division by energy output favour crops with high energy output, primarily sugarcane and maize. Again, figure 6.4 shows that the European crops generally have lower ecotoxicity scores compared to the crops grown in North and South America. However, maize scores in level with the European crops as long as the insecticide chlorpyrifos is not used. There is a significant range in impact scores caused by the various crops. Production of 1 TJ biofuel energy from rapeseed causes an ecotoxic impact score of 31 CTUe, while production of 1 TJ biofuel energy from wheat, maize (insecticide case), GM soybean and sugarcane give rise to ecotoxic impact scores 4, 10, 13 and 22 times larger, respectively.

Figures 6.3 and 6.4 show that wheat causes an ecotoxic impact more than three times that of rapeseed – both in relation to hectare and year and in relation to energy output. This is mainly due to the fungicide prothioconazole. However, the CFs of prothioconazole have been calculated and could be labelled as interim since effect data were only found for two trophic levels (see Appendix IX), for which reason this result has to be accepted with caution.

Throughout figures 6.1 – 6.4, *Salix* has the lowest, most favourable score, in all environmental performance indicators. However, the results for *Salix* are not to be compared to the results of the other biofuel feedstocks, since ethanol from woody biomass represent a future technique. Commercialisation of this technique will alter the utilisation degrees of other crops and lead to different scenarios all together. The results for *Salix* should however be interpreted as an indicator of the future potential of ethanol from woody biomass - showing that efforts to promote advanced biofuels are worthwhile.

Figure 6.5 present the ecotoxicity of the pesticides used in the various cropping systems, expressed in relation to 1 kg of the mix of AS used. This indicator has been calculated by dividing total ecotoxicity score (in CTUe/ha/yr) with the total amount of pesticides used (in kg AS/ha/yr).

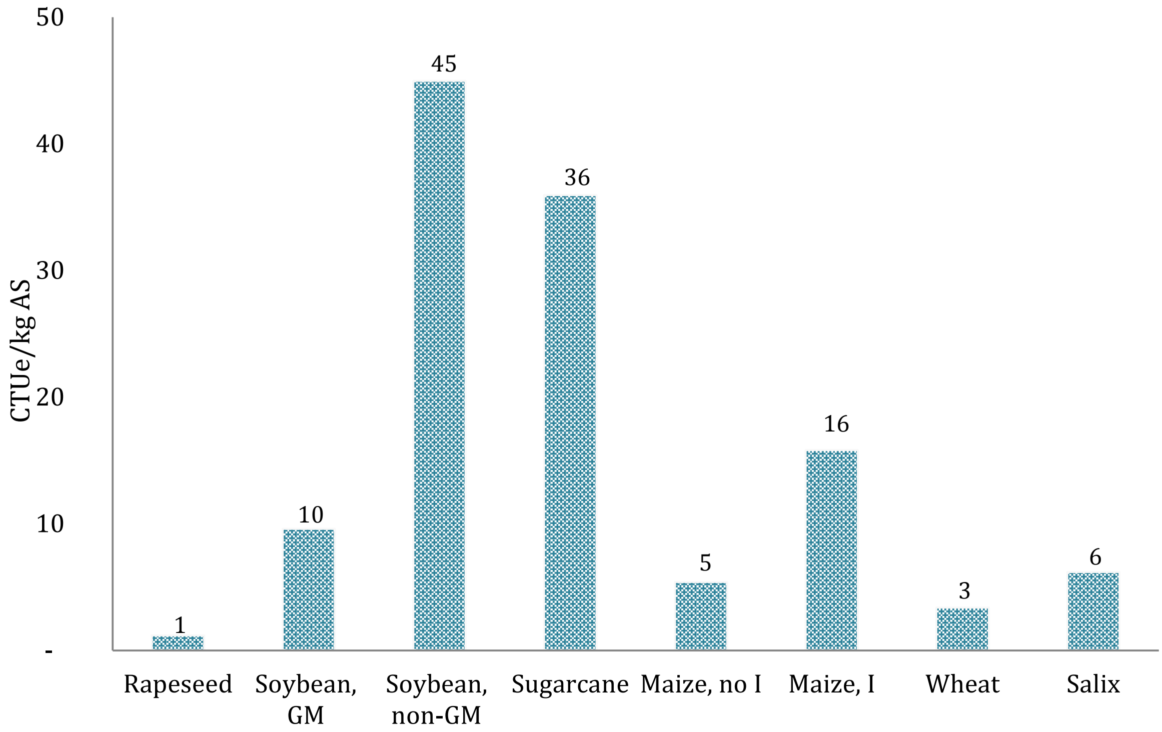


Figure 6.5 Freshwater ecotoxic impact of pesticides, in CTUe, in relation to 1 kg of the mix of the active substances used, for each of the various cropping systems.

Figure 6.5 shows that the pesticides used for cultivation of crops in North and South America generally are more toxic in relation to 1 kg of the AS used, compared to the crops grown in Europe – the exception is Bt-maize. The pesticides used for cultivation of rapeseed have the lowest ecotoxicity in relation to 1 kg of the AS used. There is no difference between allocated and unallocated versions of this indicator.

Figure 6.5 shows that there is no correlation between amount of applied pesticide (in kg) and ecotoxicity (in CTUe) and that amount of pesticide alone is a poor indicator of ecotoxicity and of environmental performance - which is sometimes assumed.

Figure 6.6 present the shares of herbicides (H), fungicides (F) and insecticides (I) in relation to the total pesticide dose and shows that herbicides dominate for all crops, ranging from 66% to 100% of the total pesticides applied. Figure 6.7 present the contributions of herbicides, fungicides and insecticides to the total ecotoxic impact.

Comparing figures 6.6 and 6.7 show that although fungicides and insecticides are applied in rather small shares, they represent larger shares of ecotoxic impact. For example, fungicides in wheat only make up 16% of the total applied dose, but make up 60% of the total ecotoxic impact. In conclusion, in relation to amount of AS, fungicides and insecticides have higher ecotoxic impact than herbicides in general.

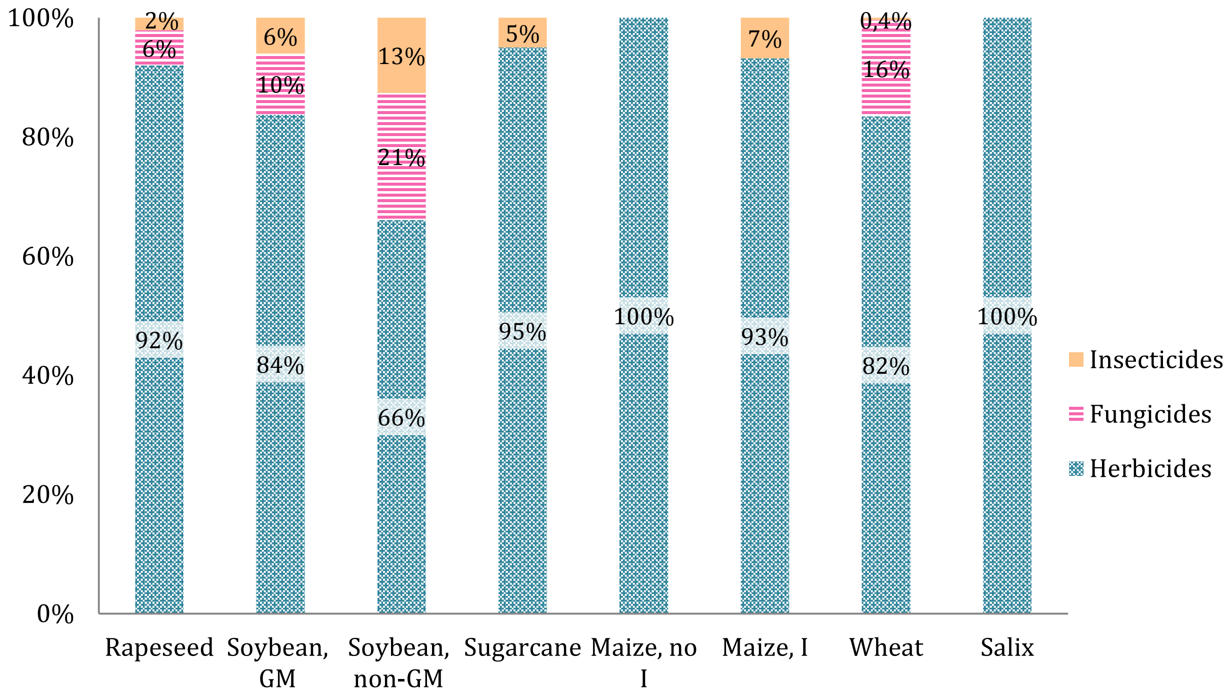


Figure 6.6 Contribution of herbicides, fungicides and insecticides to total pesticide dose, expressed as percentages.

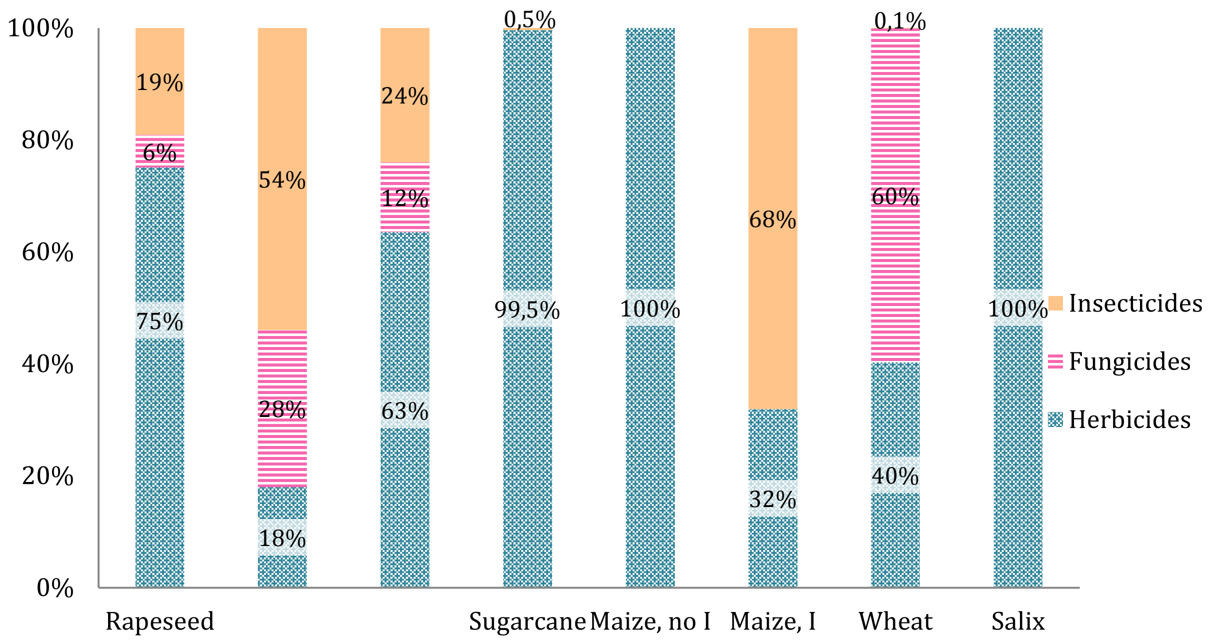


Figure 6.7 Contribution of herbicides, fungicides and insecticides to total freshwater ecotoxic impact, expressed as percentages.

6.2 Top-ten list

Table 6.2 shows the top-ten active substances (AS) with largest allocated ecotoxic impact scores per hectare and year among all crops and pesticides included in the study. In case of two rounds of application of the same pesticide in one year (as practiced in cultivation of soybean), the ecotoxicity scores have been added prior to constructing the top-ten list.

Table 6.2 Top-ten active substances with largest allocated ecotoxic impact scores per hectare and year among all crops and pesticides included in the study.

No	Active substance	Type of pesticide	Crop	Allocated ecotoxic impact score (CTUe/ha·yr)
1	Atrazine	Herbicide	Sugarcane	56.8
2	2,4-D	Herbicide	Sugarcane	17.8
3	Chlorpyrifos	Insecticide	Maize	16.1
4	Ametryn	Herbicide	Sugarcane	12.7
5	Lactofen	Herbicide	Soybean	11.3
6	Atrazine	Herbicide	Maize	7.5
7	Prothioconazole	Fungicide	Wheat	3.7
8	Alpha-cypermethrin	Insecticide	Soybean	2.9
9	Epoxiconazole	Fungicide	Soybean	2.5
10	Zeta-cypermethrin	Insecticide	Soybean	1.9

Atrazine in sugarcane, Brazil, is the pesticide-crop combination with largest ecotoxic impact score – more than three times larger than number two: 2,4-D in sugarcane. Atrazine is also found at place six in the top-ten list; applied to maize, USA. A closer look and comparison of the results of atrazine in sugarcane and maize is provided in chapter 7.2. A closer look at top-three is provided in this chapter.

Atrazine

The ecotoxicity score of atrazine in sugarcane is in equal parts due to emissions to surface water and air. Inventory results show that 1.75% of the applied amount is emitted to air and 0.07% to surface water. The CFs of atrazine are classified as recommended (Appendix IX).

Atrazine is known to be a highly leachable (PPDB, 2013) and problematic herbicide, widely used in Brazil (Arraes et al. 2008) and the second most widely used AS in the USA[41] (USEPA, 2011). The herbicide has been linked to water pollution problems in both countries. In a ground water quality study in the Serra Grande aquifer in Tianguá, the State of Ceará, Brazil, conducted between 2003 and 2006, atrazine was found in 75% of water samples from the aquifer and in concentrations above the maximum allowed values in 48% of the samples (Arreas et al. 2008).

In a US pesticide residues inventory from 2008 conducted by USDA, atrazine was found in 94% of treated drinking water samples, making atrazine the most frequently detected drinking water pollutant in the USA. The herbicide was also found in 5% of ground water samples. (USDA, 2009)

[41] Among all AS used in the agricultural sector in 2007, glyphosate was the AS used in largest amounts (USEPA, 2011).

The herbicide has also been linked to ground water contamination in the EU, but banned since 2005 after a scientific committee had identified it as such. In some countries such as Sweden, Finland, Denmark, Germany and Italy it was banned much earlier. An incident that may have contributed to the European ban took place in the rice and maize growing regions of northern Italy, in 1987, when local authorities shut down household water supplies after elevated pesticide levels in drinking water had been detected. (Ackerman, 2007) In Sweden, atrazine has been banned since 1989 (KemI, 2013). Despite that, due to the slow degradation rate of the herbicide, it was found in 7% of ground water sample in a pesticide residues inventory in south of Sweden conducted 2007 − 2010. In some samples, even in concentrations above acceptable limits. (Länsstyrelsen Skåne, 2012)

A number of physical-chemical properties contribute towards making it a potent water contaminant: its low sorption to organic soil particles, moderate solubility in water, slow degradation rate in soil and slow hydrolysis (Arreas et al. 2008). In addition to being a water contaminant, atrazine is a probable carcinogen and a suspected endocrine disruptor. (PAN North America, n.d)

2,4-D

The pesticide with second largest ecotoxic impact score is the herbicide 2,4-D applied to sugarcane, Brazil. While the CFs of 2,4-D are fairly low (compared to other CFs, see Appendix IX) the ecotoxicity score becomes high due to an extremely large share, 46%, emitted to air. 99% of the ecotoxicity score of 2,4-D is due to emissions to air. It should be noted the CFs of 2,4-D are classified as interim, since 2,4-D is dissociating, which adds a layer of uncertainty to this result.

The fact that a very large share is emitted to air is however not surprising since 2,4-D is known to be highly volatile. 2,4-D exist in several formulations; the most volatile of which have been banned, while several volatile formulations remain. 2,4-D was developed over 60 years ago and became known during the Vietnam war as an ingredient in the infamous product Agent Orange, used to defoliate the jungle. The patent on 2,4-D has run out and several low-cost 2,4-D formulations are available today from different producers, making 2,4-D one of the most popular herbicides in the world. Some crops, such as grapes, are highly sensitive to 2,4-D and can be damaged merely due to wind drift from nearby field. Special care has to be taken in application of the herbicide, avoiding windy conditions and high temperatures, to reduce emissions and protect nearby sensitive crops. (Tu et al. 2001)

2,4-D is also a water pollutants. Evidence from USA in the form of a pesticide residues inventory from 2008, conducted by USDA, show that 2,4-D was found in 85% of treated drinking water samples. (USDA, 2009)

Chlorpyrifos

The pesticide with third largest ecotoxic impact score is chlorpyrifos applied to maize, USA. 4% of the applied dose is directly emitted to air and 98% of the ecotoxicity score is due to air emissions. The fact that this insecticide is applied with aircraft is one factor contributing towards high emissions to air, which is confirmed by sensitivity test 3 (Appendix X).

Chlorpyrifos, an organophosphate insecticide that works by disturbing the nervous system of insects, was the most widely used insecticide in the agricultural sector of USA in 2007

(USEPA, 2011). Chlorpyrifos is highly to very highly toxic to several species of freshwater organisms such as aquatic invertebrates (primarily crustaceans), *Daphnia* species and fish. Its toxicity to algae has been classified as moderate. (PAN Pesticide Database, 2010) Chlorpyrifos has also been linked to effects on humans. The insecticide is classified as class II, moderately hazardous, in terms of acute risk to human health (WHO, 2010) and has been identified as one of the main causes for acute insecticide poisoning in the USA (PAN UK, 1998). The insecticide has been linked to cholinesterase[42] inhibition in humans and effects such as nausea, dizziness, respiratory paralysis and death in severe cases. Since 2000 virtually all household consumption has been banned in the USA to reduce human exposure. (USEPA, 2002)

Concluding remarks

Evidence from the literature have shown that the top-three AS with highest ecotoxic impact scores in this study are indeed known to be problematic pesticides and two of them (atrazine and 2,4-D) are particularly identified as water pollutants. The obvious link between the potential to cause water pollution and the potential to cause freshwater ecotoxic impacts together with the findings presented in chapter 6.2 lends towards the reliability of these results.

6.3 Contributions to ecotoxicity

Pie-chart figures 6.8 – 6.14 show the contributions of individual pesticides to the total freshwater ecotoxic impact score in percentage of total for each of the different crops and cases. In case of two rounds of application of the same pesticide (as practiced in cultivation of soybean), the ecotoxicity scores have been added prior to construction of the pie-charts. Pesticides with very small contribution (<1%) are not shown in the figures. All pesticides used in all crops and cases are available in Appendix II.

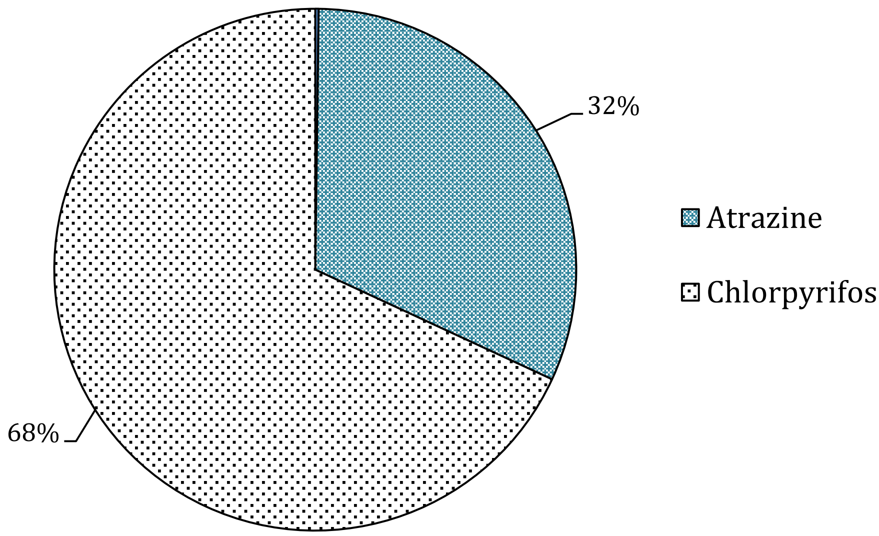


Figure 6.8 Contributions of individual pesticides to total freshwater ecotoxic impact, insecticide case of maize (genetically modified maize without Bt insect resistance).

[42] Cholinesterase is an enzymes associated with the proper functioning of the nervous system.

Figure 6.8 shows that chlorpyrifos contributes by 68% to the ecotoxicity score of maize in the insecticide-case and that atrazine make up the remaining share. In the no-insecticide case, not presented in a figure, atrazine make up 99% of the ecotoxic score. Both chlorpyrifos and atrazine are knows to be problematic pesticides (atrazine with links to water pollution), for which reason this result is not surprising. A more comprehensive record of chlorpyrifos and atrazine was presented in chapter 6.2.

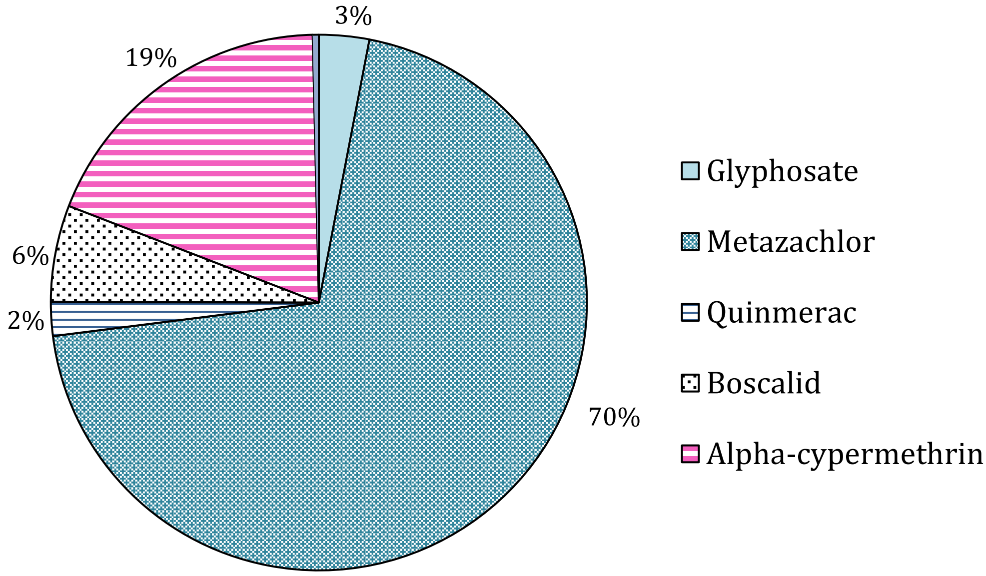


Figure 6.9 Contributions of individual pesticides to total freshwater ecotoxic impact, rapeseed.

Figure 6.9 shows that metazachlor contributes by 70% to the ecotoxicity score of rapeseed, 94% of which is due to surface water emissions. This is not surprising since metazachlor is known to be highly mobile (PPDB, 2013) and frequently found in surface water. In a pesticide monitoring study from south of Sweden, metazachlor was found in 54% of surface water samples and it was found to be the pesticide with third largest emissions from field in relation to applied amounts (0.08%) (Kreuger, 2002). According to the emission inventory results (Appendix VIII) of this study, 0.03% of the applied dose of metazachlor was emitted to surface water. Metazachlor has also been found in ground water in south of Sweden (Länstyrelsen Skåne, 2012).

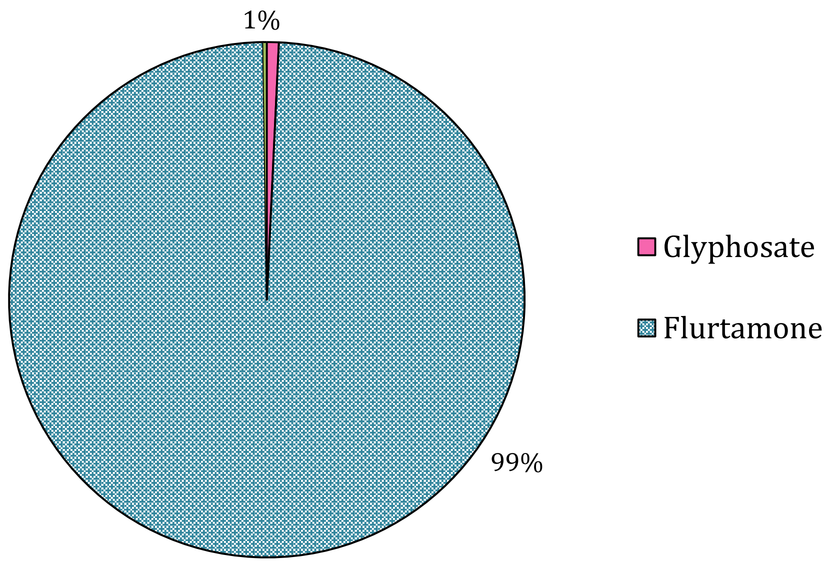


Figure 6.10 Contributions of individual pesticides to total freshwater ecotoxic impact, *Salix*.

Figure 6.10 shows that flurtamone contributes by 99% to the ecotoxicity score of *Salix*. However, there are some uncertainties with regard to this result as the CFs of diflufenican - another herbicide AS applied in *Salix* - not shown in figure 6.10 – are highly uncertain, a matter which is further discussed in chapter 7.1.

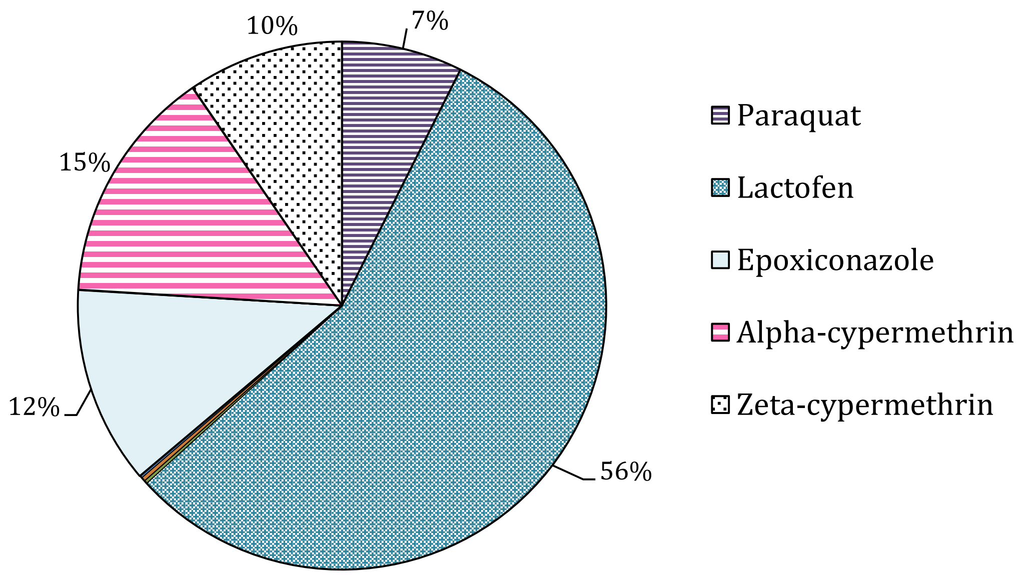


Figure 6.11 Contributions of individual pesticides to total freshwater ecotoxic impact, conventional soybean.

Figure 6.11 shows that the largest contributor to the ecotoxicity score of conventional soybean is the herbicide lactofen (56%) while the remaining share is distributed between the insecticide alpha-cypermethrin (15%), the fungicide epoxiconazole (12%), the insecticide zeta-cypermethrin (10%) and the herbicide paraquat (7%). The CFs of lactofen have been calculated but ecotoxicological effect data were only found for two freshwater species at two trophic levels which means the CFs can be classified as interim.

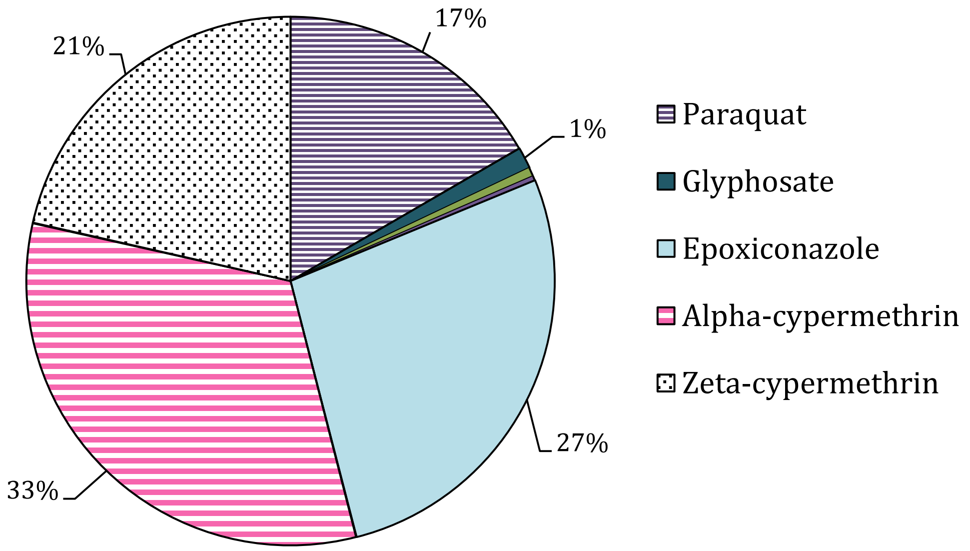


Figure 6.12 Contributions of individual pesticides to total freshwater ecotoxic impact, genetically modified glyphosate tolerant soybean.

Figure 6.12 shows the contributions to ecotoxicity for GM soybean. This distribution between pesticides resembles that of conventional soybean but without lactofen.

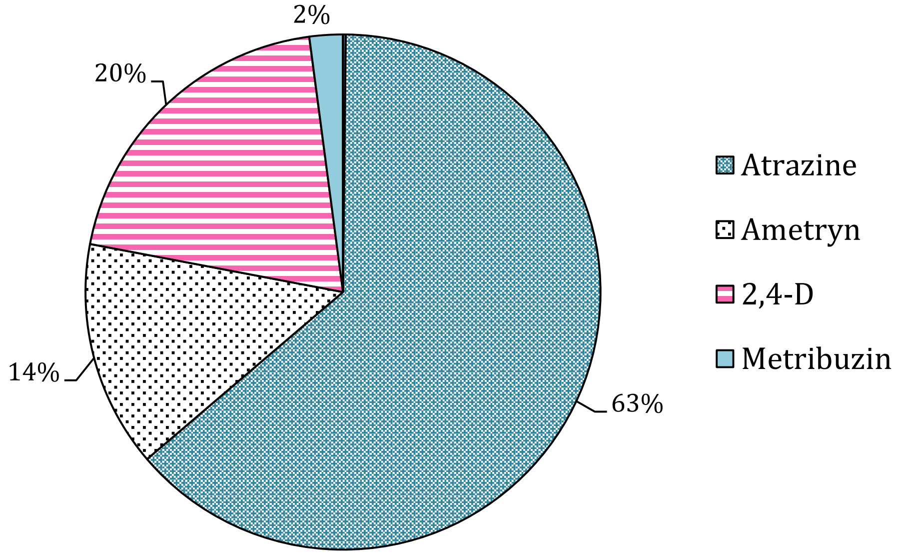


Figure 6.13 Contributions in percentage of individual pesticides to total freshwater ecotoxic impact for sugarcane.

Figure 6.13 shows that atrazine is the largest contributor (63%), followed by 2,4-D (20%) and ametryn (14%), to the ecotoxicity score of sugarcane. All three pesticides found in the top-ten list and atrazine and 2,4-D with confirmed links to water pollution (see chapter 6.2).

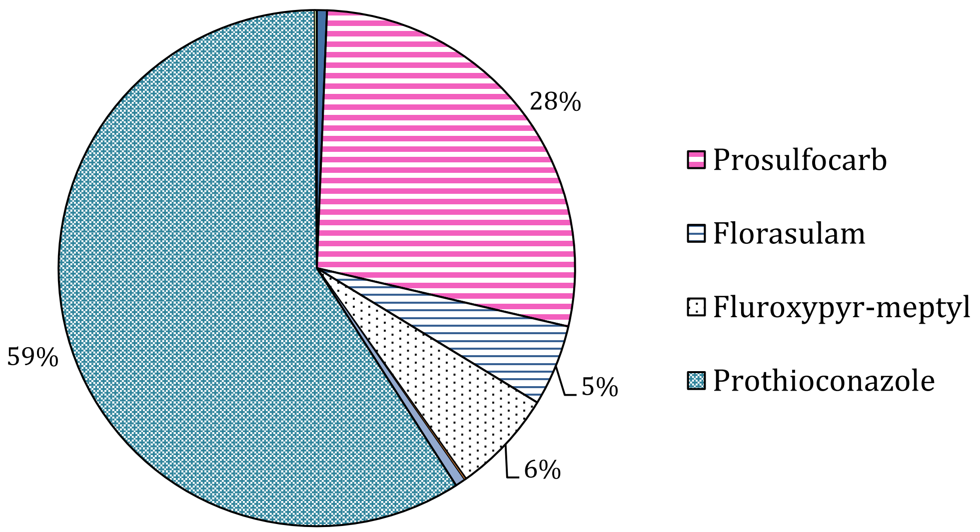


Figure 6.14 Contributions in percentage of individual pesticides to total freshwater ecotoxic impact of wheat.

Figure 6.14 shows that the largest contributor to the ecotoxicity score of wheat is the fungicide prothioconazole (59%), found at the seventh place in the top-ten list, table 6.2, followed by the herbicide prosulfocarb (28%). 99% of the impact score for prothioconazole is due to emissions to air. It should however be noted that the CFs of prothioconazole have been calculated and could be labelled as interim since effect data were only found for two trophic levels.

7. DISCUSSION

This chapter starts with a discussion on some of the challenges encountered with regard to ecotoxicological effect data. Chapter 7.2 discusses the significance of performing a detailed emission inventory. Chapter 7.3 discusses the main limitations of the present study including allocation, and proposes advancement measures. Chapter 7.4 discusses what can be done within this research area beyond the scope of this thesis and present models and includes areas for future work and recommendations.

7.1 Ecotoxicological effect data

The most challenging, and time consuming, step in the characterisation of freshwater ecotoxic impact was encountered in relation to ecotoxicological effect data. Difficulties were encountered with regard to finding, interpreting, classifying and using ecotoxicological effect data. Challenges included: limited guidelines in data collection and in relation to using data for calculation of *avlogEC50*; a large set of possible and unique databases to get familiar with - not always providing consistent values or full test details and difficulties related to classifying the data. In addition, out of the two recommended databases (Huijbregts et al. 2010a) one was difficult to obtain (Payet, 2004) and the other about to close-down (RIVM e-toxbase).

Chapter 7.1 give examples of some of the limitations, uncertainties and challenges that were encountered and ends with some concluding remarks. All ecotoxicological effect data that have been collected and used for calculation of CFs in this thesis are available in Appendix V.

Differentiation between acute and chronic

There is no scientific consensus regarding how to differentiate between acute and chronic ecotoxicological tests (Payet, 2004). The classification method used in this thesis (described in chapter 4.3.5) resulted in 3-day tests on algae and 7-day tests on aquatic plants sometimes being classified as chronic and sometimes as acute.

A test was performed for a case with prothioconazole, in order to evaluate to what degree the differentiation between acute and chronic affected the results. In the first case, a 7-day EC50-test on *Lemna Gibba* (aquatic plant) and a 3-day EC50-test on *Pseudokirchneriella subcapitata* (algae) were interpreted as chronic, in accordance with table 4.7. In the second case, both tests were interpreted as acute, as specified in PPDB, from which the test values had been collected. The results of the test are presented in table 7.1.

Table 7.1 Comparison of characterisation factors for prothioconazole when interpreting two tests on primary producers as chronic or acute.

	CF air	CF water
Both tests interpreted as chronic	3 988	85 627
Both tests interpreted as acute	5 640	121 094

Table 7.1 shows that changing from chronic to acute increased both CF air and CF water with 41% and the final ecotoxicity score (CTUe/ha·yr), in this particular case for wheat, with 21%, since prothioconazole is a major contributor to the final ecotoxicity score of wheat.

Acute-to-chronic extrapolation factors

A constant acute-to-chronic extrapolation factor of 2 was used in this thesis according to the recommendation in Huijbregts et al. (2010b). Other possible extrapolation factors have been suggested in the literature, for example 2.2 for all pesticides except carbamates and organotins, and 1.9 for other organics (Payet, 2004, p. 30). A test was performed for a case with florasulam, in order to evaluate to what degree choosing 2.2 instead of 2 affected the results. The result of the test is presented in table 7.2.

Table 7.2 Comparison of characterisation factors for florasulam with two different acute-to-chronic extrapolation factors.

	CF air	CF water
Acute-to-chronic extrapolation factor = 2	3 892	25 106
Acute-to-chronic extrapolation factor = 2.2	4 034	26 019

In this particular case with florasulam the CFs increased with 4% when changing from the lower extrapolation factor to the higher.

Inconsistencies between databases

Databases were found to not always provide consistent test values. An example is provided here for flurtamone: while both PPDB and AGRITOX have the same test values (0.0099, 0.02 and 13 mg/l), they give somewhat different test specifications. PPDB specify 7 days as test duration for the 0.0099 mg/l test-value while AGRITOX specify 14 days for the same test. And while PPDB specify the 0.02 test-value as performed on *Raphidocelis subcapitata*, AGRITOX specify the test species as "*Pseudokirchneriella subcapitata (ex. Selenastrum capricornutum)*". Additional inconsistencies and sources of confusions as well as error have been found.

Importance of correctly interpreting "similar test conditions"

A test was performed in which the CFs of lactofen were evaluated in two different cases in order to determine to what degree "similar test conditions" mattered for the result. In the first case, three apparently similar 2-day tests (8.4, 4.8 and 0.1 mg/l) on *Daphnia magna* were added separately to the calculation route[43] and in the second case the geometric mean was taken on the three test results before added to the calculation route (believed to be the correct manner of dealing with similar tests). The results of this test are presented in table 7.3.

Table 7.3 Comparison of characterisation factors for lactofen depending on how test values from similar test conditions are handled.

	CF air	CF water	Ecotoxicity score
Three apparently similar test results on *Daphnia magna* added separately to the calculation route.	6 785	271 154	5.4
A geometric mean was taken on the three test results before added to the calculation route.	42 966	1 716 987	34.5

Table 7.3 shows that the CFs of lactofen increased by a factor of 40 in the second case compared to the first, and that the ecotoxicity score of lactofen increased more than 6 times.

[43] The calculation route referred to is that of *avlogEC50*, explained in chapter 4.3.5.

Comparison between calculated CFs and CFs included in USEtox database

CFs were calculated for three pesticides already included in the USEtox database in order to compare the results. The results are presented in table 7.4.

Table 7.4 Comparison between calculated CFs and USEtox CFs for glyphosate, quinmerac and diflufenican.

Substance	CF air	CF water	Source of CFs and classification
Glyphosate	13	321	USEtox database, recommended CF
	14	324	Calculated, effect data from Payet (2004)
Quinmerac	24	505	USEtox database, interim CF
	21	445	Calculated, effect data from AGRITOX and PPDB. EC50 = 148.7 mg/l as specified in AGRITOX
	24	508	Calculated, effect data from AGRITOX and PPDB. EC50 = 100 mg/l. Specified in PPDB as >100 mg/l
Diflufenican	30	1 247	USEtox database, interim CF
	36 454	1 513 535	Calculated, effect data from AGRITOX

Table 7.4 shows that the calculated CFs for glyphosate are very close to the values given in the USEtox database.

For quinmerac, the test revealed database inconsistencies and showed that USEtox team had used less exact effect data, leading to overestimated CFs. AGRITOX specify an acute EC50-test value on *Daphnia Magna* as 148.7 mg/l, while PPDB specify the same test value simply as "*>100 mg/l*". A test was performed, presented in table 7.4, in order to evaluate to what degree choosing one value or the other impact the CFs and how these respective results compare with the USEtox database CFs for quinmerac. Table 7.4 shows that both CFs increased with 14% when choosing the lower value compared to the higher. While it is believed that it is more correct to use the higher, more exact value, this test shows that USEtox team had used the lower, more inexact figure.

For diflufenican, table 7.4 shows that there is a very large difference between calculated CFs and USEtox CFs. The entire difference has been derived to the input parameter *avlogEC50*. EC50-data represent a total of seven measurements, three species and two tropic levels. USEtox effect data are based on the same number of species and trophic levels and the CFs are classified as interim. It is not known why there is such a large difference between USEtox CFs and calculated CFs, and which pair is a better representation of ecotoxicity, but indications point towards diflufenican being highly ecotoxic, indicating in favour of the higher (calculated) pair.

In a recent field study of pesticide residues in water courses of southern Sweden, diflufenican was ranked number one in terms of ecotoxicity in a ranking based on acceptable concentrations among 25 surveyed pesticides. In the same study diflufenican was found in 32% of the water samples and the average concentration was six times higher than the maximum acceptable level. (Länsstyrelsen Skåne, 2011) According to the Swedish Chemicals Agency (KemI) the freshwater ecotoxicity of diflufenican is difficult to determine due to its low solubility in water. For example, lethal tests are not possible to perform since lethal effects are not reached at the maximum level of solubility. (KemI, 2013)

Diflufenican would enter the top-ten list (table 6.2) at place seven if the higher CFs were used and the ecotoxic impact score of *Salix* would increase by a factor of four.

Concluding remarks

The examples provided in chapter 7.1 have indicated the level of sensitivity of both CFs and ecotoxicity scores to ecotoxicological effect data and highlighted important features of the USEtox model.

It has been shown that results are highly dependent on differentiation between acute and chronic. In this thesis the method outlined in chapter 4.3.5 was used while many other differentiation systems could have been used. The fact that USEtox user manual (Huijbregts et al. 2010b) does not provide guidance in this matter calls for improved user guidelines. Further, acute-to-chronic extrapolation factors are indeed crude instruments of chronic toxic effect evaluation that can be questioned.

The examples of inconsistencies between databases indicated some of the hardships that were encountered in data collection. The importance of correctly interpreting "similar test conditions" has been shown, while the problem is that the definition of it is unclear - no clue is given in the USEtox user manual. In this thesis "similar test conditions" were interpreted as specified in chapter 4.3.5, while it could have been interpreted in many other ways – producing other results.

The comparison between the CFs for quinmerac available in USEtox database and calculated CFs showed that more can be done to improve the CFs already included in the USEtox database. The example with diflufenican illustrated the limitations of present models and the uncertainty of some of the CFs, especially those that are classified as interim, and showed that there is a need to develop ecotoxicity assessment methods to cover a wider range of chemicals and that caution should indeed be taken in interpretation of CFs classified as interim.

That ecotoxicological effect data greatly impact ecotoxic scores in USEtox is confirmed in a paper by Hendersson et al. (2011). The paper concludes that for emissions to freshwater, the effect factor (based on ecotoxicological effect data) controls CFs for freshwater emissions by up to 10 orders to magnitude, while physical-chemical properties (of relevance for fate) impact CFs by less than 2 orders of magnitude, while for emissions to soil, physical-chemical properties are more important.

7.2 Significance of detailed emissions inventory

A closer look and comparison of the results for atrazine in sugarcane and atrazine in maize at places one and six in the top-ten list (table 6.2) is provided here. Selected input data parameters in the two cases are presented in table 7.5.

Table 7.5 Comparison between input data parameters, emissions and ecotoxicity scores for atrazine applied to maize and sugarcane.

Input data parameters	Atrazine in maize	Atrazine in sugarcane
Location	Iowa, USA	Mato Grosso, Brazil
Time of application	March	October
Dose (kg/ha)	1.009	0.679
Method of application	Conventional boom bare soil	Conventional boom cereals
Crop development stage at time of application	Bare soil	Maize I
Application frequency (1/yr)	1	0.73
Emissions to air (kg/ha)	1.96E-03	1.19E-02

Share of applied dose emitted to air (%)	0.19	1.75
Emissions to surface water (kg/ha)	8.35E-05	4.45E-04
Share of applied dose emitted to surface water (%)	0.008	0.066
Ecotoxicity score (CTUe/ha/yr) (unallocated / allocated)	13.8 / 7.5	56.8 / 56.8

Table 7.5 shows that these two cases differ in all aspects, such as location, time of application, dose, frequency of application and method of application. Some parameters indicate towards a higher ecotoxic impact score of atrazine in maize – for example the fact that the dose applied to maize is almost 50% higher compared to the dose applied to sugarcane and that it is applied every year. Initially, one would also suspect that application to bare soil increases emissions from field, but sensitivity test 3 (Appendix X) shows this is not the case.

Despite many factors indicating towards higher emissions in the maize-case, emissions to air and surface water are five – six times higher for atrazine in sugarcane compared to atrazine in maize and the final unallocated ecotoxicity score more than four times larger for atrazine in sugarcane compared to atrazine in maize.

This shows that ecotoxicity is by no means a function of application doses alone and several other factors including climate, soil and time of the year are highly significant. One explanation for the higher air emissions in the sugarcane-case could be the warm climate in October in Mato Grosso, making atrazine more volatile. Climate data in Appendix VII show that the average temperature in Iowa in March is only 3 degrees. One explanation for the higher surface water emissions in Mato Grosso could be that it rains more frequently and with heavier intensity in Mato Grosso in October compared to Iowa in March.

Sensitivity test 7 (Appendix X) shows that emissions to air and surface water were four – six times higher in Mato Grosso compared to emissions in Iowa when all other modelling parameters were kept constant. This indicates that regional climate and soil conditions matter.

Sensitivity test 3 (Appendix X) shows that emissions to air and surface water were significantly higher during the warmer months of the year, compared to the colder, when all other modelling parameters were kept constant, indicating that timing also matters - in the sense that timing has to do with weather conditions such as temperatures, solar radiation and rain frequencies.

As mentioned in chapter 3.3, pesticide emission inventory analysis in the context of agricultural LCAs has up to now often been dealt with using crude assumptions regarding the shares of pesticides emitted to different compartments. Table 7.5 shows that the shares of the applied dose emitted to air and surface water were eight - nine times larger in the sugarcane-case compared to the maize-case.

The lesson that can be learnt is that it is very important to do a detailed emission inventory analysis, take into account local climate and soil characteristics and timing, and not rely on crude estimates.

7.3 Limitations of the present study and proposed advancement measures

Only the active substances of herbicides, insecticides and fungicides were included in this thesis although other types of pesticides such as nematicides and seed disinfectants are commonly used in many agricultural systems, contributing to the overall ecotoxicity, as well as and other formulation ingredients, such as surfactants and solvents.

Only aquatic freshwater ecotoxicity was evaluated since characterisation in this sub-impact category is most advanced and ILCD-recommended characterisation methods are available.

Only emissions to air and surface water were included following direct field application. Accidental spills and other emission routes were excluded. Emissions to soil and ground water could not be included since PestLCI does not give the emissions to soil and USEtox lacks characterisation methods for ground water.

With background in these limitations, it has to be remembered that the results presented here only partially account for the full ecotoxic impact caused.

While great care has been taken to ensure that the scenarios used are realistic, they are not claimed to represent any sort of national or regional averages or to be fully representative for the crops in general. Many other possible application scenarios exist, each of which would produce a unique result. It is therefore important that the result presented here be viewed as products of these particular cases and not as representative ecotoxicity scores for the crops in general.

Pesticide application and hence ecotoxicity is a difficult and highly dynamic area that depend on a range of factors that vary between farmers, regions and years – for example climate and weather, pressure from pests and diseases, legislation and culture. Commodity prices are another aspect that affect year-to-year application practices – the higher the price the lower the thresholds for application. Farm support, widely practiced in Europe, is another aspect that might influence application levels – farmers that are less dependent on actual yields to survive might apply less pesticides.

These results should not be interpreted as inherent characteristics of the crops in general, but rather as a product of cultivation practices, legislation and culture in different regions. For example, in Brazil, where fields generally are larger and monocropping practices are more widespread than in Europe, larger yields and more money are at risk in case of severe insect or disease attack - probably acting in favour of increased pesticide use.

The limited scope of this thesis has left several areas unexplored. A more exhaustive account of pesticide use in biofuel feedstock production and evaluation of freshwater ecotoxic impact, which can be done with present models, could expand into one or several of the following areas:

- include more biofuel feedstocks, such as oil palm, sugar beet, Jatropha and *Eucalypt*
- include all types of pesticides used and to the extent it is possible, also other formulation ingredients

- advance inventory of pesticide use, for example by using national or regional averages
- calculate regionalised CFs to account for geographical differences in ecotoxic impact
- conduct a more careful and wider collection of ecotoxicological effect data and aim for minimum effect data requirements to reach more reliable CFs
- consider variable biofuel production levels, pesticide application levels and variability in physical-chemical and ecotoxicological effect data.

A study taking into account all of these suggested areas of expansion would enable more far-reaching conclusions to be drawn regarding the freshwater ecotoxic impact of various conventional and advanced biofuels produced in different regions. However, in order to determine the full environmental impact of biofuels further expansions are required, including several other environmental impact categories and the entire life cycle of biofuels. Such an assessment is urgently needed since biofuels are projected to increase dramatically in the near future and decisions makers as well as industry need guidance to encourage investment in biofuels with low environmental impacts and avoid technology lock-in in biofuel production systems with high environmental impacts.

Human health aspects could also be addressed by present models, for which USEtox is appointed the best available midpoint characterisation model by ILCD (Hauschild et al. 2013). However, human health aspects in relation to production of biofuels also urgently need to be addressed by other measures than LCA to improve working conditions of farm-workers and reduce the number of pesticide intoxication cases, especially in developing countries.

Allocation

It was decided in this thesis to allocate pesticide application levels and ecotoxic impact scores through partitioning based on energy content of main product (fuel) and co-product(s), using allocation factors available in the BioGrace greenhouse gas calculation tool (2011). The allocation factor for sugarcane was 100% meaning the entire pesticide dose and ecotoxic impact was allocated to ethanol, while all other conventional crops had allocation factors in the range of 33 – 60% allocated to the fuel. Sugarcane's allocation factor can however be questioned since most modern sugarcane ethanol production plants use bagasse as a feedstock to produce local CHP and in addition often sell excessive electricity to the grid for which reason it would be reasonable to consider the energy content of this co-product. More over, other basis for allocation partitioning could possibly have been used. The analysis of effects of allocation choices on the results is however beyond the scope of this study, but is central in a more thorough study.

7.4 Future work and recommendations

Beyond what can be done with present models, several areas of future improvement potential involving development of models and characterisation methods have been identified, ranging from including more substances into models, ensuring compatibility of models to the issue of regionalisation and taking into account metabolites and cocktail effects.

Expanding toxicity characterisation models

Characterisation methods for marine and terrestrial ecotoxicity are lagging behind characterisation in the freshwater compartment and need to be developed in order to be able to characterise every aspect of ecotoxicity. To this date, no ILCD recommended characterisation method exists for terrestrial and marine ecotoxicity (Hauschild et al. 2013).

Characterisation methods for substances that are currently not handled by USEtox (all substances other than non-polar, non-ionic, organic substances) need to be developed to be able to assess the toxic effects of all chemicals, including those that are classified as interim at present. This also includes substances with very low solubility in water, for example diflufenican, a case which was discussed in chapter 7.1.

Methods for characterisation in ground water are still at an early stage of development. Research has shown that pesticides and their metabolites are frequently found in ground water (see for example Adielsson and Kreuger, 2006) for which reason it should be included as an exposure route for humans and possibly also in ecotoxicity characterisation.

More substances need to be included in the databases of both models, especially PestLCI with as little as around 100 pesticides today, to facilitate the inclusion of ecotoxicity as an impact category in agricultural LCAs at SIK and elsewhere. Most LCA practitioners do not have the time to manually add new pesticides to PestLCI or to calculate CFs for substances that are missing and will simply omit substances that are not included which will lead to underestimated impacts. In this thesis, despite dealing with fairly common pesticides, more than a third of the pesticides were not included in the USEtox database and had to be calculated.

It is recommended that model developers consider the option of using only modelled physical-chemical data instead of, as now, prioritise experimental data. It is believed that the quality of experimental data is more variable and the quality more difficult to rate, than modelled data. Also, modelled data are much easier and cheaper to produce in large quantities which would facilitate the inclusion of more substances into both models.

The user manual of USEtox (Huijbregts et al. 2010b) needs to be improved to encourage and facilitate the calculation process of CFs that are missing. The user manual of today is perceived as a theory-centred technical report with little practical guidance. Especially the section on ecotoxicological effect data collection and calculation needs to be updated with regard to the points discussed in chapter 7.1.

Best practice effect

It should be noted that in reality, farmers have the possibility to choose suitable application times and avoid inappropriate conditions. For example, 2,4-D should not be applied at windy conditions and high temperatures to avoid emissions to air (Tu et al. 2001), and ideally, farmers follow these guidelines. However, PestLCI does not take into account that farmers may follow best practice, but only considers the physical-chemical properties of the pesticide and month of application, assuming average climate conditions of that month. The impact of this effect on emission inventory results is not known but would be interesting to investigate.

Compatibility of models

That PestLCI is compatible with USEtox is assured in Dijkman et al. (2012) and the combination has been used in previously published papers (for example Ometto et al. 2009). However, Van Zelm et al. (2012) raise concerns, in a yet unpublished paper, regarding double-counting and over-lap in time and space between typical LCI and LCIA practices in agricultural LCAs of today, although PestLCI has not been mentioned specifically in the context.

That PestLCI and USEtox suggest different default databases for collection of physical-chemical has been pointed out previously. While PestLCI recommend PPDB and PhysProp (Dijkman, pers. com. 2013), USEtox suggests EPISuite (Rosenbaum et al. 2008). The main problem, besides the double data collection, is that property values given in each of the different database sometimes display considerable differences. An example is presented in table 7.6.

Table 7.6 Example of differences in physical-chemical properties between databases.

		Prothioconazole	Florasulam
Vapour pressure at 25°C (Pa)	PPDB	4.0E-7	1.0E-5
	EPISuite	4.5E-12	5.8E-7
Henry's Law constant at 25°C ($Pa{\cdot}m^3$/mole)	PPDB	3.0E-5	4.4E-7
	EPISuite	9.6E-8	1.4E-8

While it would be desirable to use a consistent physical-chemical dataset for both models it was prioritised in this thesis to follow the model developers' recommendations, although this resulted in inconsistency. The full set of physical-chemical data collected and used in this thesis for PestLCI and USEtox are available in Appendix III and IV, respectively.

Besides the inconsistent set of default databases, attention has been drawn to the fact that the two models disagree on which environmental compartments that are of concern. USEtox includes the soil compartment which PestLCI is lacking and PestLCI includes the ground water compartment which USEtox is lacking. In addition, as mentioned in chapter 3.3, the system boundaries in agricultural LCAs are not as clear cut as in traditional LCAs and the question if agricultural soil belongs to the technosphere or ecosphere is one of the most pressing issues for the international LCA community to resolve.

It is recommended that the development teams of both models increase their level of co-operation and initiate harmonisation efforts, addressing the following issues:

- databases for physical-chemical data
- environmental compartments
- system boundaries in space and time

This matter has been pointed out to representatives of both models and it has been indicated that a dialogue aimed for harmonisation might be initiated at DTU (where representatives of both development teams reside) as a result of this (Dijkman pers. com. 2013).

In Van Zelm et al. (2012) a framework for the treatment of pesticides in agricultural LCAs designed to avoid overlap between the LCI and LCIA is proposed, that might change practice in agricultural LCAs in the future. The proposed framework suggests the following system boundaries:

- Defining the system boundary of LCI as a box with a bottom area equal to the field including buffer zones, extending 10 meters up into the air and 1 cm down into the soil column.
- Setting the time scale of LCI to the same order of magnitude as the time pesticides remain inside the field box. For example, drift and volatilization can be accounted for in within a time scale of a few minutes, while other transport and degradation processes require much longer time scales. (Van Zelm et al. 2012)

Regionalisation of impact models

Chapter 7.2 stressed the importance of taking into account regional factors in inventory models. The question remains if this also applies to characterisation models. Geographical differences matter also in the characterisation step but somewhat less since emissions are likely to have dispersed over larger regional areas in the characterisation stage – the rationale for assuming average continental conditions in USEtox.

Currently, steps are taken towards spatial differentiation of impact assessment models in those impact categories for which it matters – for example toxicity. An example of this is GLOBOX (Wegener Sleeswijk, 2006) with ability to calculate spatially differentiated CFs for ecotoxicity and human toxicity down to the level of 289 different regions. To date, USEtox is site-generic but the opportunity to calculate region-specific CFs exists through modification of landscape data, which was done in Bennet (2012).

More accurate results can be achieved with regionalisation of both LCI and LCIA, but this is a matter of practicability in each specific case – regionalisation can be time consuming if default regions are not already included in models.

One way forward towards integrating spatial differentiation could be to include a selection of typical climate zones and soil profiles in USEtox – a suggestion is to start with those already included in PestLCI. Further it is recommended that PestLCI shift from weather station based locations to typical climate zones since there exist a large number of weather stations in the world, but a much smaller set of typical climate zones. A recommendation is that the development teams of both models co-operate in this area. Eventually, PestLCI need to expand beyond Europe.

Metabolites

A shortcoming of present models is that pesticides are modelled to disappear as they degrade and that model databases do not contain key metabolites. For example, USEtox with over 3000 substances, does not include even AMPA, the key metabolite of glyphosate. The PPDB (2013) database includes a section on key metabolites of pesticides and supports an attempt to include them for modelling purposes, but in practice this is difficult since physical-chemical as well as toxicity data are very scarce for most metabolites.

It is important to include metabolites in the calculation of CFs, especially for compounds that degrade rapidly into more stable compounds, some of which are more toxic than the parent compound. A recent study (Van Zelm et al. 2010) showed that when degradation products of glyphosate were included, the CFs for freshwater ecotoxicity of glyphosate increased by a factor of ten.

Cocktail effects

The knowledge about cocktail effects, arising from combination of several toxic compounds and generally larger than the sum of individual effects, is very limited and far beyond the scope of present models. Cocktail effects are not evaluated in traditional risk evaluation of chemicals, and the knowledge about cocktail effects is restricted to isolated research studies on specific combinations.

For example, several studies have showed that surfactants (a common pesticide ingredient) increase toxicity of pesticides. Sharma and Singh (2001) showed that surfactants increased toxicity of both glyphosate and 2,4-D to Brazil pusley (*Richardia brasiliensis*), a common weed in citrus plantations in Florida. Lee et al. (2009) report that while glyphosate alone is only slightly toxic to rats, in combination with surfactants, it can cause considerable health problems and death to swine and have caused death to humans upon ingestion.

Jin-Clark et al. (2002) report on the combined effect of atrazine and chlorpyrifos – two pesticides that are commonly used in combination, for example in maize, as in this study. While chlorpyrifos is toxic to *Chironomus tentans* (larva of aquatic midge) already at low concentrations, atrazine is not, even in high concentrations. But when the larvae are exposed to both pesticides at the same time, the toxicity of chlorpyrifos is enhanced by up to a factor of 1.8 through synergetic effects. The explanation is that atrazine interacts with the degradation of chlorpyrifos forming highly toxic degradation products.

That cocktail effects are of significant importance in toxicology is clear (see for example Nordic Council of Ministers, 2012), but more research is needed to determine how such effects can be integrated into models. Other effects that border to cocktail effects are background concentrations and thresholds for effects.

Linking midpoints to endpoints

One future research area is to link ecotoxicity midpoints, represented by measures such as CTUe, to endpoints, for example biodiversity. No methods linking midpoints to endpoints exist in ecotoxicity today (Hauschild et al. 2013). One effort in line with this suggestion is presented in Rundlöf et al. (2012) in which the effects of pesticides on biodiversity in evaluated. Endpoints make concepts easier to grasp but introduce additional layers of uncertainty.

The dual challenge for model developers

The suggested improvement areas discussed above will undoubtedly lead to models becoming more complex. At the same time, the inclusion of ecotoxicity as an impact category in LCA at SIK and elsewhere is not facilitated by models becoming more complex, difficult to understand and work with. Model developers indeed face dual demands in making models transparent and easy to work with, and at the same time, advanced enough to incorporate state-of-the art research in toxicity and provide reliable and comparable results, preferably within several environmental compartments and regions and for tens of thousands of chemicals.

8. CONCLUSIONS

This study has showed that:

- sugarcane and maize have the highest energy output per hectare and year while soybean has the lowest.
- all crops are subject to fairly similar application levels per hectare and year (unallocated levels) - except *Salix* that by far has the lowest pesticide active substance (AS) application rate.
- *Salix* has the lowest intensity of application (once every three years with herbicides) while wheat and soybean has the highest (pesticides applied to soybean up to 12 times per growing season).
- sugarcane, soybean (conventional case) and maize (both cases) all require almost the same amount (18−19 g) of pesticide AS for production of 1 GJ biofuel energy while rapeseed and wheat require 40% and 80% more respectively. *Salix* requires by far the least amount: 4 g AS for production of 1 GJ biofuel energy.
- rapeseed and *Salix* have the lowest freshwater ecotoxic impacts per hectare and year (1 and 2 CTUe/ha/yr respectively).
- sugarcane has the highest freshwater ecotoxic impact per hectare and year (89 CTUe/ha/yr) – more than three times larger than that of any other biofuel feedstock. The high score of sugarcane is associated with the use of the herbicides atrazine, 2,4-D and ametryn. Another contributing cause is that the entire impact is allocated to sugarcane ethanol, while the impact scores of the other feedstocks (besides *Salix*) are partially allocated to co-products.
- in relation to energy output, the impact score of sugarcane is significantly better in relation to the other crops due to high energy output.
- there is a significant range in freshwater ecotoxic impacts in relation to energy output caused by the various crops: production of 1 TJ biofuel energy from rapeseed causes an ecotoxic impact score of 31 CTUe, while production of 1 TJ biofuel energy from wheat, maize (insecticide case), GM soybean and sugarcane give rise to ecotoxic impact scores 4, 10, 13 and 22 times larger, respectively.
- the large difference between the two soybean cases is due to the herbicide lactofen applied to conventional soybean – the characterisation factors (CFs) of which have been calculated and are uncertain due to insufficient effect data.
- the European cases have lower ecotoxicity scores in general compared to the North and South American cases – probably an effect of stricter pesticide legislation in Europe. However, in relation to energy output, Bt-maize (not using chlorpyrifos) also scores in level with the European crops.
- the large difference between the two maize cases is due to the insecticide chlorpyrifos – applied in the non-Bt case.
- wheat causes an ecotoxic impact almost four times larger than that of rapeseed, both in relation to hectare and year and in relation to energy output. However, this is primarily due to the fungicide prothioconazole – the CFs of which have been calculated and are uncertain due to insufficient effect data.
- the pesticides used for cultivation of crops in North and South America are generally more toxic in relation to amount of AS used compared to crops cultivated in Europe – the exception are pesticides used on Bt-maize.
- there is no correlation between amount of pesticides used and ecotoxic impact caused.

- fungicides and insecticides have higher ecotoxic impact in relation to amount of AS in general, compared to herbicides.
- there is a large variation in application rates and freshwater ecotoxic impacts of the assessed alternatives. Allocation and choice of impact metric (per hectare and year or energy output) influence the results significantly.
- the top-three AS with highest ecotoxic impact scores are atrazine (sugarcane, 56.8 CTUe/ha/yr), 2,4-D (sugarcane, 17.8 CTUe/ha/yr) and chlorpyrifos (maize, 16.1 CTUe/ha/yr) – all three of them known to be problematic and two of them (atrazine and 2,4-D) identified water pollutants, lending towards the reliability of these results.
- *Salix* has the lowest (most favourable) score in all environmental performance indicators and it is likely that future biofuels from *Salix* would be associated with lower freshwater ecotoxic impacts compared to the other alternatives.

The results need to be interpreted with the following in mind:

- the cases presented here represent "typical" and realistic application scenarios but do not claim to be any sort of national or regional averages. The ecotoxic impacts should therefore not be interpreted as representative for the crops in general. Neither do the results reflect inherent characteristics of the crops. The results should be interpreted as products of these particular cases and in the light of regional agricultural practices and pesticide legislation.
- pesticide application and ecotoxic impact scores of sugarcane is allocated entirely to ethanol, while all other conventional feedstocks have allocation factors in the range 33 – 60% to the fuel. The allocation factor of sugarcane can be questioned.
- the results for *Salix* are not to be compared with the other biofuel feedstocks, but should be interpreted as an indication of the future potential of ethanol from woody biomass.
- pesticide use and ecotoxic impact is highly dynamic and depend on a range of factors that vary between farmers, regions and years, for example climate, pressure from disease and pests, legislation, culture etc – stressing the need for regionalisation of models and inventory.
- results only partially account for the full ecotoxic impact caused and an even smaller part of the full environmental impact – but this study is one important contributor towards a full environmental assessment of biofuels, needed by industry and policy makers.

The discussion arrived at the following conclusions:

- the most challenging, and time consuming, step in the characterisation of freshwater ecotoxic impact was encountered in relation to ecotoxicological effect data. Challenges ranged from difficulties in finding, interpreting, differentiating and using effect data. Tests showed that CFs and ecotoxic impacts scores are highly dependent on effect data and the differentiation between acute and chronic tests.
- location and timing are highly significant for emissions to various compartments and hence ecotoxic impact scores. Therefore it is very important to perform a detailed emission inventory, as done in this thesis, taking into account local climate and soil characteristics and timing, besides application amounts, and not rely on crude estimates.

- models are still immature and further research is needed to develop and harmonise models. Key research areas include: terrestrial and marine ecotoxicity, substances currently not handled by USEtox, regionalisation, metabolites of substances and cocktail effects. In addition, more substances need to be included in the databases of both models – especially PestLCI. Harmonisation efforts should strive for a consistent set of physical-chemical data and environmental compartments.

With regard to aim the following can be concluded:

- this thesis has fulfilled aim (a) and (b) through comparison of several indicators based on pesticide use, gross energy output and freshwater ecotoxic impacts and evaluation of the environmental performance of six biofuel crops.
- this thesis has explored and applied the methodology needed to characterise ecotoxicity and spread the knowledge at SIK, thus made a contribution to methodology development within the ecotoxic impact category in LCA at SIK and fulfilled aim (c).

REFERENCES

Ackerman F. (2007) *The Economics of Atrazine.* The International Journal of Occupational and Environmental Health, 13 (4): 437 − 445.

Adielsson S, Kreuger J. (2006) *Bekämpningsmedel hittas i åar och grundvatten*. Fakta Jordbruk no 9. SLU, Swedish University of Agricultural Sciences: Uppsala

AGRITOX (2012) *Guide: Definitions of the properties given on the fact sheets*. [online] Available at: <http://www.dive.afssa.fr/agritox /guides/guide-agritox-anglais.html> [Accessed 2013-02-28] French National Institute for Agricultural Research.

AGRITOX (2013) AGRITOX: database on plant protection substances. [online] Available at: <http://www.dive.afssa.fr/agritox/index.php> [Accessed 2013-02-28] [In French] French National Institute for Agricultural Research

Alkabbashi A.N, Alam Md. Z, Mirghani M.E.S, Al-Fusaiel A.M.A. (2009) *Biodiesel production from crude palm oil by transesterification process.* Journal of Applied Sciences, 9 (17): 3166 − 3170.

APS (2013) *Common names of plant diseases*. [online] Available at: <http://www.apsnet.org/publications/commonnames/Pages/CornorMaize.aspx> [Accessed 2013-01-11] The American Phytopathological Society.

Arraes A, Barreto F.M, de Araújo, J.C. (2008) *Use of Atrazine and groundwater availability in Brazil: case study Tianguá*. Article presented at the 13th IWRA (International Water Resource Association) World Water Congress, 1 − 4 September 2008, Montpellier, France

de Armas E.D, Monteiro R.T.S, Amâncio A.V, Correa R.M.L, Guercio M.A. (2005*) The use of pesticides in sugar cane at the Corumbataí river basin and the risk of water pollution*. Química Nova, 28 (6): 975 – 982. [In Portugese]

Barker T, Bashmakov I, Bernstein L, Bogner J.E, Bosch P.R, Dave R, Davidson O.R, Fisher B.S, Gupta S, Halsnæs K, Heij G.J, Kahn Ribeiro S, Kobayashi S, Levine M.D, Martino D.L, Masera O, Metz B, Meyer L.A, Nabuurs G.-J, Najam A, Nakicenovic N, Rogner H.-H, Roy J, Sathaye J, Schock R, Shukla P, Sims R.E.H, Smith P, Tirpak D.A, Urge-Vorsatz D, Zhou D. (2007) *Technical Summary.* In: *Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Metz B, Davidson O.R, Bosch P.R, Dave R, Meyer L.A. (eds)] Cambridge University Press: Cambridge and New York

BASF (201-) *BASF Växtskydd 2012/2013*. [online] Available at: <http://www.agro.basf.se/agroportal/se/media/migrated/se/product_files/produkth_ndbog _2012_13/BASF_Vaxtskydd.pdf> [Accessed 2013-05-03] BASF Crop Protection Sverige

Batjes N.H. (2008) *ISRIC-WISE Harmonized Global Soil Profile Dataset (Ver. 3.0).* ISRIC - World Soil Information (Report 2008/2): Wageningen

Batjes N.H. (2009) *Harmonized soil profile data for applications at global and continental scales: updates to the WISE database*. Soil Use and Management, 25 (2): 124 – 127

Baumann H. Tillman A-M. (2004) *The Hitch Hiker's Guide to LCA.* Studentlitteratur: Lund

Bayer CropScience (201-) *Vi kan gräsogräs.* [online] Available at: <http://www.bayercropscience.se/uploads/media/gr%C3%A4sogr%C3%A4sinfo_WEB.pdf> [Accessed 2012-11-09]

Bayer CropScience (2012) Bayer CropScience Crop Compendium. [online] Available at: <http://compendium.bayercropscience.com> [Accessed 2013-05-02]

Bennet S.M.P (2012) *Ecotoxicity in LCA – A review of methods and an assessment of the ecotoxic impact of pesticide use in Swedish winter wheat and Brazilian soybean production*. MSc Thesis. SIK, Swedish Institute for Food and Biotechnology: Göteborg

Berry P, Cook S, Ellis S, Gladders P, Roques S. (2012) *Oilseed rape guide - Summer 2012.* [Boys E. (ed.)] Cereals and oilseeds division (HGCA) of the Agriculture and Horticulture Development Board (AHDB): Warwickshire

BioGrace (2011) BioGrace GHG calculation tool developed in the BioGrace project 2010 – 2012, funded within the Intelligent Energy Europe Programme. Excel tool available at: <www.biograce.net> Follow the links: GHG calculation tool, calculation tool. [Accessed 2013-05-04]

Birkved M, Hauschild M.Z. (2006) *PestLCI—A model for estimating field emissions of pesticides in agricultural LCA*. Ecological Modelling, 198 (3-4): 433 – 451

Björkman C, Eklund K. (2004) *Skörd stör biologisk kontroll av skadeinsekter.* Fakta Jordbruk no 3. SLU, Swedish University of Agricultural Sciences: Uppsala

BNDES and CGEE (2008) *Sugarcane bioethanol in Brazil*. In: *Sugarcane-based* bioethanol - Energy for sustainable development. BNDES, Brazilian Development Bank and CGEE, Center for Strategic Studies and Management Science, Technology and Innovation (coordination) in cooperation with FAO, Food and Agriculture Organisation and ECLAC, the Economic Commission for Latin America and the Caribbean: Rio de Janeiro.

Boundy B, Diegel S.W, Wright L, Davis S.C. (2011) *Lower and Higher heating values of Gas, Liquid and Solid Fuels.* Appendix A in: *Biomass Energy Data Book*. Fourth edition. Prepared by the Oak Ridge National Laboratory: Tennessee, for the US Department of Energy

Carlson A, Antonson H. (2011) *Andra generationens biodrivmedel - En litteraturöversikt*. VTI, Swedish National Road and Transport Research Institute: Linköping

Cederberg C, Wivstad M, Sonesson U. (2007) *Bekämpningsmedelsanvändning i höstvete odlat enligt Svenskt Sigill åren 2002 – 2004.* SIK, The Swedish Institute for Food and Biotechnology, (SR report no 776): Göteborg

CERA (2012) GM Crop Database. [online] Available at: <http://cera-gmc.org/index.php?action=gm_crop_database> [Accessed 2012-11-26] Center for Environmental Risk Assessment, ILSI Research Foundation: Washington

Dijkman T.J, Birkved M, Hauschild M.Z. (2012) *PestLCI 2.0: a second generation model for estimating emissions of pesticides from arable land in LCA.* The International Journal of Life Cycle Assessment, 17 (8): 973 – 986.

EC (2009a) *Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.* Official Journal of the European Union L 140: 16 − 62

EC (2009b) *Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC.* Official Journal of the European Union L 140: 88 − 113

Ekbom, B. (2002) *Resistens mot insektsbekämpningsmedel.* Faktablad om växtskydd no 109. SLU, Swedish University of Agricultural Sciences: Uppsala

EPPO (2007) *Conclusions and Recommendations.* Workshop paper from *Ad hoc* EPPO Workshop on insecticide resistance of *Meligethes* spp. (pollen beetle) on oilseed rape. BBA, Berlin-Dahlem, September 3-5, 2007. EPPO, European and Mediterranean Plant Protection Organisation

Ericsson K, Rosenqvist H, Nilsson L.J. (2009) *Energy crop production costs in the EU.* Biomass and Bioenergy, 33 (11): 1577 – 1586.

EU-JRC (2010) *International Reference Life Cycle Data System (ILCD) Handbook - Framework and Requirements for Life Cycle Impact Assessment Models and Indicators.* First edition. European Commission - Joint Research Centre - Institute for Environment and Sustainability: Luxembourg.

Eurostat (2008) *A common methodology for the collection of pesticide usage statistics within agriculture and horticulture*. Methodologies and Working paper. Statistical office of the European Union. Office for Official Publications of the European Communities: Luxembourg

Eurostat (2010) *Europe in figures - Eurostat yearbook 2010*. Statistical office of the European Union. Publications Office of the European Union: Luxembourg

Everest J.W, Patterson M.G, Ortiz B.V, Walker R.H, Wehtje G. (2012) *Corn - Insect, Disease, Nematode, and Weed Control Recommendations for 2012.* Alabama Cooperative Extension System, Alabama A&M University and Auburn University

FAO (1996) *Pesticides as water pollutants*. In: *Control of water pollution from agriculture.* FAO irrigation and drainage paper 55. [Ongley E.D] Natural Resources Management and Environment Department, Food and Agriculture Organisation of the United Nations: Rome.

FAO (1999) *Guidelines for the management of small quantities of unwanted and obsolete pesticides.* FAO Pesticide Disposal Series 7, Food and Agriculture Organisation of the United Nations: Rome.

FAO (2002) *Insects in wheat-based systems*. [Miller R.H, Pike K.S] In: *Bread Wheat – Improvement and Production*. [Curtis B.C, Rajaram S, Gómez Macpherson H. (eds)] FAO Plant Production and Protection Series no 30. Food and Agriculture Organisation of the United Nations: Rome.

FAO (2003) *International Code of Conduct on the Distribution and Use of Pesticides*. Adopted by the Hundred and Twenty-third Session of the FAO Council in November 2002. Food and Agriculture Organisation of the United Nations: Rome.

FAO (2007) *Designing national pesticide legislation*. [Vapnek J, Pagotto I, Kwoko M.] FAO Legislative study 97. Legal Office, Food and Agriculture Organisation of the United

FAOSTAT (2012) FAOSTAT, the FAO statistical database. [online] Available at: <http://faostat.fao.org/> Statistics Division of the Food and Agriculture Organisation of the United Nations: Rome
Nations: Rome.

Fediol (n.d) *Rapeseed.* [online] Available at: <http://www.fediol.eu> Follow the links: About our products, Raw materials, Rapeseed. [Accessed 2013-05-03] The EU vegetable Oil and Proteinmeal Industry

Flickr (2013) Electronic images available under the Creative Commons-license. [online] Available at: <www.flickr.com>

Gassmann A, Weber P (2012) *2011 Evaluation of insecticides and plant-incorporated protectants*. Corn Pests Research Project. Department of Entomology, Iowa State University of Science and Technology: Ames

Goedkoop M, Spriensma R. (2000) *The Eco-indicator 99: A Damage Oriented Method for Life Cycle Assessment*. Methodology Report, second edition. Pré Consultants: Amersfoort

Goedkoop M.J, Heijungs R, Huijbregts M.A.J, de Schryver A, Struijs J, Van Zelm R. (2009) *ReCiPe 2008 - A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level*. First edition. Report I: Characterisation. Ministry of Housing, Spatial Planning and Environment (VROM): The Hauge

Government Offices (2008) *En sammanhållen klimat- och energipolitik - Klimat*. Government bill 2008/09:162. Stockholm

Greenpeace and GM Freeze (2011) *Herbicide tolerance and GM crops. Why the world should be Ready to Round Up glyphosate.* Greenpeace: Amsterdam and GM Freeze: Barnsley

Hallenbeck W.H, Cunningham-Burns K.M. (1985) *Pesticides and human health*. Springer-Verlag New York Inc.: New York

Hauschild M.Z, Goedkoop M, Guinée J, Heijungs R, Huijbregts M.A.J, Jolliet O, Margni M, de Schryver A, Humbert S, Laurent A, Sala S, Pant R. (2013) *Identifying best existing practice for characterization modeling in life cycle impact assessment.* The International Journal of Life Cycle Assessment, 18 (3): 683 – 697.

Hauschild M.Z, Jolliet O, Huijbregts M.A.J. (2011) *A bright future for addressing chemical emissions in life cycles assessment.* The International Journal of Life Cycle Assessments, 16 (8): 697 – 700.

Heap I. (2013) *The International survey of herbicide resistant weeds.*[online] Available at: http://www.weedscience.org/ [Accessed 2013-03-08]

Heller M.C, Keoleian G.A, Volk T.A. (2003) *Life cycle assessment of a willow bioenergy cropping system.* Biomass and Bioenergy, 25 (2): 147–165.

Hendersson A.D, Hauschild M.Z, Van de Meent D, Huijbregts M.A.J, Larsen H.F, Margni M, McKone T.E, Payet J, Rosenbaum R, Jolliet O. (2011) *USEtox fate and ecotoxicity factors for comparative assessment of toxic emissions in life cycle analysis: sensitivity to key chemical properties*. The International Journal of Life Cycle Assessment, 16 (8): 701 – 709.

Höglund S, Eklund K, Björkman C. (1999) *Insektsskadegörare i Salixodlingar – bladbaggar*. Växtskyddsnotiser 63: 20-26. SLU, Swedish University of Agricultural Sciences: Uppsala

Huijbregts M.A.J, Hauschild M, Jolliet O, Margni M, McKone T, Rosenbaum R, Van de Meent D. (2010b) *USEtox™ User manual.* Report version 1.01.

Huijbregts M.A.J, Margni M, Van de Meent D, Jolliet O, Rosenbaum R, McKone T, Hauschild M. (2010a) *USEtox™ Chemical database: organics*. Report version 1.01.

ICARDA (2011) *Strategies to reduce the emerging wheat stripe rust disease*. Synthesis of a dialog between policy makers and scientists from 31 countries at: International Wheat Stripe Rust Symposium, Aleppo, Syria, April 2011. Organised by ICARDA, the International Center for Agricultural Research in the Dry Areas: Aleppo

IEA (2011) *Technology Roadmap, Biofuels for Transport*. [Eisentraut A. (co-ordinator)] International Energy Agency: Paris

IEA Bioenergy (2009) *Bioenergy - a sustainable and reliable energy source. A review of status and prospects*. [Bauen A, Berndes G, Junginger M, Londo M, Vuille F.] International Energy Agency Bioenergy (Report 2009:06): Rotorua

IEA Bioenergy (2012) *Short rotation coppice willow - Best practice guidelines*. [Caslin B, Finnan J, McCracken A. (eds.)] International Energy Agency Bioenergy (Task 43 report 2012:03): Rotorua

IPCC (2007) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment*. Intergovernmental Panel on Climate Change [Solomon S.D, Qin M, Manning Z, Chen M, Marquis K.B, Averyt M, Tignor, Miller H.L. (eds.)] Cambridge University Press: Cambridge, New York

IPCC (2011) *Bioenergy*. In: *IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation* [Edenhofer O, Pichs-Madruga R, Sokona Y, Seyboth K, Matschoss P, Kadner S, Zwickel T, Eickemeier P, Hansen G, Schlomer S, Von Stechow C. (eds.)] Cambridge University Press: Cambridge, New York

IRAG UK (2012) *IRAG Grain Aphid Guidance – kdr Resistance in Grain Aphids*. [online] Available at: <http://www.pesticides.gov.uk/Resources/CRD/Migrated-Resources/Documents/I/IRAG_Grain_Aphid_Guidance_Sept_2012.pdf > [Accessed 2013-05-03] Insecticide Resistance Action Group UK

ISUST (2009) *Corn field guide*. Iowa State University of Science and Technology, University Extension: Ames

Jin-Clark Y, Lydy M.J, Zhu K.Y. (2002) *Effects of atrazine and cyanazine on chlorpyrifos toxicity in Chironomus tentans (Diptera: Chironomidae).* Environmental Toxicology and Chemistry, 21 (3): 598 - 603.

Jolliet O, Margni M, Charles R, Humbert S, Payet J, Rebitzer G, Rosenbaum R. (2003) *IMPACT 2002+: A new life cycle impact assessment methodology*. The International Journal of Life Cycle Assessment, 8 (6): 324-330.

Jørgensen L.N, Jahn M, Kühn J, Clark B, Antichi D, Góral T, Schepers H, Lucas P, Gouache D, Hornok L. (2008) *Best control practices of disease in winter wheat in 8 countries in the EU.* Deliverable D 1.2 of: *Endure – wheat case study.* ENDURE, European Network for Durable Exploitation of Crop Protection Strategies

KemI (2012) *Försålda kvantiteter av bekämpningsmedel 2011*. [Edell Å, Würtz R.] The Swedish Chemicals Agency: Sundbyberg

KemI (2013) Bekämpningsmedelsregistret. [online] Available at: <http://apps.kemi.se/bkmregoff/> The Swedish Chemicals Agency: Sundbyberg

Kew (n.d) *Saccharum officinarum (sugar cane)*. [online] Available at:< http://www.kew.org/ plants-fungi/Saccharum-officinarum.htm> [Accessed 2012-12-19] Royal Botanic Gardens: London.

Kolm S.B, Björkman C, Bonosi L, Ghelardini L, Lehrman A, Nordh N.E, Rönnberg-Wästljung A.C, Samils B, Stenberg J.A, Stenlid J, Weih M, Åhman I, von Arnold S. (2011) *Nya salixsorter med modern växtförädlingsteknik.* Fakta Jordbruk no 1. SLU, Swedish University of Agricultural Sciences: Uppsala

Kreuger J. (2002) *Övervakning av bekämpningsmedel i vatten från ett avrinningsområde i Skåne. Årsredovisning för Vemmenhögsprojektet 2001.* Division of Water Quality Management, SLU, Swedish University of Agricultural Sciences: Uppsala

Lee H.L, Kan C.D, Tsai C.L, Liou M.J, Guo H.R. (2009) *Comparative effects of the formulation of glyphosate-surfactant herbicides on hemodynamics in swine.* Clinical Toxicology, 47 (7): 651−658.

Lehrman A. (2012) *Workshop: Neonikotinoider – välsignelse eller hot?* Växtskyddsnotiser, 67: 1 − 4. SLU, Swedish University of Agricultural Sciences: Uppsala

Lehtonen M. (2009) *Status report on sugar cane agrochemicals management. Agrochemicals in the sugarcane industries: health and environmental challenges and solutions.* [Goebel F.R (co-ordination)] Ethanol & Sugar Impact Analysis (ESIA) and Agricultural Research for Development (CIRAD).

LMC International (2010) *The 2010 Update to Soybean Meal Evaluation*. Report for US soybean export council. LMC International: Oxford, New York, Kuala Lumpur.

Länsstyrelsen Skåne (2011) *Bekämpningsmedel i skånska vattendrag – resultat från den regionala miljöövervakningen 2010.* [Pirzadeh P.] Länsstyrelsen Skåne: Malmö

Länsstyrelsen Skåne (2012) *Grundvattenkvalitet i Skåne län – utvärdering av regional provtagning av grundvatten 2007-2010.* [Virgin H.] Länsstyrelsen Skåne: Malmö

MASTER (20--) *Target pests*. [online] Available at: <http://www.rothamsted.ac.uk/pie/master/targetpests.htm> [Accessed 2013-05-03] MASTER, Management Strategies for European Rape Pests project, supported by the European Commission under the 5th Framework Programme

McKone T.E, Enoch K.G. (2002) *CalTOX, A Multimedia Total-Exposure Model Spreadsheet User's Guide, Version 4.0 (Beta).* Ernest Orlando Lawrence Berkeley National Laboratory: Berkeley

Meyer D, Cederberg C. (2010) *Pesticide use and glyphosate resistant weeds – a case study of Brazilian soybean production*. SIK, The Swedish Institute for Food and Biotechnology (Report 809): Göteborg

Monsanto Company (2005) *History of Monsanto's Glyphosate Herbicides*. [online] Available at: http://www.monsanto.com/products/Documents/glyphosate-background-materials/back_history.pdf [Accessed 2012-11-26]

Monsanto Company (2008) *Doseringar*. [online] Available at: http://www.monsanto.se/ Follow the links: Växtskydd, Roundup, Rekommendationer, Doseringar. [Accessed: 2013-01-18]

Monsanto Company (2013) *Annual R&D pipeline review*. [online] Available at: http://www.monsanto.com/investors/Documents/2013/2013.01.08_Pipeline_Q1FY13.pdf [Accessed 2013-01-16]

Monsanto Company (n.d) *Roundup Ready System*. [online] Available at: http://www.monsanto.com/weedmanagement/Pages/roundup-ready-system.aspx [Accessed 2012-11-26]

NCGA (2012) *2012 - World of Corn.* National Corn Growers Association: Chesterfield, Washington

Nilsson C. (2001) *Miljönyckeltal: Kemiska bekämpningsmedel*. Fakta Jordbruk no 6. SLU, Swedish University of Agricultural Sciences: Uppsala

Nordic Council of Ministers (2012) *Chemical cocktails – a serious matter of concern*. Nordic Council of Ministers (ANP 2012:711): Copenhagen

Oerke E.C, Dehne H.W, Schönbeck F, Weber A. (1994) *Crop production and crop protection. Estimated losses in major food and cash crops.* Elsevier Science: Amsterdam

Ometto A.R, Hauschild M.Z, Roma W.N.L. (2009) *Lifecycle assessment of fuel ethanol from sugarcane in Brazil*. The International Journal of Life Cycle Assessments, 14 (3): 236 − 247.

PAN Germany (2002) *From law to field – Wheat study: Obstacles and the Potential for Pesticide Reduction.* [Mücke M.] Second edition. Pesticide Action Network Germany: Hamburg

PAN North America (n.d) *Atrazine*. [online] Available at: http://www.panna.org/resources/specific-pesticides/atrazine [Accessed 2013-03-22] Pesticide Action Network North America: Oakland

PAN Pesticide Database (2010) Pesticide Action Network Pesticide Database. [Kegley S.E, Hill B.R, Orme S, Choi A.H. (eds.)] [online] Available at: <http:www.pesticideinfo.org>

PAN UK (1998) *Chlorpyrifos*. [online] Available at: http://www.pan-uk.org/pestnews/Actives/chlorpyr.htm [Accessed 2013-04-10] Pesticide Action Network United Kingdom: London

Payet J. (2004) *Assessing toxic impacts on aquatic ecosystems in life cycle assessment (LCA).* Ecole Polytechnique Fédérale de Lausanne: Lausanne. PhD thesis. Available upon request to the author by email: jerome.payet@cycleco.eu.

PIC (2012) Paraquat Information Center, on behalf of Syngenta Crop Protection AG. [online] Available at: <www.paraquat.com> [Accessed 2012-11-25]

Pires A. Schechtman R. (2010) *International biofuel policies*. In: *Ethanol and Bioelectricity: Sugarcane in the Future of the Energy Matrix.* [de Sousa E.L.L, Macedo I.C. (coordination and organisation)] São Paulo Sugar Cane Agroindustry Union (UNICA): São Paulo

PPDB (2009) *The PPDB – Background and support information.* [online] Available at: <http://sitem.herts.ac.uk/aeru/footprint/en/index.htm> [Accessed 2013-03-12] Agriculture & Environment Research Unit (AERU), University of Hertfordshire, Herts.

PPDB (2013) The Pesticide Properties DataBase (PPDB). [online] Available at: <http://sitem.herts.ac.uk/aeru/footprint/en/index.htm> [Accessed 2013-03-12] Agriculture & Environment Research Unit (AERU), University of Hertfordshire, Herts

Ramstedt M. (1999) *Bladrost – det allvarligaste sjukdomsproblemet för Salix*. Växtskyddsnotiser 63: 27 − 32. SLU, Swedish University of Agricultural Sciences: Uppsala

Rosenbaum R.K, Bachmann T.M, Gold L.S, Huijbregts M.A.J, Jolliet O, Juraske R, Koehler A, Larsen H.F, MacLeod M, Margni M, McKone T.E, Payet J, Schumacher M, Van de Meent D, Hauschild M,Z. (2008) *USEtox – the UNEP-SETAC toxicity model: recommended characterization factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment*. The International Journal of Life Cycle Assessment, 13 (7): 532 − 546.

Rundlöf M, Lundin O, Bommarco R. (2012) *Växtskyddsmedlens påverkan på biologisk mångfald i jordbrukslandskapet*. The Center for Chemical Pesticides (CKB report 2012:2). SLU, Swedish University of Agricultural Sciences: Uppsala

Sala S, Marinov D, Pennington D. (2011) S*patial differentiation of chemical removal rates from air in life cycle impact assessment.* The International Journal of Life Cycle Assessment, 16 (8): 748 − 760.

SalixEnergi Europa (n.d.) *Att odla energiskog* [online] Available at: <http://www.salixenergi.se/uploads/Broschyr_SEE.pdf> [Accessed 2012-11-19] SalixEnergi Europa: Svalöv

Sattler C, Kächele H, Verch G. (2006) *Assessing the intensity of pesticide use in agriculture*. Agriculture, Ecosystems and Environment, 119 (3-4): 299 − 304.

SCB and KemI (2012) *Växtskyddsmedel i jordbruket 2011, beräknat antal hektardoser*. Statistics Sweden: Stockholm and Örebro and The Swedish Chemicals Agency: Sundbyberg

Schmidt J.H. (2007) *Life cycle assessment of rapeseed oil and palm oil*. PhD thesis. Aalborg University.

SEAB (2012) Information about registered pesticides in the state of Paraná, Brazil. [online] Available at: <http://www.agricultura.pr.gov.br/arquivos/File/defis/DFI/Bulas/> [Accessed 2013-03-24] Secretariat of Agriculture and Supply: Curitiba [In Portugese]

Sharma S.D, Singh, M. (2001) *Surfactants Increase Toxicity of Glyphosate and 2,4-D to Brazil Pusley*. Hort Science, 36 (4): 726-728.

Sheil D, Casson A, Meijaard E, Van Nordwijk M, Gaskell J, Sunderland-Groves J, Wertz K Kanninen M. (2009) *The impacts and opportunities of oil palm in Southeast Asia: What do we know and what do we need to know?* Center for International Forestry Research, CIFOR (Occasional paper no 51): Bogor Barat

SJV (2006) *Marknadsöversikt, Biodiesel – ett fordonsbränsle på frammarsch?* [Johnsson B, Lagerkvist Tolke C.] SJV, The Swedish Board of Agriculture (Report 2006:21): Jönköping

SJV (2011) *Förnybara drivmedel från jordbruket – etanol, biodiesel, biogas*. [Lagerkvist Tolke C, Einarson E, Eklöf, P.] SJV, The Swedish Board of Agriculture (Report 2011:14): Jönköping

SJV (2012) *Handbok för Salixodlare*. [Hollsten R, Arkelöf O, Ingelman G.] SJV, The Swedish Board of Agriculture: Jönköping

SJV and KemI (2002) *Förslag till handlingsprogram för användningen av bekämpningsmedel i jordbruket och trädgårdsnäringen till år 2006*. [Emmerman A, Franzén M, Sundgren A, Bergqvist P.] SJV, The Swedish Board of Agriculture (Report 2002:7): Jönköping and KemI, The Swedish Chemicals Agency: Sundbyberg

SJV, LRF and HIR (20--) *Resistens*. [online] Available at: <http://www.jordbruksverket.se/download/18.84b1402123cbbb742680009932/> [Accessed 2013-05-08]

SRC (2013) The Physical Properties Database (PHYSPROP). [online] Available at: http://www.srcinc.com/what-we-do/product.aspx?id=133 [Accessed 2013-05-03] Syracuse Research Centre

Soyatech (n.d) *Soybean and oilseed facts.* [online] Available at: <http://www.soyatech.com/soy_oilseed_facts.htm> [Accessed 2013-05-03]

Soy Stats (2012) *World statistics.* [online] Available at: <http://www.soystats.com/2012/Default-frames.htm> [Accessed 2012-11-24] The American Soybean Association

Syngenta (2009) *Our commitment to soybean.* [online] Available at: <http://www.syngenta.com/global/corporate/SiteCollectionDocuments/pdf/publications/products/20090724-en-our-commitment-to-soybean.pdf> [Accessed 2012-11-24]

Thompson H.M (1996) *Interactions between pesticides; a review of reported effects and their implications for wildlife risk assessment*. Ecotoxicology, 5 (2): 59 – 81.

Tu M, Hurd C, Randall J.M and The Nature Conservancy (2001) *2,4-D.* In: *Weed Control Methods Handbook: Tools & Techniques for Use in Natural Areas.* All U.S. Government Documents (Utah Regional Depository) (Paper 533). The Nature Conservancy: Arlington

UM Extension (2008) *Bt Corn & European Corn Borer - Long-Term Success Through Resistance Management.* [online] Available at: http://www.extension.umn.edu/ distribution/cropsystems/dc7055.html#ch11 [Accessed 2013-03-15] University of Minnesota Extension: St. Paul

UNICA (2007) *Sugar Cane's Energy – Twelve studies on Brazilian sugarcane agribusiness and its sustainability*. Second edition. [Macedo I.C. (organiser)] São Paulo Sugar Cane Agroindustry Union (UNICA): São Paulo

USDA (2009) *Pesticide Data Program - Annual Summary, Calendar Year 2008*. Agricultural Marketing Service, United States Department of Agriculture: Washington

USDA NASS (2011) *Agricultural chemical use: Corn, upland cotton and fall potatoes 2010*. United States Department of Agriculture National Agricultural Statistics Service: Washington

USDA NASS (2012) United States Department of Agriculture National Agricultural Statistics Service Quick Stats Database. [online] Available at: <http://quickstats.nass.usda.gov/>

USEPA (2002) *Chlorpyrifos facts.* [online] Available at: http://www.epa.gov/oppsrrd1/ REDs/factsheets/chlorpyrifos_fs.htm [Accessed 2013-04-10] United States Environmental Protection Agency: Washington

USEPA (2007) *Renewable Fuel Standard (RFS).* [online] Available at: <http://www.epa.gov/ otaq/fuels/renewablefuels/index.htm> Office of Transportation and Air Quality, United States Environmental Protection Agency: Washington

USEPA (2011) *Pesticides Industry Sales and Usage - 2006 and 2007 Market Estimates.* [Grube A, Donaldson D, Kiely T, Wu L.] Biological and Economic Analysis Division, Office of Pesticide Programs, United States Environmental Protection Agency: Washington

USEPA (2012) Estimation Programs Interface EPISuite^{TM}. Download setup file available at: http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm. [Accessed 2013-02-13]

USEPA (2013) ECOTOXicology (ECOTOX) Database Version 4.0. [online] Available at: <http:/www.epa.gov/ecotox/> United States Environmental Protection Agency: Washington

Van Zelm R, Huijbregts M.A.J, Van de Meent D. (2009) *USES-LCA 2.0−a global nested multimedia fate, exposure, and effects model.* International Journal of Life Cycle Assessment, 14 (3): 282–284.

Van Zelm R, Huijbregts M.A.J, Van de Meent D. (2010) *Transformation products in the life cycle impact assessment of chemicals*. Environmental Science and Technology, 44 (33): 1004 – 1009.

Van Zelm R, Larrey-Lassalle P, Roux P. (2012) *Bridging the gap between Life Cycle Inventory and Impact Assessment for toxicological assessments of pesticides used in crop production*. The International Journal of Life Cycle Assessment. (Submitted October 2012)

Volk T.A, Verwijst T, Tharakan P.J, Abrahamson L.P, White E.H. (2004) *Growing fuel: a sustainability assessment of willow biomass crops.* Frontiers in Ecology and the Environment, 2 (8): 411 – 418.

Wegener Sleeswijk, A. (2006) *GLOBOX–A spatially differentiated multimedia fate and exposure model*. The International Journal of Life Cycle Assessment 11 (2): 141.

Weidow B. (2008) *Växtodlingens grunder*. Natur & Kultur: Helsingborg

Weiss E.A. (1983) *Oilseed crops*. Tropical agriculture series. Longman Group Ltd: London

Wenzel H, Hauschild M, Alting L. (1997) *Environmental Assessment of Products, Vol.1: Methodology, Tools and Case Studies in Product Development*. Institute of Product Development. Kluwer Academic Publishers: Hingham.

Wivstad M. (2010) *Klimatförändringarna – en utmaning för jordbruket och Giftfri miljö*. The Swedish Chemicals Agency: Sundbyberg

WHO (2010) *The WHO recommended classification of pesticides by hazard and guidelines to classification 2009.* World Health Organisation: Geneva

Åkerblom N. (2004) *Agricultural pesticide toxicity to aquatic organisms – a literature review*. SLU, Swedish University of Agricultural Sciences (Report 2004:16): Uppsala

Personal communication

Beckman, Börje	Lantmännen Agroetanol, Sweden
Björkman, Christer	Swedish University of Agricultural Sciences, Sweden
Cederberg, Christel	The Swedish Institute for Food and Biotechnology and Chalmers
Dijkman, Teunis	PestLCI team member and PhD-student, Technical University of Denmark
Egeskog, Andrea	PhD student, Chalmers University of Technology
Ertl, David	Iowa Corn Promotion Board, USA
Fantke, Peter	USEtox manager, Technical University of Denmark (DTU), Denmark
Huijbregts, Mark	member of USEtox team, Department of Environmental Science, Radboud University Nijmegen, The Netherlands
Gerlach, Erik	USDA NASS, USA
Meyer, Daniel	Round Table on Responsible Soy Association, Brazil
Ramstedt, Mauritz	Swedish University of Agricultural Sciences, Sweden
Yngvesson, Nils	Hushållningssällskapet Malmöhus, Sweden
Van Zelm, Rosalie	Department of Environmental Science, Radboud University Nijmegen, The Netherlands
Wallman, Magdalena	The Swedish Institute for Food and Biotechnology, Sweden
Wintersen, Arjen	National Institute for Public Health and the Environment, RIVM, the Netherlands
Åsheim, Per	SalixEnergi Europa, Sweden

APPENDICES

Appendix I. All pesticide active substances covered in this thesis

	CAS	Common name of active substance	Type of pesticide	Chemical class
1	52315-07-8	(Zeta)-cypermethrin	Insecticide	Pyrethroid
2	94-75-7	2,4-D[1]	Herbicide	Alkylchlorophenoxy
3	67375-30-8	Alpha-cypermethrin	Insecticide	Pyrethroid
4	834-12-8	Ametryn	Herbicide	Triazine
5	1912-24-9	Atrazine	Herbicide	Triazine
6	188425-85-6	Boscalid	Fungicide	Anilide
7	90982-32-4	Chlorimuron-ethyl	Herbicide	Sulfonylurea
8	2921-88-2	Chlorpyrifos	Insecticide	Organophosphate
9	99129-21-2	Clethodim	Herbicide	Cyclohexanedione
10	101205-02-1	Cycloxydim	Herbicide	Cyclohexanedione
11	83164-33-4	Diflufenican	Herbicide	Anilide
12	133855-98-8	Epoxiconazole	Fungicide	Triazole
13	66230-04-4	Esfenvalerate	Insecticide	Pyrethroid
14	67564-91-4	Fenpropimorph	Fungicide	Morpholine
15	120068-37-3	Fipronil	Insecticide	Pyrazole
16	145701-23-1	Florasulam	Herbicide	Triazolopyrimidine
17	272451-65-7	Flubendiamide	Insecticide	Anthranilic diamide
18	81406-37-3	Fluroxypyr-meptyl[2]	Herbicide	Pyridinecarboxylic acid
19	96525-23-4	Flurtamone	Herbicide	Unclassified
20	1071-83-6	Glyphosate	Herbicide	Phosphonoglycine
21	81335-77-5	Imazethapyr	Herbicide	Imidazolinone
22	77501-63-4	Lactofen	Herbicide	Diphenyl ether
23	67129-08-2	Metazachlor	Herbicide	Chloroacetanilide
24	21087-64-9	Metribuzin	Herbicide	Triazinone
25	4685-14-7	Paraquat	Herbicide	Bipyridylium
26	60207-90-1	Propiconazole	Fungicide	Azole
27	52888-80-9	Prosulfocarb	Herbicide	Thiocarbamate
28	178928-70-6	Prothioconazole	Fungicide	Azole
29	175013-18-0	Pyraclostrobin	Fungicide	Strobin
30	90717-03-6	Quinmerac	Herbicide	Quinoline
31	83121-18-0	Teflubenzuron	Insecticide	Benzoylurea
32	111988-49-9	Thiacloprid	Insecticide	Neonicotinoid
33	153719-23-4	Thiamethoxam	Insecticide	Neonicotinoid
34	101200-48-0	Tribenuron-methyl	Herbicide	Sulfonylurea
35	141517-21-7	Trifloxystrobin	Fungicide	Strobin

1) Full name: 2,4-dichlorophenoxy acetic acid
2) Also called: fluroxypyr 1-methylheptyl ester

Appendix II. Pesticide application scenarios for all crops and cases

Maize

Active substance	Frequency [1/yr]	Dose per application [kgAS/ha]	Yearly average [gAS/ha·yr]	Crop type and development stage	Application method	Application time	Comment
Atrazine	1	1.0090	1009	Bare soil – pre-emergence	Conv. boom bare soil	March	Applied pre-plant.
Glyphosate	1	1.5490	1549	Maize II	Conv. boom sugar beet[1]	June	Applied when plants are ~ 50 cm tall
			Tot H: 2558				
Chlorpyrifos	1	0.1870	187	Maize III	Pest LCI Aircraft	July	Applied at time of tasslling, in the insecticide case
			Tot I: 187				

1) The IMAG conventional boom sugar beet was chosen as application method since the wind drift curve for this application method has been derived for sugar beet crops at an average height of 50 cm (Dijkman, pers. com. 2013).

Rapeseed

Product name	Active substance	Dose product [l/ha or g/ha]	AS content [gAS/l] or [gAS/g]	Frequency [1/yr]	Dose per application [kgAS/ha]	Yearly average [gAS/ha·yr]	Crop type and development stage	Application method	Application time
RoundUp Bio[1]	Glyphosate	6.75	360	0.25	2.4300	607.5	Bare soil – pre-emergence	Conv. boom bare soil	Aug.
Butisan Top	Metazachlor	3	375	1	1.1250	1125	Bare soil – pre-emergence	Conv. boom bare soil	Aug.
	Quinmerac	3	125	1	0.3750	375	Bare soil – pre-emergence	Conv. boom bare soil	Aug.
Focus Ultra[2]	Cycloxydim	2.25	100	1	0.2250	225	Oilseed rape I	Conv. boom cereals	Sept.
						Tot H: 2333			
Cantus[3]	Boscalid	1000	0.5	0.3	0.500	150	Oilseed rape III	Conv. boom cereals	May
						Tot F: 150			
Fastac 50[4]	Alpha-cypermethrin	0.25	50	0.45	0.0125	5.625	Oilseed rape I	Conv. boom cereals	Sept.
Biscaya OD 240[5]	Thiacloprid	0.3	240	0.67	0.0720	48	Oilseed rape II	Conv. boom cereals	April
						Tot I: 54			

1) Applied on average every fourth year against couch grass.
2) Against voluntary cereals from previous season.
3) Applied to on average 30% of fields every year against fungal diseases.
4) Against flea beetles, three years of five in three quarters of a full dose.
5) Against pollen beetles, two years of three.

Salix									
Product Name	**Active substance**	**Dose product [l/ha or g/ha]**	**AS content [gAS/l] or [gAS/g]**	**Frequency [1/yr]**	**Dose per application [kgAS/ha]**	**Yearly average [gAS/ha·yr]**	**Crop type and development stage**	**Application method**	**Application time**
Roundup Bio[1]	Glyphosate	4.50	360	0.048	1.620	77.14	Bare soil – pre-emergence	Conv. boom bare soil	Oct.
Bacara[2]	Flurtamone	1.25	250	0.33	0.3125	104.2	Bare soil – pre-emergence	Conv. boom bare soil	April
	Diflufenican	1.25	100	0.33	0.1250	41.67	Bare soil – pre-emergence	Conv. boom bare soil	April
						Tot H: 223			

1) Applied once before field establishment.
2) Applied once prior to planting and subsequently after every harvest.

Soybean										
Application ID	**Product name**	**Active substance**	**Dose product [l/ha or g/ha]**	**AS content [gAS/l] or [gAS/g]**	**Frequency [1/yr]**	**Dose per application [kgAS/ha]**	**Yearly average [gAS/ha·yr]**	**Crop type and development stage**	**Application method**	**Application time**
CASE: GM soy										
H 1	Gromoxone[1]	Paraquat	1.5	200	1	0.300	300	Bare soil – pre-emergence	Conv. boom bare soil	Sep.
H 2	RoundUp Original[2]	Glyphosate	2.5	360	1	0.900	900	Soybean I	Conv. boom cereals	Oct.
H 3	RoundUp Original[3]	Glyphosate	2.5	360	1	0.900	900	Soybean I	Conv. boom cereals	Oct.
H 4	Gromoxone[4]	Paraquat	1.5	200	1	0.300	300	Soybean III	Conv. boom cereals	Feb.
CASE: conventional soy				**Tot H case GM soy: 2400**						
H 1	Gromoxone[5]	Paraquat	1.5	200	1	0.300	300	Bare soil – pre-emergence	Conv. boom bare soil	Sept.
H 2	Several[6]	Lactofen	0.5	240	1	0.1200	120	Soybean I	Conv. boom cereals	Oct.
	Several	Chlorimuron-ethyl	50	0.25	1	0.0125	12.5	Soybean I	Conv. boom cereals	Oct.
	Several	Imazethapyr	0.3	100	1	0.0300	30	Soybean I	Conv. boom cereals	Oct.
H 3	Select[7]	Clethodim	0.3	240	1	0.0720	72	Soybean I	Conv. boom cereals	Oct.
H 4	Select[8]	Clethodim	0.3	240	1	0.0720	72	Soybean I	Conv. boom cereals	Nov.
H 5	Gromoxone[4]	Paraquat	1.5	200	1	0.300	300	Soybean III	Conv. boom cereals	Feb.
Fungicides same in both cases			**Tot H case conventional soy: 907**							
F 1	Fox[9]	Prothio-conazole	0.15	175	1	0.02625	26.3	Soybean I	Conv. boom cereals	Nov.
		Trifloxy-strobin	0.15	150	1	0.0225	22.5	Soybean I	Conv. boom cereals	Nov.
F 2	Opera[10]	Epoxiconazole	0.5	50	1	0.0250	25	Soybean II	Conv. boom cereals	Nov.
		Pyraclostro-bin	0.5	133	1	0.06650	66.5	Soybean II	Conv. boom cereals	Nov.

F 3	Fox[11]	Prothio-conazole	0.3	175	1	0.0525	52.5	Soybean II	Conv. boom cereals	Dec.
		Trifloxy-strobin	0.3	150	1	0.0450	45	Soybean II	Conv. boom cereals	Dec.
F 4	Opera[12]	Epoxiconazole	0.3	50	1	0.0150	15	Soybean III	Conv. boom cereals	Jan.
		Pyraclostro-bin	0.3	133	1	0.03990	39.9	Soybean III	Conv. boom cereals	Jan.
Insecticides same in both cases				**Tot F both cases: 293**						
I 1	Belt[13]	Fluben-diamide	0.075	480	1	0.0360	36	Soybean I	Conv. boom cereals	Oct.
I 2	Premium[14]	Alpha-cypermethrin	0.07	100	1	0.0070	7	Soybean II	Conv. boom cereals	Nov.
	Nomolt	Teflu-benzuron	0.15	150	1	0.02250	22.5	Soybean II	Conv. boom cereals	Nov.
I 3	Fury[15]	Zeta-cypermethrin	0.15	400	1	0.0600	60	Soybean II	Conv. boom cereals	Dec.
	Belt	Fluben-diamide	0.1	480	1	0.0480	48	Soybean II	Conv. boom cereals	Dec.
				Tot I both cases: 174						

1) To clear the field from all vegetation prior to sowing
2) 15 days after sowing
3) 15 days after H 2
4) To kill the plant and enable harvest
5) To clear the field from all vegetation prior to sowing
6) 15 days after sowing
7) 15 days after H 2
8) 15 days after H 3
9) 40 days after sowing
10) 15 days after F 1
11) 20 days after F 2
12) 20 days after F 3
13) 15 days post-emergence
14) 30 days after I 1
15) 15 days after I 2

Sugarcane						
Active substance	**Frequency [1/yr]**	**Dose per application [kgAS/ha]**	**Yearly average [gAS/ha·yr]**	**Crop type and development stage**	**Application method**	**Application time**
Glyphosate	0.182	3.7620	684	Bare soil – pre-emergence	Conv. boom bare soil	Jan.
Ametryn	0.727	0.67375	490	Maize I[1]	Conv. boom cereals	Oct.
Atrazine	0.727	0.67925	494	Maize I	Conv. boom cereals	Oct.
2,4-D	0.727	0.51150	372	Maize I	Conv. boom cereals	Oct.
Metribuzin	0.727	0.440	320	Maize I	Conv. boom cereals	Oct.
		Tot H: 2360				
Fipronil	0.727	0.08594	62.5	Maize II	Conv. boom cereals	Nov.
Thiamethoxam	0.727	0.08594	62.5	Maize II	Conv. boom cereals	Nov.
		Tot I: 125				

1) Maize was chosen as the crop morphology in closest resemblance of sugarcane at time of application.

Wheat									
Product name	**Active substance**	**Dose product [l/ha or g/ha]**	**AS content [gAS/l] or [gAS/g]**	**Frequency [1/yr]**	**Dose per application [kgAS/ha]**	**Yearly average [gAS/ha·yr]**	**Crop type and development stage**	**Application method**	**Application time**
RoundUp Bio[1]	Glyphosate	6.75	360	0.25	2.4300	607.5	Bare soil – pre-emergence	Conv. boom bare soil	Sept.
Boxer	Prosulfocarb	2.25	800	1	1.800	1800	Cereals I	Conv. boom cereals	Oct.
Starane XL[2]	Florasulam	1.125	2.5	1	0.0028	2.8125	Cereals II	Conv. boom cereals	April
	Fluroxypyr-meptyl	1.125	144.1	1	0.16211	162.11	Cereals II	Conv. boom cereals	April
Express 50	Tribenuron methyl	11.25	0.5	1	0.00563	5.625	Cereals II	Conv. boom cereals	April
					Tot H: 2578				
Tilt Top 500 EC[3]	Fenpropimorph	1	375	0.5	0.3750	187.5	Cereals III	Conv. boom cereals	May
	Propiconazole	1	125	0.5	0.1250	62.5	Cereals III	Conv. boom cereals	May
Proline EC 250[4]	Prothioconazole	1	250	1	0.2500	250	Cereals III	Conv. boom cereals	June
					Tot F: 500				
Sumi-Alpha 5 FW	Esfenvalerate	0.25	50	1	0.0125	12.5	Cereals III	Conv. boom cereals	June
					Tot I: 13				

1) Applied on average every fourth year against couch grass
2) Starane XL applied in mix with Express.
3) Tilt top applied before inflorescence against yellow rust.
4) Proline applied in mix with Sumi-alpha.

<u>Keys to crop development stage</u>
Maize I - leaf development
Maize II – stem elongation
Maize III – inflorescence emergence / flowering
Oilseed rape I - leaf development
Oilseed rape II – side shoot formation / stem elongation
Oilseed rape III - inflorescence emergence / ripening
Soybean I – leaf / harvestable plant parts development
Soybean II – side shoot and harvestable part development
Soybean III - inflorescence emergence / senescence
Cereals I – leaf development
Cereals II - tillering
Cereals III – stem elongation

Appendix III. Physical-chemical data used in PestLCI

Property (unit)	Florasulam	Fluroxypyr-meptyl	Prothio-conazole	Quinmerac	Cycloxydim
Molecular weight (g/mol)	3.59E+02	3.67E+02	3.44E+02	2.22E+02	3.25E+02
Solubility in water (g/l)	6.36E+00	1.36E-04	3.00E-01	1.07E+02	5.30E-02
Ref. temp solubility (^oC)	2.00E+01	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Vapour pressure (Pa)	1.00E-05	1.00E-05	4.00E-07	1.00E-10	1.00E-05
Ref. temp vapour pressure (^oC)	2.50E+01	2.50E+01	2.50E+01	2.50E+01	2.50E+01
pKa (-)	4.54E+00	Not applicable	6.90E+00	4.31E+00	4.17E+00
Log Kow (-)	-1.22E+00	5.04E+00	3.82E+00	-1.41E+00	1.36E+00
Koc (l/kg)	2.20E+01	2.46E+04	1.77E+03	8.60E+01	5.90E+01
Soil $t_{½}$ (days)	8.50E+00	1.00E+00	5.00E-01	3.00E+01	6.50E-01
Ref. temp. biodegradation (^oC)	2.00E+01	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Atmospheric OH rate (cm^3/molecules/sec)	6.27E-12	3.68E-11	1.13E-10	4.37E-12	1.42E-10
Atmospheric OH rate ref. temp (^oC)	2.50E+01	2.50E+01	2.50E+01	2.50E+01	2.50E+01

Property (unit)	Boscalid	Flurtamone	Ametryn	Fipronil	Lactofen
Molecular weight (g/mol)	3.43E+02	3.33E+02	2.27E+02	4.37E+02	4.62E+02
Solubility in water (g/l)	4.60E-03	1.07E-02	2.00E-01	3.78E-03	5.00E-04
Ref. temp solubility (^oC)	2.00E+01	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Vapour pressure (Pa)	7.20E-07	4.50E-07	3.65E-04	2.00E-06	9.30E-06
Ref. temp vapour pressure (^oC)	2.50E+01	2.50E+01	2.50E+01	2.50E+01	2.50E+01
pKa (-)	Not applicable	Not applicable	1.01E+01	Not applicable	Not applicable
Log Kow (-)	2.96E+00	3.20E+00	2.63E+00	3.75E+00	4.81E+00
Koc (l/kg)	1.23E+03	4.47E+03	3.16E+02	8.38E+02	1.00E+04
Soil $t_{½}$ (days)	2.00E+02	5.60E+01	3.70E+01	1.42E+02	4.00E+00
Ref. temp. biodegradation (^oC)	2.00E+01	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Atmospheric OH rate (cm^3/molecules/sec)	2.60E-11	8.92E-11	2.85E-11	9.61E-11	3.21E-12
Atmospheric OH rate ref. temp (^oC)	2.50E+01	2.50E+01	2.50E+01	2.50E+01	2.50E+01

Property (unit)	Imazethapyr	Clethodim	Pyraclostrobin	Flubendiamide
Molecular weight (g/mol)	2.89E+02	3.60E+02	3.88E+02	6.82E+02
Solubility in water (g/l)	1.40E+00	5.45E+00	1.90E-03	2.90E-05
Ref. temp solubility (^oC)	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Vapour pressure (Pa)	1.33E-05	2.08E-06	2.60E-08	5.51E-14
Ref. temp vapour pressure (^oC)	2.50E+01	2.50E+01	2.50E+01	2.50E+01
pKa (-)	2.10E+00	4.47E+00	Not applicable	Not applicable
Log Kow (-)	1.49E+00	4.14E+00	3.99E+00	4.20E+00
Koc (l/kg)	5.20E+01	1.50E+05	9.30E+03	2.20E+03
Soil $t_{½}$ (days)	9.00E+01	5.50E-01	3.20E+01	8.00E+00
Ref. temp. biodegradation (^oC)	2.00E+01	2.00E+01	2.00E+01	2.00E+01
Atmospheric OH rate (cm^3/molecules/sec)	1.59E-11	1.55E-10	2.06E-10	2.92E-11
Atmospheric OH rate ref. temp (^0C)	2.50E+01	2.50E+01	2.50E+01	2.50E+01

Appendix IV. Physical-chemical data used in USEtox

AS common name	MW (g/mole)	Kow (-)	Koc (l/kg)	K_H25C (Pa·m^3/mole)	Pvap25 (Pa)
Flurtamone	3.33E+02	5.75E+03	4.47E+03		5.05E-05
Thiacloprid	2.53E+02	2.14E+02	1.12E+03		1.51E-04
Boscalid	3.43E+02	9.12E+02	9.46E+03		9.19E-09
Florasulam	3.59E+02	1.35E+02	1.61E+02		5.77E-07
Prothioconazole	3.44E+02	4.07E+03	2.92E+03		4.45E-12
Glyphosate	1.69E+02	3.98E-04	1.00E+00	2.13E-07	1.31E-05
Diflufenican	3.94E+02	7.94E+04	2.43E+04	3.29E-02	4.24E-06
Quinmerac	2.22E+02	6.03E+00	4.70E+02		1.83E-05
Chlorpyrifos	3.51E+02	9.12E+04	5.01E+03	2.97E-01	2.71E-03
Thiamethoxam	2.92E+02	6.27E+00	2.66E+02		5.43E-05
Trifloxystrobin	4.08E+02	3.16E+04	3.04E+06		7.49E-06
Lactofen	4.62E+02	6.5E+04	1.00E+04	4.78E-02	9.33E-06
Chlorimuron-ethyl	4.15E+02	3.2E+02	1.10E+02	1.84E-10	5.33E-10
Epoxiconazole	3.30E+02	2.75E+03	2.27E+04		3.75E-05
Pyraclostrobin	3.88E+02	9.77E+03	4.79E+04		1.10E-07
Flubendiamide	6.82E+02	4.79E+04	1.60E+04		5.52E-14

AS common name	Sol25 (mg/l)	$kdeg_A$ (1/s)	$kdeg_W$ (1/s)	$kdeg_{Sd}$ (1/s)	$kdeg_{Sl}$ (1/s)
Flurtamone	4.87E+01	6.77E-06	1.30E-07	1.44E-08	6.50E-08
Thiacloprid	2.32E+02	6.70E-05	1.30E-07	1.44E-08	6.50E-08
Boscalid	2.02E+01	6.78E-06	1.30E-07	1.44E-08	6.50E-08
Florasulam	8.24E+01	4.70E-06	4.50E-08	5.00E-09	2.25E-08
Prothioconazole	5.53E+00	8.47E-05	4.50E-08	5.00E-09	2.25E-08
Glyphosate	1.05E+04	5.93E-05	5.30E-07	5.89E-08	2.65E-07
Diflufenican	5.00E-02	2.40E-06	4.50E-08	5.00E-09	2.25E-08
Quinmerac	2.23E+02	2.73E-06	2.10E-07	2.33E-08	1.05E-07
Chlorpyrifos	1.12E+00	6.88E-05	4.50E-08	5.00E-09	2.25E-08
Thiamethoxam	2.86E+03	1.87E-04	2.10E-07	2.33E-08	1.05E-07
Trifloxystrobin	3.90E-01	5.28E-06	1.30E-07	1.44E-08	6.50E-08
Lactofen	1.00E-01	2.40E-06	4.50E-08	5.00E-09	2.25E-08
Chlorimuron-ethyl	1.20E+03	3.20E-05	1.30E-07	1.44E-08	6.50E-08
Epoxiconazole	6.63E+00	6.58E-06	4.50E-08	5.00E-09	2.25E-08
Pyraclostrobin	1.43E+00	1.55E-04	1.30E-07	1.44E-08	6.50E-08
Flubendiamide	4.66E-03	2.19E-05	4.50E-08	5.00E-09	2.25E-08

Appendix V. Ecotoxicological effect data used for calculation of CFs

Florasulam						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna Gibba*	14	0.00118		AGRITOX	-2.928117993
Algae	*Skeletonema costatum*	5	43.1		AGRITOX	1.63447727
Algae	*Navicula pelliculosa*	5	1.38		AGRITOX	0.139879086
Algae	*Pseudokirchneriella subcapitata*	3	0.00894		AGRITOX	-2.048662481
Algae	*Anabaena flos-aquae*	5	0.363		AGRITOX	-0.440093375
Aquatic invertebrate	*Daphnia magna*	2	146	292	AGRITOX	2.164352856
Aquatic invertebrate	*Palaemonetes pugio*	4	60	120	AGRITOX	1.77815125
Aquatic invertebrate	*Crassostrea virginica*	4	62.5	125	AGRITOX	1.795880017
						***AvlogEC50* = 0.261983329**

Diflufenican						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plants	*Lemna gibba, 2 tests*	14	0.04673		AGRITOX	-1.330373683
Algae	*Scenedesmus subspicatus, 4 tests*	3	0.00106		AGRITOX	-2.974134594
Aquatic invertebrate	*Daphnia magna*	2	0.12	0.24	AGRITOX	-0.920818754
						***AvlogEC50* = -1.741775677**

Flubendiamide						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna Gibba*	7	0.0273	0.0546	PPDB	-1.563837353
Aquatic invertebrate	*Daphnia magna*	2	0.0274	0.0548	PPDB	-1.562249437
Algae	*Unspecified*	3	0.03465	0.0693	PPDB	-1.460296761
						***AvlogEC50* = -1.528794517**

Boscalid						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Algae	*Pseudokirchneriella subcapitata*	3	1.875	3.75	PPDB	0.273001272
Algae	*Pseudokirchneriella subcapitata*	4	1.34		AGRITOX and [1]	0.127104798
Aquatic invertebrate	*Daphnia magna*	2	2.665	5.33	AGRITOX	0.425697213
Fish	*Unspecified*	n.a	1.35	2.7	[1]	0.130333768
						***AvlogEC50* = 0,239034263**

Thiamethoxam						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Algae	*Pseudokirchneriella subcapitata*	3	81.8		AGRITOX	1.912753304
Algae	*Pseudokirchneriella subcapitata*	4	100		AGRITOX	2
Aquatic plant	*Lemna gibba*	7	45	90	PPDB	1.653212514
Aquatic invertebrate	*Crassostrea virginica*	4	59.5	119	AGRITOX	1.774516966
Aquatic invertebrate	*Daphnia magna*	2	50	100	AGRITOX	1.698970004
Aquatic invertebrate	*Daphnia pulex*	1	50	100	AGRITOX	1.698970004
Aquatic invertebrate	*Thamnocephalus platyurus*	1	50	100	AGRITOX	1.698970004
Aquatic invertebrate	*Mysidopsis bahia*	4	3.45	6.9	AGRITOX	0.537819095
Aquatic invertebrate	*Gammarus sp*	2	1.4	2.8	AGRITOX	0.146128036
Aquatic invertebrate	*Asellus aquaticus*	2	0.16	0.32	AGRITOX	-0.795880017
Aquatic invertebrate	*Ostracoda*	2	0.09	0.18	AGRITOX	-1.045757491
Aquatic invertebrate	*Lymnea stagnalis*	2	50	100	AGRITOX	1.698970004
Aquatic invertebrate	*Radix peregra*	2	50	100	AGRITOX	1.698970004
Aquatic invertebrate	*Chaoborus crystallinus*	2	3.65	7.3	AGRITOX	0.562292864
Aquatic invertebrate	*Crangonyx pseudogracillis, 2 tests*	2	0.395537	0.791075	AGRITOX	-0.402812216
Aquatic invertebrate	*Lymnea stagnalis*	2	50	100	AGRITOX	1.698970004
Aquatic invertebrate	*Chironomus riparius, 3 tests*	2	0.024089	0.048177	AGRITOX	-1.618183693
Aquatic invertebrate	*Dyticidae, 2 tests*	2	0.028474	0.056947	AGRITOX	-1.545556521
Aquatic invertebrate	*Cloeon dipterum, 2 tests*	2	0.015199	0.030397	AGRITOX	-1.81819401
Aquatic invertebrate	*Brachionus calyciflorus*	1	50	100	AGRITOX	1.698970004
						***AvlogEC50* = 0.662656443**

Epoxiconazole						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna gibba, 3 tests*	7	0.00470	0.00940	AGRITOX/ PPDB	-2.32787147
Aquatic invertebrate	*Daphnia magna*	2	4.345	8.69	PPDB	0.637989781
Algae	*Pseudokirchneriella subcapitata, 2 tests*	3	1.7248188	3.449637	AGRITOX/ PPDB	0.236743485
Aquatic invertebrate	*Chironomus riparius*	28	0.0625		AGRITOX	-1.204119983
Aquatic invertebrate	*Daphnia magna*	21	0.63		AGRITOX	-0.200659451
						***AvlogEC50* = -0.571583527**

Prothioconazole						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna gibba*	7	0.037	0.074	PPDB	-1.431798276
Algae	*Pseudokirchneriella subcapitata, 2 tests*	3	0.774274	1.548548	PPDB and [2]	-0.111105406
Aquatic invertebrate	*Daphnia magna*	2	0.65	1.3	AGRITOX	-0.187086643
Algae	*Cyprinus carpio*	4	0.88		[3]	-0.055517328
						AvlogEC50 **= -0.446376913**

Thiacloprid						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna gibba*	15	95.4		AGRITOX	1.979548375
Algae	*Scenedesmus subspicatus*	3	44.7		AGRITOX	1.650307523
Algae	*Pseudokirchneriella subcapitata*	5	60.6		AGRITOX	1.782472624
Aquatic invertebrate	*Daphnia magna*	2	42.55	85.1	AGRITOX	1.628899564
Aquatic invertebrate	*Hyalella azteca*	4	0.02035	0.0407	AGRITOX	-1.691435586
Freshwater Insect	*Cheumatopsyche brevilineata*	2	0.002635	0.00527	ECOTOX	-2.57921938
						AvlogEC50 **= 0.461762187**

Lactofen						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic invertebrate	*Daphnia magna, 3 tests*	2	0.795811	1.591623	PPDB/ ECOTOX	-0.099189821
Aquatic plant	*Skeletonema costatum*	n.a	0.000495	0.00099	[4]	-3.305394801
						AvlogEC50 **= -1.702292311**

Chlorimuron-ethyl						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna gibba*	7	0.000225	0.00045	PPDB	-3.647817482
Aquatic invertebrate	*Daphnia magna*	2	50	100	PPDB /ECOTOX	1.698970004
Algae	*Chlorella pyrenoidosa*	4	15.308		ECOTOX	1.184918454
Algae	*Scenedesmus acutus*	4	11.832		ECOTOX	1.073058161
Algae	*Scenedesmus quadricauda*	4	0.1		ECOTOX	-1
Algae	*Chlorella vulgaris*	4	19.236		ECOTOX	1.284114768
Algae	*Pseudokirchneriella subcapitata*	4	5.5348		ECOTOX	0.743101932
						AvlogEC50 **= 0.190906548**

Quinmerac						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plants	*Lemna gibba*	7	48	96	PPDB	1.681241237
Algae	*Chlorella fusca*	3	24.25	48.5	PPDB	1.384711743
Aquatic invertebrate	*Daphnia magna*	2	74.35	148.7	AGRITOX	1.871280973
						AvlogEC50 **= 1.645744651**

Pyraclostrobin						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna gibba*	7	0.86	1.72	PPDB	-0.065501549
Aquatic invertebrate	*Daphnia magna*	2	0.00785	0.0157	AGRITOX	-2.105130343
Algea	*Pseudokirchneriella subcapitata*	3	0.4215	0.843	PPDB	-0.375202421
Algea	*Pseudokirchneriella subcapitata*	4	0.152		AGRITOX	-0.818156412
Molluscs	*Lampsilis siliquoidea*	4	0.015	0.03	ECOTOX	-1.823908741
Molluscs	*Lampsilis siliquoidea*	1	0.24	0.48	ECOTOX	-0.619788758
Molluscs	*Lampsilis siliquoidea*	2	0.04	0.08	ECOTOX	-1.397940009
						AvlogEC50 **= -1.029375462**

Flurtamone						
Group of organism	**Species**	**Days**	**EC50 chronic [mg/l]**	**EC50 acute [mg/l]**	**Source**	**Log of chronic EC50**
Aquatic plant	*Lemna gibba*	14	0.0099		AGRITOX	-2.004364805
Algea	*Raphidocelis subcapitata*	3	0.01	0.02	AGRITOX/ PPDB	-2
Aquatic invertebrate	*Daphnia magna*	2	6.5	13	AGRITOX	0.812913357
						AvlogEC50 **= -1.06381715**

AvlogEC50**s from Payet (2004)**	
Active substance	***AvlogEC50***
Trifloxystrobin	-1.22
Chlorpyrifos	-1.99
Glyphosate	1.466

Additional sources:
[1] http://ec.europa.eu/food/plant/protection/evaluation/newactive/boscalid.pdf
[2] http://www.bayercropscience.co.uk/assets/Uploads/Redigo_Twin.pdf
[3] http://www.lookchem.com/msds/2011-06%2f1%2f34232(178928-70-6).pdf
[4] http://www.epa.gov/oppsrrd1/registration_review/lactofen/lactofen_summary.pdf

Appendix VI. Soil data for regionalisation of PestLCI

Soil parameter	Value	Soil parameter	Value
start layer 1 (m)	0	f(silt) layer 6	-
start layer 2 (m)	0.2	f(sand) layer 6	-
start layer 3 (m)	0.33	f(clay) layer 7	-
start layer 4 (m)	0.53	f(silt) layer 7	-
start layer 5 (m)	0.76	f(sand) layer 7	-
start layer 6 (m)	1	f(clay) layer 8	-
start layer 7 (m)	-	f(silt) layer 8	-
start layer 8 (m)	-	f(sand) layer 8	-
start layer 9 (m)	-	f(clay) layer 9	-
start layer 10 (m)	-	f(silt) layer 9	-
end layer 10 (m)	-	f(sand) layer 9	-
pH layer 1	6.1	f(clay) layer 10	-
pH layer 2	6.4	f(silt) layer 10	-
pH layer 3	6.2	f(sand) layer 10	-
pH layer 4	6	f(OC) layer 1 (%)	2.32
pH layer 5	6.1	f(OC) layer 2 (%)	1.32
pH layer 6	-	f(OC) layer 3 (%)	0.79
pH layer 7	-	f(OC) layer 4 (%)	0.40
pH layer 8	-	f(OC) layer 5 (%)	0.23
pH layer 9	-	f(OC) layer 6 (%)	-
pH layer 10	-	f(OC) layer 7 (%)	-
f(clay) layer 1	0.31	f(OC) layer 8 (%)	-
f(silt) layer 1	0.66	f(OC) layer 9 (%)	-
f(sand) layer 1	0.03	f(OC) layer 10 (%)	-
f(clay) layer 2	0.34	Soil bulk density	n.a
f(silt) layer 2	0.63	Name layer 1	Ap
f(sand) layer 2	0.03	Name layer 2	Bt1
f(clay) layer 3	0.33	Name layer 3	Bt2
f(silt) layer 3	0.63	Name layer 4	Bt3
f(sand) layer 3	0.04	Name layer 5	Bt4
f(clay) layer 4	0.31	Name layer 6	-
f(silt) layer 4	0.65	Name layer 7	-
f(sand) layer 4	0.04	Name layer 8	-
f(clay) layer 5	0.27	Name layer 9	-
f(silt) layer 5	0.67	Name layer 10	-
f(sand) layer 5	0.06	Soil type	n.a
f(clay) layer 6	-		

Source to soil data: ISRIC-WISE Harmonized Global soil Profile Dataset v.3 (Batjes, 2008).

The WISE-3 soil sample ID is USO323, and the sample is located at latitude 42.21 N longitude 92.47 W, in Grundy County Iowa. The soil sample is classified as a “mollic hapludalf” according to the USDA soil taxanomy classification and represent a welldrained, rainfed arable culture land at a slope of 5%.

Appendix VII. Climate data for regionalisation of PestLCI

Location: Iowa City, USA
Station Id: Iowa City, Johnson County, CDC TD 9641 Clim 81.

Row no.	Climate parameter	Value	Row no.	Climate parameter	Value
3	Latitude	41.65° N	57	Total (mm)	922.6
4	Longitude	91.53° W	58	Rain days (>1mm) Jan	18.0
5	Elevation (m)	195	59	Rain days (>1mm) Feb	15.0
6	TG jan (degC)	-6.3	60	Rain days (>1mm) Mar	13.0
7	TG feb (degC)	-3.3	61	Rain days (>1mm) Apr	18.0
8	TG mar (degC)	3.4	62	Rain days (>1mm) May	17.0
9	TG apr (degC)	10.9	63	Rain days (>1mm) Jun	18.0
10	TG may (degC)	17.1	64	Rain days (>1mm) July	13.0
11	TG jun (degC)	22.2	65	Rain days (>1mm) Aug	16.0
12	TG jul (degC)	24.6	66	Rain days (>1mm) Sep	9.0
13	TG aug (degC)	23.1	67	Rain days (>1mm) Oct	12.0
14	TG sept (degC)	18.8	68	Rain days (>1mm) Nov	12.0
15	TG oct (degC)	12.5	69	Rain days (>1mm)	18.0
16	TG nov (degC)	4.6	70	Rain days (>1mm) Average	14.9
17	TG dec (degC)	-3.3	71	Average rainfall on rainy day Jan (mm)	1.4
18	TG average (degC)	10.4	72	Average rainfall on rainy day Feb (mm)	1.6
19	TMIN jan (degC)	-11.3	73	Average rainfall on rainy day Mar (mm)	4.6
20	TMIN feb (degC)	-8.6	74	Average rainfall on rainy day Apr (mm)	5.2
21	TMIN mar (degC)	-2.1	75	Average rainfall on rainy day May (mm)	6.0
22	TMIN apr (degC)	4.5	76	Average rainfall on rainy day Jun (mm)	6.4
23	TMIN may (degC)	10.5	77	Average rainfall on rainy day Jul (mm)	9.6
24	TMIN jun (degC)	15.7	78	Average rainfall on rainy day Aug (mm)	7.0
25	TMIN jul (degC)	18.3	79	Average rainfall on rainy day Sep (mm)	11.1
26	TMIN aug (degC)	16.8	80	Average rainfall on rainy day Oct (mm)	6.0
27	TMIN sept (degC)	12.4	81	Average rainfall on rainy day Nov (mm)	4.5
28	TMIN oct (degC)	6.0	82	Average rainfall on rainy day Dec (mm)	2.2
29	TMIN nov (degC)	-0.4	83	Average rainfall on rainy day Average (mm)	5.5
30	TMIN dec (degC)	-7.9	84	Rain frequency Jan (day^{-1})	1.7
31	TMIN average (degC)	4.5	85	Rain frequency Feb (day^{-1})	1.9
32	TMAX jan (degC)	-1.2	86	Rain frequency Mar (day^{-1})	2.4
33	TMAX feb (degC)	1.8	87	Rain frequency Apr (day^{-1})	1.7
34	TMAX mar (degC)	9.0	88	Rain frequency May (day^{-1})	1.8
35	TMAX apr (degC)	17.4	89	Rain frequency Jun (day^{-1})	1.7
36	TMAX may (degC)	23.7	90	Rain frequency Jul (day^{-1})	2.4
37	TMAX jun (degC)	28.7	91	Rain frequency Aug (day^{-1})	1.9
38	TMAX july (degC)	30.8	92	Rain frequency Sep (day^{-1})	3.3
39	TMAX aug (degC)	29.5	93	Rain frequency Oct (day^{-1})	2.6
40	TMAX sept (degC)	25.3	94	Rain frequency Nov (day^{-1})	2.5
41	TMAX oct (degC)	19.0	95	Rain frequency Dec (day^{-1})	1.7
42	TMAX nov (degC)	9.7	96	Rain frequency Average (day^{-1})	2.1
43	TMAX dec (degC)	1.1	97	Annual potential evaporation (mm)	n.a
44	TMAX average (degC)	16.2	98	Solar irradiation Jan ($Wh/m^2/day$)	1 980
45	Rainfall Jan (mm)	25.4	99	Solar irradiation Feb ($Wh/m^2/day$)	2 810
46	Rainfall Feb (mm)	24.3	100	Solar irradiation Mar ($Wh/m^2/day$)	3 690
47	Rainfall Mar (mm)	59.9	101	Solar irradiation Apr ($Wh/m^2/day$)	5 100
48	Rainfall Apr (mm)	93.7	102	Solar irradiation May ($Wh/m^2/day$)	5 840
49	Rainfall May (mm)	102.6	103	Solar irradiation Jun ($Wh/m^2/day$)	6 320
50	Rainfall Jun (mm)	115.3	104	Solar irradiation July ($Wh/m^2/day$)	6 250
51	Rainfall July (mm)	124.7	105	Solar irradiation Aug ($Wh/m^2/day$)	5 360
52	Rainfall Aug (mm)	112.0	106	Solar irradiation Sep ($Wh/m^2/day$)	4 360

53	Rainfall Sep (mm)	99.7	107	Solar irradiation Oct (Wh/m^2/day)	3 090
54	Rainfall Oct (mm)	71.6	108	Solar irradiation Nov (Wh/m^2/day)	1 960
55	Rainfall Nov (mm)	53.8	109	Solar irradiation Dec (Wh/m^2/day)	1 660
56	Rainfall Dec (mm)	39.6	110	Solar irradiation Average (Wh/m^2/day)	4 035

TG = average temperature
TMIN = minimum temperature
TMAX = maximum temperature

Source to climate data

Row no.	Source / calculation procedure	Comments
3-56	http://www.worldclimate.com/cgi-bin/grid.pl?gr=N41W091	Data derived from NCDC TD 9641 Clim 81. Normals from 30 years between 1961 and 1990.
57	Calculated, summation.	
58-69	http://www.zoover.co.uk/united-states-of-america/iowa/iowa-city/weather	
70	Calculated, average.	
71-83	Calculated by dividing the monthly average rainfall by the number of rain days (> 1mm) for every month.	Average rainfall on a rainy day, monthly average, for every month
84-96	Calculated by dividing the number of days in each month with the number of rain days (> 1 mm) in the same month.	Rain frequency, monthly average, for every month
97	Annual potential evaporation not supplied.	Can be calculated by the Thornthwaite equation if minimum and maximum air temperature, latitude and elevation are provided.
98-109	http://rredc.nrel.gov/solar/calculators/PVWATTS/version2/pvwattsv2.cgi	Data based on spatial interpolation of solar radiation values derived from the 1961-1990 National Solar Radiation Data Base (NSRDB), from Iowa state, latitude 41.8 longitude 91.6.
110	Calculated, average.	

Appendix VIII. Emission inventory results from PestLCI

Maize	Type	Emissions to air (kg/ha)	Emissions to surface water (kg/ha)
Glyphosate	H	8.35E-05	2.66E-04
Atrazine	H	1.96E-03	8.35E-05
Chlorpyrifos	I	7.53E-03	1.79E-07

Rapeseed	Type	Emissions to air (kg/ha)	Emissions to surface water (kg/ha)
Glyphosate	H	4.70E-03	1.30E-03
Metazachlor	H	2.22E-03	3.56E-04
Quinmerac	H	7.25E-04	1.46E-04
Cycloxydim	H	1.03E-03	6.29E-07
Boscalid	F	2.23E-03	5.72E-07
Alpha-cypermethrin	I	6.50E-06	9.39E-11
Thiacloprid	I	3.20E-04	7.54E-08

Salix	Type	Emissions to air (kg/ha)	Emissions to surface water (kg/ha)
Glyphosate	H	3.13E-03	5.43E-04
Flurtamone	H	6.04E-04	1.79E-06
Diflufenican	H	2.42E-04	1.62E-06

Soybean	Type and ID[1]	Emissions to air (kg/ha)	Emissions to surface water (kg/ha)
Paraquat	H1	2.32E-05	2.32E-05
Glyphosate	H2	2.32E-05	5.75E-04
Glyphosate	H3	2.68E-04	5.39E-04
Paraquat	H4	1.34E-03	2.63E-09
Paraquat	H1	2.32E-05	2.32E-05
Lactofen	H2	8.02E-04	1.70E-09
Chlorimuron-ethyl	H2	2.25E-06	6.64E-06
Imazethapyr	H2	6.64E-06	2.10E-07
Clethodim	H3	1.42E-05	2.73E-13
Clethodim	H4	1.06E-05	6.01E-12
Paraquat	H5	1.34E-03	2.63E-09
Prothioconazole	F1	7.76E-06	2.88E-09
Trifloxystrobin	F1	1.67E-04	2.03E-07
Epoxiconazole	F2	1.62E-03	2.10E-07
Pyraclostrobin	F2	4.03E-07	8.15E-10
Prothioconazole	F3	1.88E-05	1.17E-08
Trifloxystrobin	F3	3.93E-04	3.41E-07
Epoxiconazole	F4	1.84E-03	1.10E-07
Pyraclostrobin	F4	1.10E-07	1.16E-10
Flubendiamide	I1	1.17E-10	2.71E-09
Alpha-cypermethrin	I2	3.51E-05	8.71E-11
Teflubenzuron	I2	2.88E-09	9.87E-09
Zeta-cypermethrin	I3	1.54E-05	1.11E-10
Flubendiamide	I3	1.60E-10	2.33E-09

1) ID number notation as in Appendix II.

Sugarcane	Type	Emissions to air (kg/ha)	Emissions to surface water (kg/ha)
Glyphosate	H	3.09E-04	2.66E-03
Atrazine	H	1.19E-02	4.45E-04
Ametryn	H	9.67E-03	4.39E-07
2,4-D	H	2.35E-01	2.46E-04
Metribuzin	H	3.42E-03	3.43E-05
Fipronil	I	4.07E-05	1.51E-08
Thiamethoxam	I	1.54E-05	1.23E-05

Wheat	Type	Emissions to air (kg/ha)	Emissions to surface water (kg/ha)
Glyphosate	H	4.70E-03	6.40E-04
Prosulfocarb	H	3.42E-03	5.83E-05
Florasulam	H	1.39E-04	7.06E-08
Fluroxypyr-meptyl	H	7.62E-04	5.56E-10
Tribenuron methyl	H	2.64E-05	1.84E-07
Fenpropimorph	F	3.21E-03	8.16E-09
Propiconazole	F	4.12E-04	2.01E-07
Prothioconazole	F	1.11E-03	3.19E-09
Esfenvalerate	I	2.57E-08	3.95E-10

Appendix IX. Characterisation factors used in this thesis

AS name	CF air (CTUe/kg)	CF water (CTUe/kg)	Classification[1]	If interim; reason[2]	No. of trophic levels	No. of species
Metazachlor	70	7 364	recommended	-	3	6
Glyphosate	13	321	recommended	-	4	38
Alpha-cypermethrin	254 034	35 089 624	interim	Ecotox EF	2	11
Prosulfocarb	308	33 087	recommended	-	3	11
Tribenuron-methyl	155	680	recommended	probably interim?	1	1
Propiconazole	295	22 312	recommended	-	4	24
Esfenvalerate	259 126	19 043 938	recommended	-	3	11
Diflufenican	30	1 247	interim	Ecotox EF	2	3
Quinmerac	21	445	calculated		2	3
Cycloxydim	1	292	interim	dissociating	3	4
Fluroxypyr-meptyl	905	77 290	recommended	-	3	4
Fenpropimorph	7	7 380	interim	dissociating	3	6
Flurtamone	5 921	289 763	calculated	-	2	3
Thiacloprid	67	9 253	calculated	-	?	6
Boscalid	342	13 215	calculated	-	2	3
Florasulam	3 892	25 106	calculated	-	?	8
Prothioconazole	5 640	121 094	calculated	-	2	4
Chlorpyrifos	3 862	2 517 779	calculated	-	?	29
Atrazine	3 288	87 654	recommended	-	4	128
Ametryn	1 804	76 179	recommended	-	3	38
2,4-D	103	860	interim	dissociating	4	65
Metribuzin	659	9 492	recommended	-	4	21
Fipronil	11 724	2 012 897	recommended	-	n.a	n.a
Thiamethoxam	31	4 300	calculated	-	?	>15
Lactofen	42 966	1 716 987	calculated	-	2	2
(Zeta)-cypermethrin	381 628	50 408 636	recommended	-	4	79
Chlorimuron-ethyl	2 806	17 642	calculated	-	2	7
Imazethapyr	96	1 164	interim	dissociating	n.a	n.a
Clethodim	11	3 291	interim	dissociating	n.a	n.a
Paraquat	1 334	118 762	interim	dissociating	3	34
Trifloxystrobin	131	7 146	calculated	-	n.a	n.a
Epoxiconazole	2 148	111 316	calculated	-	2	4
Pyraclostrobin	447	147 269	calculated	-	?	4
Flubendiamide	31 352	1 114 768	calculated	-	2	3
Teflubenzuron	50 982	971 086	interim	Ecotox EF	2	3

1) Classification into either of three categories: Recommended, Interim or Calculated. CFs classified as recommended and interim are taken from USEtox database. Calculated CFs have not been classified as recommended or interim but the number of species and trophic levels are provided to assist in interpretation. The number of trophic levels is however not always known. All species are available in Appendix V for determination of number of trophic levels.
2) Reasons for interim: “Ecotox EF” refer to insufficient ecotoxicological effect data (species covering less than three trophic levels) “Dissociating” refer to substances that split into atoms or ions and are classified as interim in USEtox due to uncertainties in the modelling of fate and exposure (Rosenbaum et al. 2008).

Appendix X. PestLCI sensitivity analysis

A sensitivity analysis was carried out for PestLCI to learn more about the model's behaviour in terms of input parameter response and contribute to the interpretation of the results. The results of the sensitivity analysis are presented here, in table as well as figure formats. Tests with constant response are not displayed in figure formats.

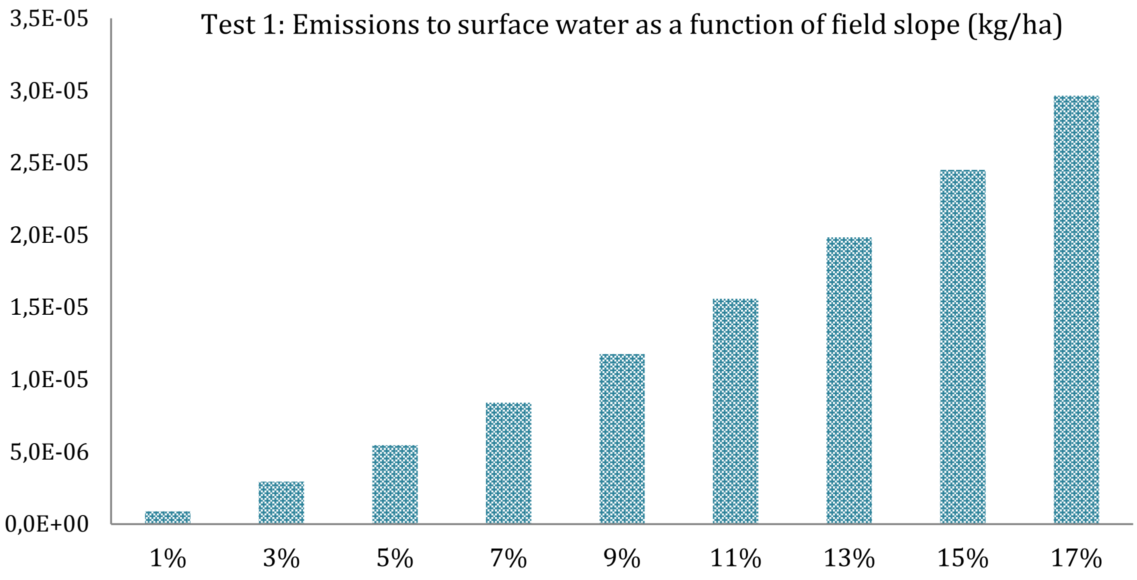
Emissions to air and surface water were analysed in terms of sensitivity to the following model parameters:

- field slope (test 1)
- month of application (test 2)
- application method (test 3)
- crop type and development stage at time of application (test 4)
- tillage type (test 5)
- field size (test 6)
- climate (test 7)

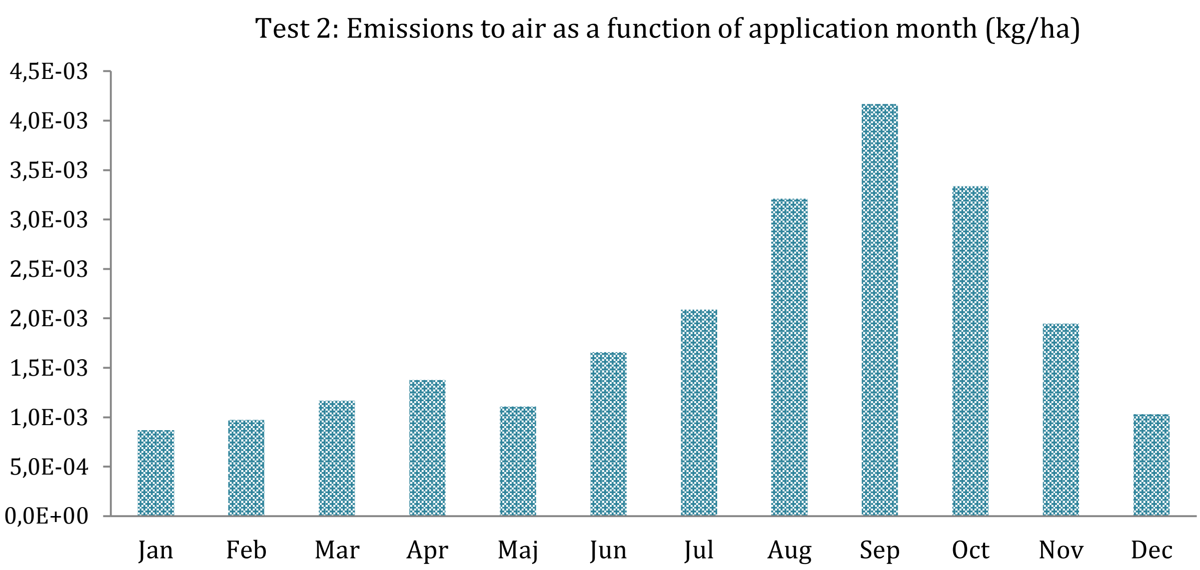
During the various tests only one parameter was varied at a time and all other model parameters were kept constant. The other parameters were set as follow in all tests:

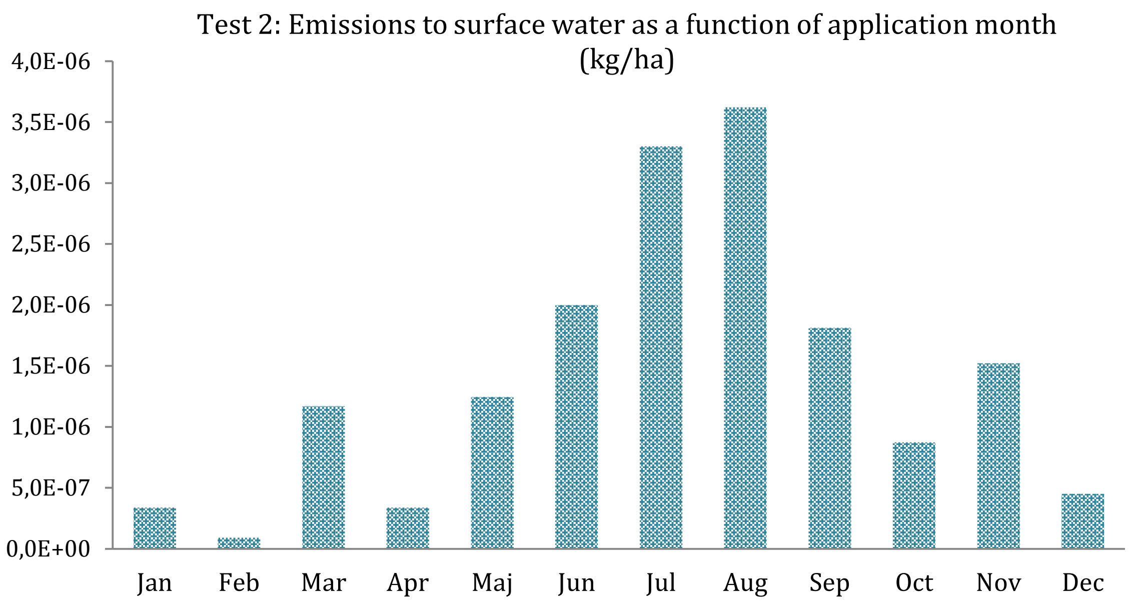
Size: 10 ha (500×200 m^2)
Climate: Görlitz, Germany
Drainage: 0%
Tillage: conventional
Slope: 1%
Soil: average
Annual irrigation: 0 mm
Application method: IMAG conventional boom cereals
Crop type and development stage: cereals I – leaf development
Month of application: October
Pesticide: prosulfocarb in tests 1 - 6, atrazine in test 7
Application rate: 1,5 kg/ha
Adjustable model parameters as default.

Test 1: Sensitivity to field slope		
Field slope (%)	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
1	3.34E-03	8.74E-07
3	3.34E-03	2.95E-06
5	3.34E-03	5.46E-06
7	3.34E-03	8.40E-06
9	3.34E-03	1.18E-05
11	3.34E-03	1.56E-05
13	3.34E-03	1.98E-05
15	3.34E-03	2.45E-05
17	3.34E-03	2.96E-05

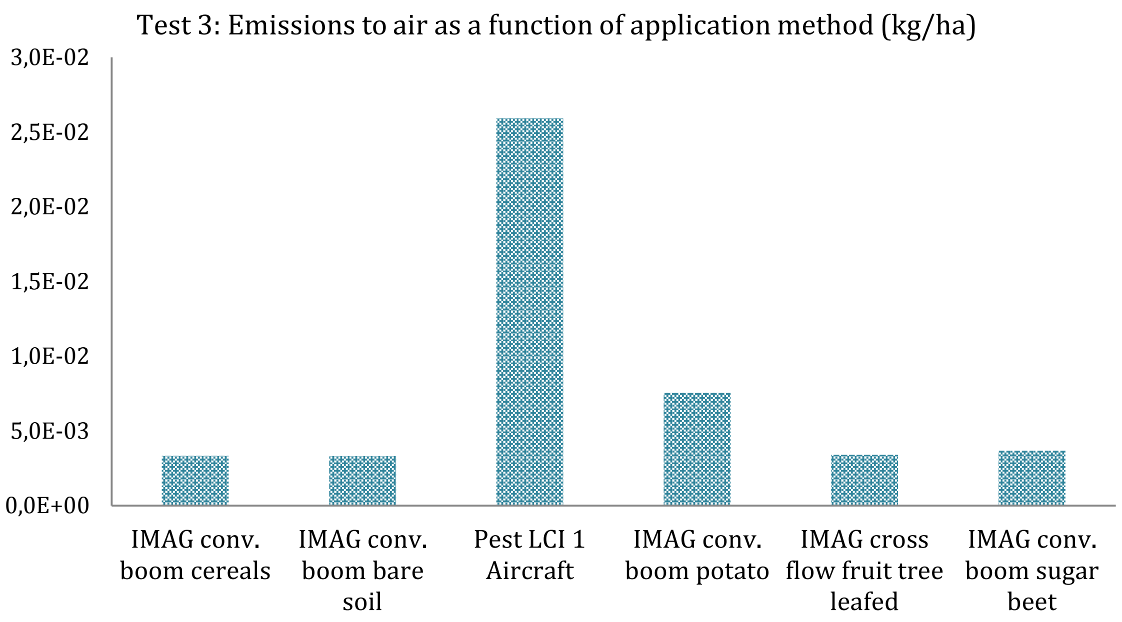


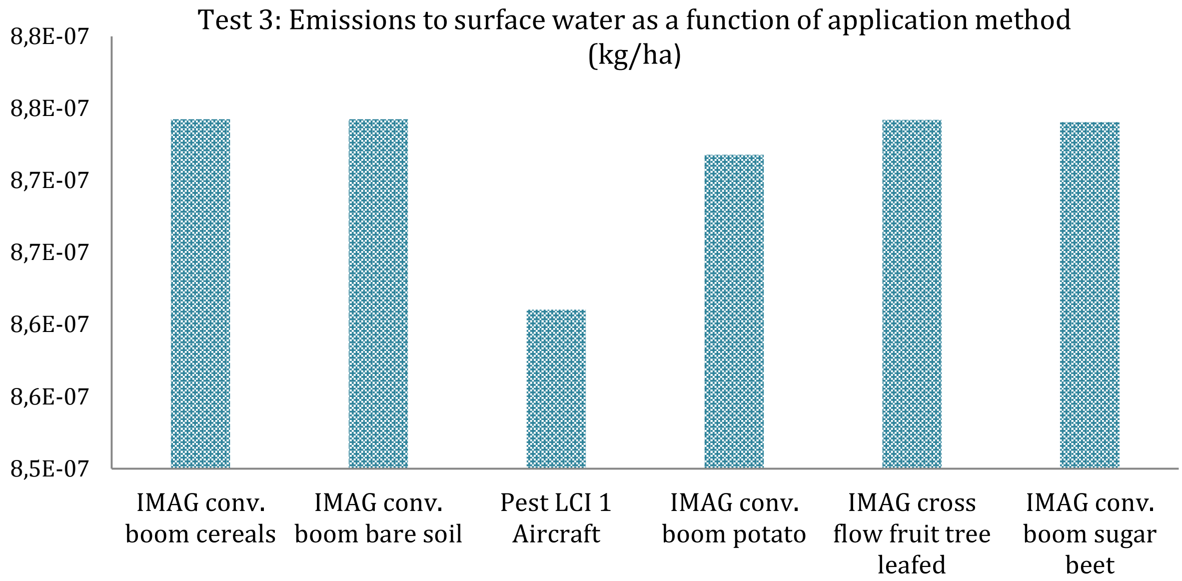
Test 2: Sensitivity to month of application		
Month	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
Jan.	8.68E-04	3.37E-07
Feb.	9.73E-04	8.99E-08
March	1.17E-03	1.17E-06
April	1.38E-03	3.38E-07
May	1.11E-03	1.25E-06
June	1.66E-03	2.00E-06
July	2.09E-03	3.30E-06
Aug.	3.21E-03	3.62E-06
Sept.	4.17E-03	1.81E-06
Oct.	3.34E-03	8.74E-07
Nov.	1.95E-03	1.52E-06
Dec.	1.03E-03	4.51E-07



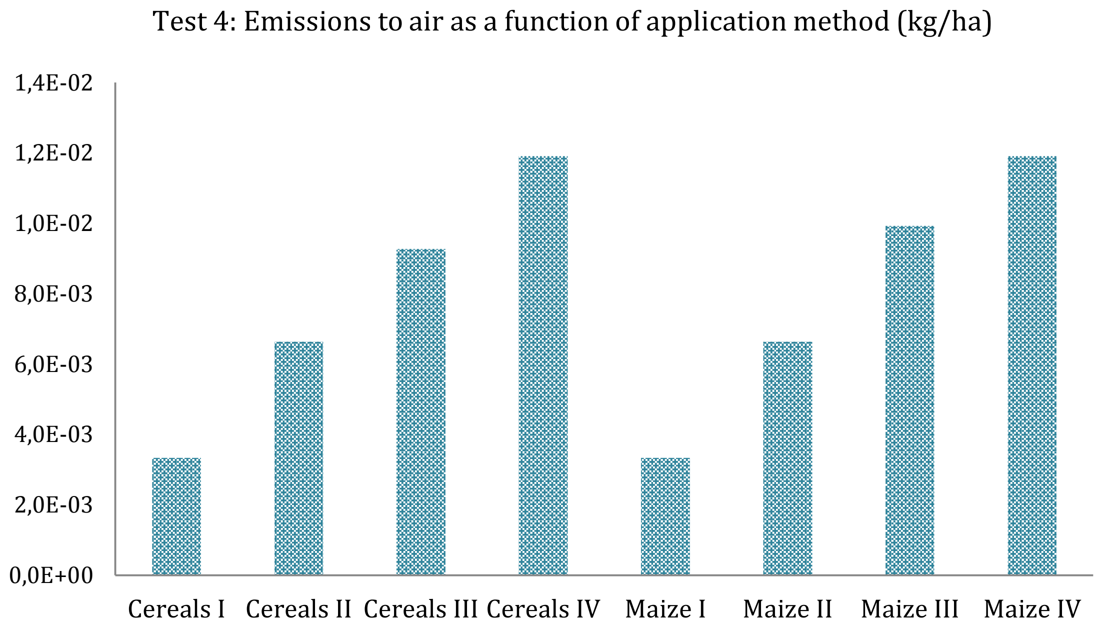


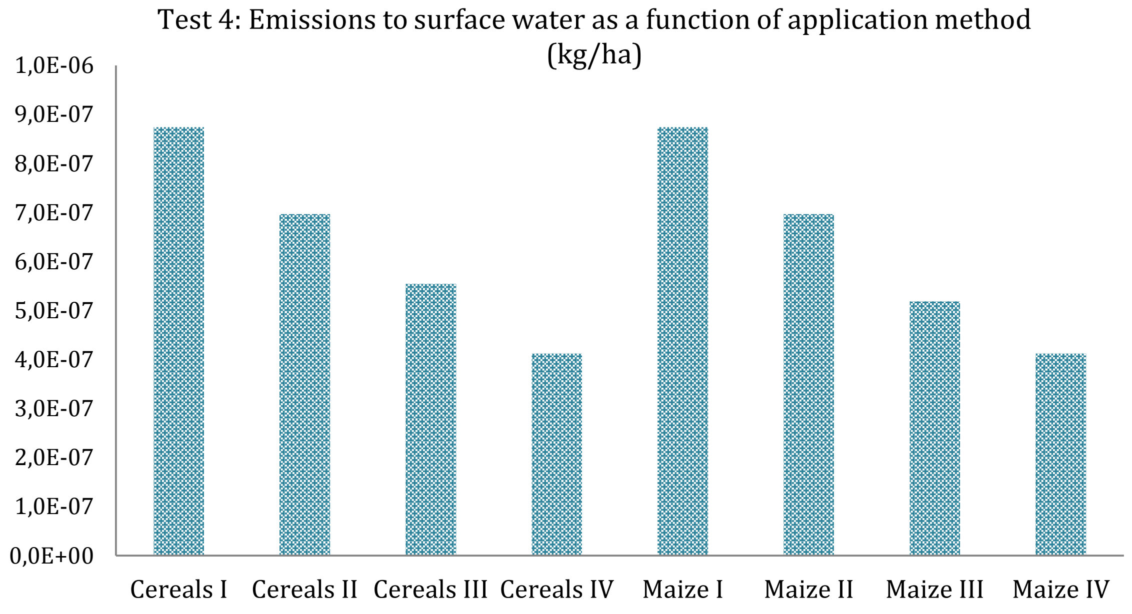
Test 3: Sensitivity to application method		
Application method	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
IMAG conv. boom cereals	3.34E-03	8.74E-07
IMAB conv. boom bare soil	3.31E-03	8.74E-07
Pest LCI 1 Aircraft	2.59E-02	8.61E-07
IMAG conv. boom potato	7.56E-03	8.72E-07
IMAG cross flow fruit tree leafed	3.40E-03	8.74E-07
IMAG conv. boom sugar beet	3.67E-03	8.74E-07





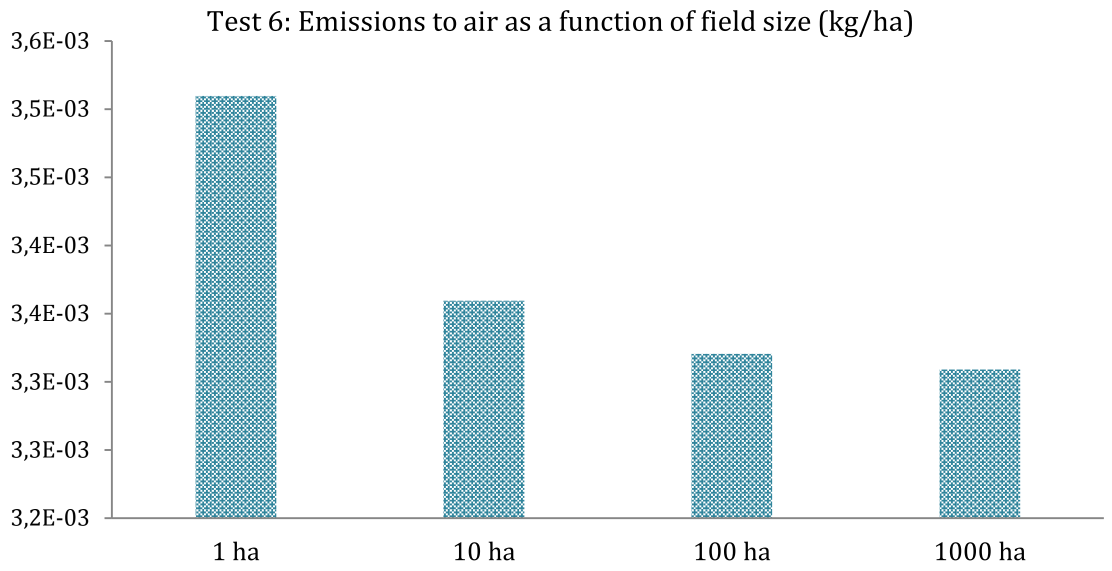
Test 4: Sensitivity to crop type and development stage at time of application		
Crop type and development stage at time of application	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
Cereals I	3.34E-03	8.74E-07
Cereals II	6.64E-03	6.97E-07
Cereals III	9.27E-03	5.55E-07
Cereals IV	1.19E-02	4.13E-07
Maize I	3.34E-03	8.74E-07
Maize II	6.64E-03	6.97E-07
Maize III	9.93E-03	5.19E-07
Maize IV	1.19E-02	4.13E-07



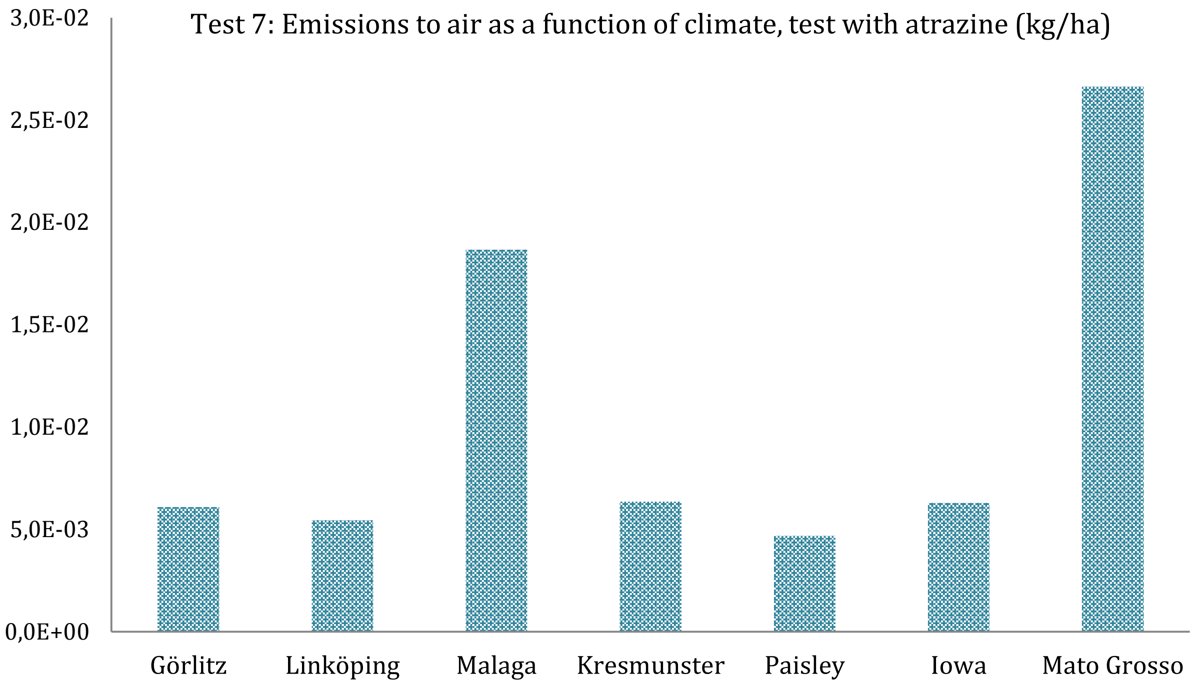


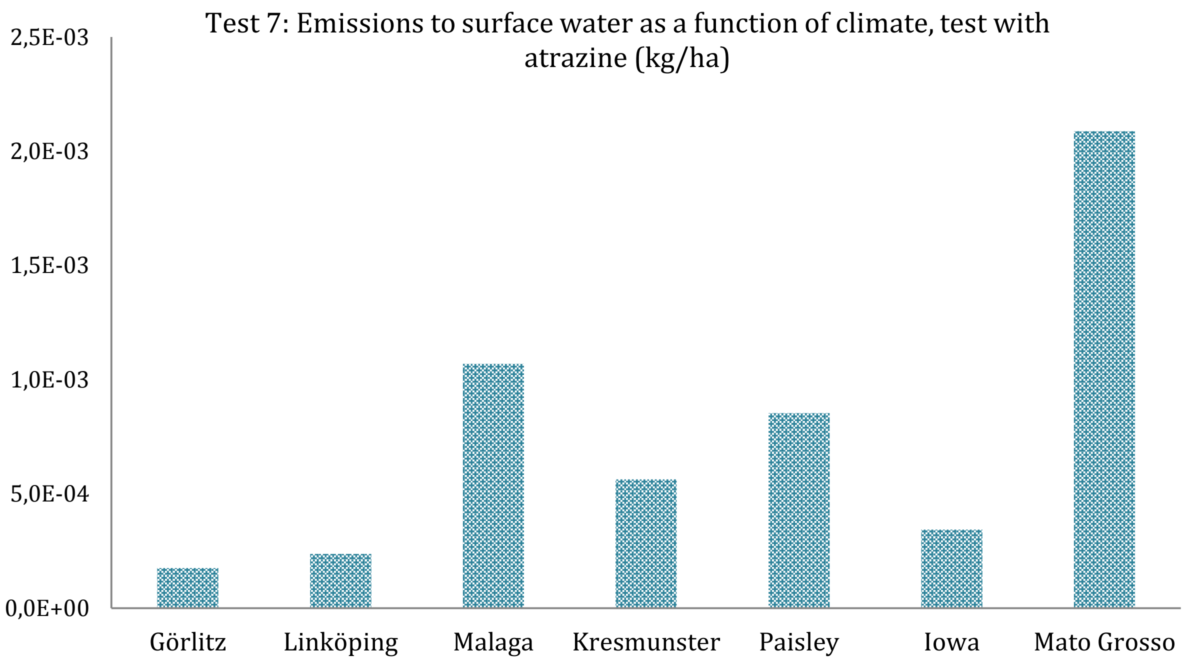
Test 5: Sensitivity to tillage type		
Tillage type	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
Conventional	3.3380E-03	8.7423E-07
Reduced	3.3380E-03	8.7423E-07
No till	3.3380E-03	8.7423E-07

Test 6: Sensitivity to field size, assuming all field sides of equal length		
Field size (ha)	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
1	3.510E-03	8.741E-07
10	3.359E-03	8.742E-07
100	3.320E-03	8.742E-07
1000	3.309E-03	8.742E-07



Test 7: Sensitivity to climate, test with atrazine. Other model parameters as specified above.		
Climate profile	**Emissions air (kg/ha)**	**Emissions water (kg/ha)**
Görlitz	6.09E-03	1.76E-04
Linköping	5.45E-03	2.38E-04
Malaga	1.87E-02	1.07E-03
Kresmünster	6.36E-03	5.65E-04
Paisley	4.68E-03	8.55E-04
Iowa	6.29E-03	3.45E-04
Mato Grosso	2.66E-02	2.09E-03





Key to climate profiles, notation as in PestLCI:
Continental 2 1: Görlitz (DE)
North European and continental 1: Linköping (SE)
Mediterranean 2 1: Malaga (ES)
Sub-alpine continental: Kresmünster (AT)
Wet maritime: Paisley (GB)
Iowa State (USA)
Mato Grosso (BR)