Freshwater ecotoxicity assessment of pesticide use in crop production: Testing the influence of modeling choices

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ABSTRACT

Pesticides help to control weeds, pests and diseases contributing, therefore, to food availability. However, pesticide fractions not reaching the intended target may have adverse effects on the environment and the field ecosystems. Modeling pesticide emissions and the alignment with characterizing associated impacts is currently one of the main challenges in Life Cycle Assessment (LCA) of agricultural systems. To address this challenge, this study takes advantage of the latest recommendations for pesticide emission inventory and impact assessment and frames a suitable interface for those LCA stages and the related mass distribution of pesticide avoiding a temporal overlapping. Here, freshwater ecotoxicity impacts in the production of feed crops (maize, grass, winter wheat, spring barley, rapeseed and peas) in Denmark are evaluated during a 3-year period, testing the effects of inventory modelling choice and recent updates of the characterization method (USEtox). Potential freshwater ecotoxicity impacts were calculated in two functional units to consider crop impact profiles and cultivation intensity. According to the results, ecotoxicity impacts decreased over the period, mainly because of the reduction of insecticide active ingredients (*e.g.,* cypermethrine). Three different emission modelling choices were tested; they differ on the underlining assumptions and data requirements. The median results for the resulting emission fractions vary ~4 orders of magnitude for the different models. Main aspects influencing impact results are the interface between inventory estimates and impact assessment, and the consideration of intermedia processes, such as crop growth development and pesticide application method. Statistical differences were found in the impact results with 2 of emission model tested, thereby indicating the influence of modelling choices on ecotoxicity impact assessment.

Keywords: Pesticide emission factors, inventory modeling, ecotoxicity characterization, life cycle impact assessment (LCIA), feed crops, agriculture.*[1]

[1] Abbreviations
AI: Active ingredient
AS: Alternative scenario
BS: Reference scenario
CF: Characterization factors
DK: Denmark
EF: Effect factor
FF: Fate factor
Fun: Fungicides
GAP: Good agricultural practices
Gly_agri: Total agricultural use of glyphosate
Hrb: Herbicides
Ins: Insecticides
IS: Impact scores
LAI: Leaf area index
NAP: National Action Plans
Pgr: Plant growth regulators
XF: Exposure factor

1 INTRODUCTION

With the increased global demand for agricultural products for food, fiber and bioenergy, and the interrelated concerns on the environmental impact hereof, there is a need to have efficient tools to evaluate the environmental performance profiles of agricultural production, to facilitate a move towards more sustainable production systems. Life Cycle Assessment (LCA) is a widely applied and standardized framework to quantify potential impacts of products and systems along their entire life cycles. One of the main challenges in assessing the environmental performance of agricultural systems in LCA is modeling emissions from pesticide use and the subsequent coupling with the impact characterization model (van Zelm et al., 2014). Over the past years, a significant number of LCA studies on agricultural systems were conducted; however, ecotoxicity impacts as currently modelled may lead to inconsistent results and wrong conclusions in few cases (*e.g.*, comparing conventional and organic farming), mostly due to the lack of agreement and precise definitions on the modeling framework for this impact category (Notarnicola et al., 2017).

The development of the life cycle inventory (LCI) analysis and subsequent life cycle impact assessment (LCIA) (*e.g.*, pesticide emission quantification and related characterization of ecotoxicity impacts) are the core phases of any LCA study. The robustness and reliability of the LCA results depend mainly on the quality and representativeness of the LCI and LCIA data and models selected. Different modeling options, hence, will affect the impact profiles of a study, and this is especially relevant for agricultural systems (Anton et al., 2014).

Quantifying the chemical emissions to the environment in the LCI phase is typically based on generic assumptions, often based on standard emission factors (*e.g.*, expressed in percentages of applied mass) or dynamic models based on specific application scenarios that describe the emission distribution of organic pesticides. The consensus effort on the delimitation between pesticide emission inventory and impact assessment for LCA already provides guidelines on what should be quantified in those LCA steps but explicitly exclude how to do it avoiding recommendations on specific models (Rosenbaum et al., 2015). The implications of choosing different emission models in the LCA of crop production have been discussed for some agricultural systems (Goglio et al., 2018; Schmidt Rivera et al., 2017; van Zelm et al., 2014). However, no studies are addressing the influence of the pesticide emission modeling approach, nor the evaluation of recent developments in impact assessment methods to determine pesticide ecotoxicity impact profiles in different crop production systems. Thus, there is a need to test different choices on how to quantify pesticide emission fractions (i.e. different modeling approaches) and the recent developments on the recommended method for freshwater ecotoxicity characterization in the production of feed crops. The purpose of the present study is to contribute to the evaluation of the ecotoxicological burden on freshwater ecosystems from pesticide use in crop production using the pesticide use in Denmark as example. It is focused on assessing the influence of pesticides on the environmental impact profiles of feed crops (maize, grass, wheat, barley, rapeseed and peas) during the period 2013-2015, testing the effects of the LCI choice and the developments of LCIA methodology.

2 MATERIALS AND METHODS

This study followed the LCA methodology to evaluate the potential ecotoxicity impacts on freshwater ecosystems from pesticide use in Denmark´s (DK) crop production. This bottom-up analysis focuses on the evaluation and influence of pesticide application on the environmental impact profiles of maize, winter wheat, grass, spring barley, rapeseed and peas during the period 2013-2015, testing the effects of the choice of the emission modeling framework and the recent updates of the characterization method. For the later, we use the global consensus model USEtox (http://usetox.org).

2.1 Definition of ecotoxicity impact scores

The quantification of ecotoxicity impact scores for freshwater ecosystems includes 1) detailed LCI reporting on the pesticide active ingredient (AI), application methods, time and mass, location, agricultural practices and crop stage development; 2) quantified AI emission fractions for both on-field and off-field; and 3) mesures to avoid double counting of multimedia transfers considered in the quantification of emission fractions and the impact assessment fate modeling (Rosenbaum et al., 2015). Accordingly, the freshwater ecotoxicity impact scores (IS) can be described as:

$$IS = \sum_{i,x}(CF_{i,x} \cdot m_{i,x}) \quad (1)$$

Where $CF_{i,x}$ is the characterization factor for freshwater ecotoxicity [PAF m^3 d $\mathrm{kg}_{\mathrm{emitted}}^{-1}$], and $m_{i,x}$ is the mass of AI *x* emitted to compartment *i* per area treated [$\mathrm{kg}_{\mathrm{emitted}}$ ha^{-1}]. Potential freshwater ecotoxicity impacts (IS_{crop_ha}) [PAF m^3 d ha^{-1}] were determined in relation to 1 hectare [ha] of crop in a given year *t* within 2013 and 2015 (cultivation intensity). Additionally, freshwater ecotoxicity impact profiles at country or regional level (IS_{crop}) [PAF m^3 d crop^{-1}] from pesticide use were derived from the product of crop impact scores and the total crop area in a given year in DK.

The interface between LCI and LCIA and related mass distribution for pesticide application in crop production are presented in Figure 1. This approach follows the proposed framework for pesticide inventory and impact assessment (Rosenbaum et al., 2015; van Zelm et al., 2014).

Figure 1.

This interface considers the boundaries between the emission inventory and impact assessment, setting also spatial and time dimensions, to quantify the AI emission fractions (in air, freshwater and soil) and characterize ecotoxicity impacts, avoiding any overlap or double counting of the chemical fate process. Furthermore, the emission flows, both on and off the field, are clearly indicated and their link to the characterization factors for the impact pathway (i.e. freshwater ecotoxicity).

2.2 Pesticide emission inventory

Pesticide application practices in DK for the selected crops were determined. Concrete active ingredients were used throughout the study, meaning, that the chemical that is the biologically active part in any pesticide was assessed (European Commission, 2017). The mass applied per AI was derived from the annual statistical report on pesticide use by crop in DK for 2013 (Ørum and Samsøe-Petersen, 2014), 2014 (Ørum and Hossy, 2015) and 2015 (Ørum and Holtze, 2017); for further information see Supporting information (SI-1). We addressed nearly 60 different AIs from four distinct target classes, herbicides (Hrb), plant growth regulators (Pgr), fungicides (Fun), and insecticides (Ins). Additionally, glyphosate (CAS-RN107-83-6) use is not allocated to any specific crop cultivation, and it was assessed as the total agricultural use of the AI per 1 hectare [ha] in a given year, hereafter identified as ($Gly_{\_agri}$). All AI identification (CAS registry numbers-RN and names), and class are reported in SI, Table S1.

2.3 Pesticide emission quantification

Crops are treated by foliar spray application (typically boom sprayers), and the reported DK statistics on pesticides were used for agricultural practices. The agricultural field is considered as part of the ecosphere and emissions to environmental media after spraying were modeled via initial distribution (primary processes like initial drift deposition) and secondary emission transfers (*e.g.*, re-volatilization after deposition). The total emission fraction of an AI [kg kg^{-1}] is quantified as the sum of the fractions emitted to air, freshwater and soil:

$$f_{em} = \frac{m_{em}}{m_{app}} = f_{em\_air} + f_{em\_fw} + f_{em\_soil.agri} + f_{em\_soil.other} \qquad (2)$$

Where f_{em} is the fraction of the applied mass of pesticide that becomes an emission to the environment, m_{em} the mass emitted, m_{app} the mass of pesticide applied, f_{em_air} the fraction of applied mass that is emitted to air, f_{em_fw} the fraction of applied mass that is emitted to freshwater, $f_{em\_soil.agri}$ the fraction of applied mass that is emitted to on-field soil and $f_{em\_soil.other}$ the emission fraction reaching off-field soil and other surfaces.

Primary distribution

The primary distribution processes between compartments occur during the initial minutes after pesticide application. This primary process are emission by wind drift (f_{d_lost}), pesticide deposition process and the fraction intercepted by the crop or weed. Since the fractions from initial distribution to environmental media should sum up to 100% of the applied mass, considering losses via degradation during the initial minutes negligible, the aggregated emission fractions will be equal to one (Fantke et al., 2011a; Juraske et al., 2007). Consequently, the crop/weed interception fraction ($f_{\text{int\_crop}}$) of an AI directly after the application is given by:

$$f_{\text{int\_crop}} = 1 - \left(f_{d\_lost} + f_{dep\_soil.agri}\right) \quad (3)$$

The fraction lost by wind drift $f_{\text{d\_lost}}$ [kg/kg], depends on the application method, i.e. the spray equipment and elevation, and wind speed. Based on models for conventional spray equipment on field crops and deposition curve parameters assuming good agricultural practices (GAP), the $f_{\text{d\_lost}}$ was fixed to a value of 0.1 (Gil et al., 2014; Gil and Sinfort, 2005; Gyldenkrne et al., 1999; van de Zande et al., 2007). The soil deposition $f_{\text{dep\_soil.agri}}$ [kg kg^{-1}], depends on crop-specific leaf area index (LAI), thereby also affecting fractions reaching soil surfaces of the treated field area (Fantke et al., 2011b). With an exponential model (Gyldenkærne et al., 2000; Juraske et al., 2007), based on crop growth stage and capture efficacy, the fraction reaching the soil surface is described as:

$$f_{dep\_soil.agri} = e^{-k_p \times LAI} \quad (4)$$

Where kp is the capture coefficient [-] and set to 0.55 for pesticide spray solutions prepared with adjuvants (Gyldenkrne et al., 1999). Pesticide target class and specific application time were used to define crop-specific growth stages in the selected crops. The LAI was derived for plant growth regulators, insecticides and fungicides distinctly as a value dependent on the target class/crop growth stage/application time combination, (Fantke et al., 2011b; Itoiz et al., 2012; Olesen and Jensen, 2013); for herbicide application on weeds the corresponding LAI of 0.5 is used. This value is based on the reported leaf cover factor for fallow lands (Panagos et al., 2015). Further details presented in SI, Table S2.

Secondary distribution

The subsequent secondary emission transfers include re-volatilization after deposition and off-field emissions allocation. The volatilization from fractions deposited in the different compartments is derived from the default Tier 1 emission factors per AI from their vapor pressures (Webb et al., 2016) see Table S1 and S3 in SI. The emission factor emF was calculated for each AI (see, SI Table S1), the inter-media transfer and the final emission factors are presented in SI, SI-1 and SI-2. Finally, the water to soil area ratio for DK (0.016) was used to allocate the off-field emissions (i.e. drift fraction deposited in off-field surfaces) see SI, Table S2. This value is based on reported data of the Danish ministry of environment (Stockmarr and Thomsen, 2009).

2.4 Freshwater ecotoxicity characterization

For assessing the ecotoxicity of pesticides on freshwater ecosystems, we followed the LCIA emission-to-damage framework that links emissions to impacts through environmental fate, exposure and effects (Jolliet et al., 2004). According to (Hauschild and Huijbregts, 2015; Rosenbaum et al., 2008) characterization factors CF for freshwater ecotoxicity of chemical emissions can be expressed as:

$$\mathrm{CF}_{i,x} = FF_{i\rightarrow fw,x} \times XF_{fw,x} \times EF_{fw,x} \tag{5}$$

Where $FF_{i\rightarrow fw,x}$ is the fate factor in [d] describing the mass transport, distribution and degradation in the environment. The ecosystem exposure factor, $XF_{fw,x}$, is defined as the bioavailable fraction of a chemical in freshwater; and an effect factor ($EF_{fw,x}$) expressing the ecotoxicological effects in the exposed ecosystems integrated over the exposed water volume. CFs were estimated with USEtox 2.02 as characterization model, with the specific European landscape dataset (i.e. representing DK conditions) (Fantke et al., 2017; Westh et al., 2015). New CFs for 10 additional AIs, following the procedure in Fantke et al. (2017) were derived. A detailed description of the resulting CF and the data used can be found in SI, SI-3. Furthermore, the recent developments for the characterization model between USEtox versions 1.01 and 2.02 were evaluated.

2.5 Sensitivity analysis definition

Two types of local sensitivity tests were conducted. First, a scenario sensitivity analysis was performed to test the effect of LCI modeling choices on the impact profile of the selected crops on the three-year period. Three scenarios were considered, the above-described scenario was selected as a reference case (BS) and two alternative scenarios (AS1-AS2) that represent different modeling approaches to quantify emissions from pesticide use. The alternative scenario AS1 followed Margni et al. (2002), which represents a usually used pesticide emission modeling, and furthermore is one of the first approaches that account for pesticide emission distribution in different environmental media in LCA studies for agricultural systems. In this approach, the pesticide emissions are distributed in environmental media based on fixed share percentages. They assume that the fraction of AI emitted to the soil will be 85% of the total application, 5% will stay on leaves and the remaining 10% is lost into the air across crops and pesticides. The second tested scenario AS2 represents fixed emission fractions dependent on the foliar spray application and drift distributions for field crops. This approach was chosen to represent a modeling framework where the initial distribution (i.e. application method and crop relation) is taken into account but also allowing the inclusion of field emissions in the assessment (Balsari et al., 2007; Felsot et al., 2010; Gil and Sinfort, 2005). Table 1 displays the emission fractions in the three scenarios considered.

Table 1.

Second, the sensitivity of the proposed modeling approach was tested by evaluating the change in the impact scores (propagated from the change in emission fractions) as a function of the variation of several input parameters by a factor of 2 larger of their initial values, one at the time. Local sensitivity to input S_{in} [-] was further expressed as the effect on the model output due to a change in an input parameter (for further details see SI, SI-5).

3 RESULTS AND DISCUSSION

3.1 Pesticides use in Danish crop production (2013-2015)

The AI considered in the study covers 98.3% of the total pesticide applications in terms of mass applied for the selected crops: maize, winter wheat, grass, spring barley, rapeseed, peas and the agricultural use of glyphosate ($Gly_{\_agri}$). The total pesticide use was 3165 tons in 2013, 1438 tons in 2014 and 2105 tons in 2015. The average pesticide application rates per crop vary between 2 and 3 orders of magnitude (SI, Table S6). Grass is the crop with the lowest application rates and pesticide use; together, fungicides and insecticides represent nearly 20% of the total use in grass-2013; additionally, in 2014-2015, there was no use of insecticides, and fungicides use was reduced by less than 2.5%. Gly_agri sum up to 2722 tons in the 3 years and represents near 40% of the total use of pesticides in DK. Winter wheat (2672 tons) is the crop with higher pesticide use followed by spring barley (748 tons) (SI, Table S7). The most used pesticide target class is Herb and prosulfocarb is the most used AI after Gly_agri on this target class.

3.2 Ecotoxicity impact profiles of feed crops (2013-2015)

The IS_{crop} from pesticide use decreased over the three years (Figure 2). The reduction of the IS_{crop} was more apparent in 2014 (59%) than in 2015 (33%) with respect to the base year (2013). Most of the decrease in the IS_{crop} was due to the non-use of a single substance: cypermethrin. This insecticide was the major contributor to IS_{crop} in 2013 across crops (*e.g.,* 87% in maize, 60% in spring barley and 47% in winter wheat) and was no longer used in 2014-2015 (see Table S8 in SI). Furthermore, the fact that maize and grass did not require the use of insecticides in 2015 also contributes to the reduction of IS_{crop}, but it is essential to note that this may be the result of unfavourable climatic conditions for the emergence of pests, among many other different reasons.

Figure 2.

After winter wheat-2013 ($1.6x10^9$ PAF m^3 d $crop^{-1}$), spring barley-2013 ($1.4x10^9$ PAF m^3 d $crop^{-1}$) and rapeseed-2013 ($3.3x10^8$ PAF m^3 d $crop^{-1}$) present the higher IS_{crop} (Figure 2). The larger IS_{crop} in those crops is associated with the use of insecticides (*e.g.*, cypermethrin, pendimethalin and lambda-cyhalothrin) and fungicides (*e.g.*, pyraclostrobin, azoxystrobin and folpet), AIs with relatively high CF, and the more extensive cultivation practices (i.e. cultivated area). Consequently, substance prioritization by LCA impact assessment helps to identify potentially harmful AI for ecosystems and, with the restriction of their use or the implementation of more sustainable practices, significant changes in the impact profiles of the crops can be made more apparent (*e.g.*, cypermethrin). In this sense, if farmers choose to use pesticides AI causing lower impacts, the load on agricultural systems will decline, even if they continue to spray their fields as usual for pests and disease control. Moreover, linking this decision with integrated pest management (IPM) will further contribute to lowering the ecotoxicological burden on freshwater ecosystems from pesticide use.

3.3 Pressure of pesticide impacts by hectare and class (2013-2015)

When calculating the potential ecotoxicity impacts on freshwater ecosystems per 1 hectare of crop per year (IS_{crop_ha}) [PAF m^3 d ha^{-1}] the cultivation intensity can be addressed, and thus, their interaction of agricultural systems and practices is more apparent. Different ranking and patterns than the presented in section 3.1 are found. Furthermore, the variations in pesticide use (almost 3 orders of magnitude) and impact scores for individual AIs (up to 9 orders of magnitude) are significant. Therefore, in the same year, the two indicators can move in different directions (Figure 3), meaning that pesticide use or application rates is not an adequate indicator of potential impacts (e.g., Gly_agri and rapeseed), since toxicity potentials might be higher for pesticides that are applied in lesser amounts (Fantke and Jolliet, 2016).

Figure 3.

In terms of cultivation intensity, peas appeared as the crop with the highest pressure by hectare cultivated in the entire period, with the maximum value (6440 PAF m^3 d ha^{-1}) in 2015.

In 2013 rapeseed, spring barley and winter wheat showed IS_{crop_ha} between 64% and 54% lower than peas, in 2014 the difference for the same crops was among 70% and 85% lower and for 2015 all crops showed IS_{crop_ha} 80% lower than peas (see Figure 4).

Figure 4.

The IS_{crop_ha} for the study varies up to 3.5 orders of magnitude, and the substances cypermethrin (Ins), aclonifen (Hrb), pendimethalin (Hrb) and lambda-cyhalothrin (Ins) present the most significant contribution to IS_{crop_ha}, which his nearly 70% (see Table S9 in SI). The large IS_{crop_ha} for peas-2015, almost double than precedent years, is mainly explained by the bloated use of aclonifen (Hrb). This intensification of herbicide treatments in 2015 could be potentially associated with the emergence of weed infestation in peas productions fields. Moreover, the sharp increment on IS_{crop_ha} in part is explained by the dose increment by hectare and the relatively high CF for direct emissions to surface water of aclonifen (SI, Table S5), which is driven by a significant EF ($1.3x10^{+4}$ PAF m^3 kg^{-1}). Furthermore, it is important to note that even if some substances have a high CF; their use could be justified at low doses, because of their agronomic importance and effectiveness of pest or disease control.

The contribution by pesticide target class to freshwater IS_{crop_ha} can be observed in Figure 5. Insecticides is the class that contributes in more significant proportion (56%) to impact scores, followed by herbicides (36.4%) and fungicides (7%); plant growth regulators were not included in Figure 5 as their contribution to IS_{crop_ha} and IS_{crop_DK} was lower than 1%.

Figure 5.

It is well known that pesticide treatments are a highly dynamic activity that varies year by year. Although, it could be more static for herbicides than for the other classes (i.e. insecticides and fungicides) that are more closely correlated with the specific climatic conditions on the area and year of study and thus also the emergence of any specific pest or disease. If these dynamics are to be considered in LCI and LCIA modeling choices, the relevant data (on, *e.g.*, pesticide treatment and crop characteristics) have to be consistently reported (Fantke et al., 2016). As mentioned before IS_{crop_ha} did not follow the same trends of pesticide use, likewise, IS_{crop_ha} did not correlate with use by crop (R2=0.0006) or by AI. Similar trends of crop impacts on freshwater ecosystems (unallocated values by hectare and year) are obtained by Nordborg et al. (2014) for the cultivation of maize, rapeseed and winter wheat for biofuel feedstock production; Parajuli et al. 2017 for grass, maize and winter wheat straw for bio-refinery, and Schmidt Rivera et al. 2017 for barley production in Italy and Denmark. The studies above mentioned use PestLCI (version 1 or 2) as inventory model and USEtox 1.01 as characterization method for the impact assessment. Therefore, using a less data demanding a simplified approach could lead to same results for substance prioritization. Despite the similarities in the trends of IS_{crop_ha}, when comparing the results with the absolute values of AI use per 1 ha in a given crop, the IS_{crop_ha} are up to 2.2 orders of magnitude higher; considering the uncertainty range of the characterization method (between 1-2 orders of magnitude) this difference might be moderately significant, and more probably associated with the difference in the LCI and the emission modeling framework.

3.4 Effects of modeling choices on ecotoxicity impact assessment

3.4.1 Comparing the LCI modeling choices

There are very different approaches and assumptions in order to provide emission estimates for quantifying lifecycle emission inventories of pesticides in any LCA study involving agricultural systems. The most simplified approaches are based on generic assumptions regarding varying percentages for pesticide application, the modeling framework of Margni et al., (2002) is used in several agricultural LCA studies. A different approach is the dynamic emission modeling used in PestLCI. This model estimates emissions to three environmental compartments: air, surface water and groundwater. It considers the agricultural field down to 1 m depth into the soil and up 100 m into the air as part of the technosphere, thus excluding emissions to soil on-field and off-field (Birkved and Hauschild, 2006; Dijkman et al., 2012). The main differences between the methods are the underlining assumptions, the definition and alignment between LCI and LCIA and the data requirements for quantifying pesticides emissions. In this sense, modeling approaches that allowed the inclusion of agricultural soil in the assessment and that involve simplified assumptions for at least application methods were selected in order to test the effects on the impact scores from the emission model choice. The selected methodologies are described in section 2.5, and the results between the three approaches (BS, AS1 and AS2) were compared between the five crops in the 3-year period. The median results for f_{em} in the BS are 2.5 and 1.5 orders of magnitude lower than the emissions for the AS1 and AS2. When modeling f_{em_air} the difference is smaller in comparison with the variations of f_{em_fw} between the three scenarios. Consequently, the variations in the emission fractions lead to further changes in the estimated impact scores.

Results for IS_{crop_ha} in [PAF m^3 d ha^{-1}] with the BS and the AS1 and AS2 are summarized in Table 2. BS presented the lowest impact results across all crops and years; the highest impact results appear in AS1, whereas, AS2 showed higher impacts than BS but within 1 order of magnitude of difference. High variability in IS_{crop_ha} results within BS and AS2 approaches were observed.

Table 2.

The Tukey test was conducted to determine statistical differences in the impact assessment of the three modeling approaches tested. The differences in results of BS and AS1 are statistically significant. Meanwhile, the results for AS2 were statistically similar to BS.

The delineation between pesticide emission inventory and the impact assessment has shown to have considerable influence on the estimation of ecotoxicity impacts of AI and the impact profiles of crop production (Rosenbaum et al., 2015; van Zelm et al., 2014). However, that alone is not the only explanatory reason for the lower IS_{crop_ha} results. The consideration of intermedia processes, crop growth development and application method allow for a more accurate estimation of the real phenomena, which are also the aspects that usually have the highest influence on LCI and LCIA models (Dijkman et al., 2012; Fantke et al., 2012).

Furthermore, the consistency showed for trend results of others studies using PestLCI (a more sophisticated emission modeling approach) compared to the BS results are satisfactory (see section 3.3). Keeping in mind that such a model is much more data demanding and since IS_{crop_ha} represent potential impacts rather than actual damages, the substance prioritization with a simplified method as the BS may serve as a first proxy in LCA studies when more detailed data are lacking.

3.4.2 Variation from LCIA characterization method version

The range of variation for the CF of all AI in the study with USEtox 2.02 was almost 9 orders of magnitude. FF and XF vary by near 2 orders of magnitude, while EF varies up to 7 orders of magnitude indicating substantial differences in pesticide-specific ecotoxicity potential. The variation in the CF for direct emissions to surface water, continental air or agricultural soil was near to 10 orders of magnitude, but CF for direct emissions to continental air and agricultural soil was lower than the CF for direct emissions to freshwater (3 and 2 orders of magnitude, respectively). From which, the importance of modeling the impacts of the dose applied, with a coherent coupling of the LCI to the LCIA model results (i.e. characterized results).

Results for IS_{crop_ha} in the base scenario (BS) and USEtox version 1.0 and 2.02 are summarized in Table 3. The more substantial differences in the impact results from both USEtox versions are the AI coverage, with version 1.01 covering fewer AI; thus, IS_{crop_ha} characterized with v 1.0 are lower in most of the cases due to AI coverage, as expected. Furthermore, significant improvements and scientific consensus have been achieved for the new features introduced in the USEtox version 2.02 among which substances and updated substance data and continent-specific landscape parameters contribute to further improving the accuracy in the quantification of CFs. An example of this, are the results for Peas 2013 to 2015, were all IA were included in both USEtox versions, and IS_{crop_ha} were within the same order of magnitude but between 3 to 6 times larger.

Table 3.

3.4.3 Sensitivity analysis

The results on the evaluation of ecotoxicity impact profiles in Danish crop production demonstrate that modeling freshwater ecotoxicity impacts with the BS and USEtox 2.0 allows to recognize trends of different pesticides treatments and burdens on freshwater ecosystems, thus accounting for interactions between different compartments and a defined clear interface between LCI and LCIA (Figure 1).

The variations of the emission fractions to air, surface water and soil were 6 orders of magnitude. Given the input parameter sensitivity analysis presented in the Supplementary material SI, SI-5, the primary sources of uncertainty in the proposed emission modeling framework are identified as i) the application method and the drift fractions, and ii) the allocation for the off-field emission, specifically the water to soil ratio (as shown in figure 6). Although, the uncertainty range associated with pesticide emissions have not yet been quantified and is beyond the scope of the present study.

The uncertainty of CFs (USEtox 2.02) due to emissions to air, freshwater and agricultural soil is 176, 18 and 103 GSD^2 (Rosenbaum, 2016). The major sources of uncertainty are substances half-lives and ecotoxicity EF (Henderson et al., 2011). Furthermore, in comparison with the FF and XF, the EF shows a substantial variation among the substances covered in this study, explaining a large part of the variations in the CFs for the AI after emissions to freshwater.

4 CONCLUSIONS

LCI modeling options do affect the ecotoxicological burden on freshwater ecosystems from pesticide use, and directly affects substance prioritization in LCA studies. Furthermore, the updated CF with the continent-specific landscape parameters contributes to a broader assessment. In the case of scenario and sensitivity analysis, the main findings identified application method and allocation for the off-field emission, as the main descriptors for modeling emissions of pesticides. The use of the modeling framework presented in this study allows delivering more robust results and accurately evaluation of ecotoxicity impacts. Finally, to provide consumers and policymakers with more reliable information on the environmental performances of agricultural systems, LCA studies need to include all relevant emission outputs; therefore, a final consensus needs to be reached with a specific emission model recommendation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the PhD stage of Nancy Peña at the Agroecology department of Aarhus University financed by the European Commission under the Seventh Framework Program FP7-KBBE.2010.1.2-02, for the Collaborative Project SOLID (Sustainable Organic Low-Input Dairying; grant agreement no. 266367). This work was financially supported by a scholarship granted by the Colombian Government through COLCIENCIAS. Authors would also thank the support from "*CERCA Program Generalitat de Catalunya*" and Erica Montemayor for the proofreading.

APPENDIX A. SUPORTING INFORMATION

The following is the supplementary material related to this article. Detailed information of scenarios, physicochemical properties and data on pesticide active ingredients, further annotations on pesticide emission quantification, data and sources for the derivation of new CFs, as well as supporting materials for results and sensitivity analysis included in the study are provided in the Supporting information.

REFERENCES

Anton, A., Torrellas, M., Nuñez, M., Sevigne, E., Amores, M.J., Muñoz, P., Montero, J.I., 2014. Improvement of Agricultural Life Cycle Assessment Studies through Spatial Di ff erentiation and New Impact Categories: Case Study on Greenhouse Tomato Production. Environ. Sci. Technol. 48, 9454–9462.

Balsari, P., Marucco, P., Tamagnone, M., 2007. A test bench for the classification of boom sprayers according to drift risk. Crop Prot. 26, 1482–1489. doi:10.1016/j.cropro.2006.12.012

Birkved, M., Hauschild, M.Z., 2006. PestLCI-A model for estimating field emissions of pesticides in agricultural LCA. Ecol. Modell. 198, 433–451. doi:10.1016/j.ecolmodel.2006.05.035

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. Int. J. Life Cycle Assess. 17, 973–986. doi:10.1007/s11367-012-0439-2

European Commission, 2017. Food Safety - Plants-Pesticides [WWW Document]. URL https://ec.europa.eu/food/plant/pesticides_en (accessed 10.20.17).

Fantke, P. (Ed), Bijster, M., Guignard, C., Hauschild, M., Huijbregts, M., Jolliet, O., Kounina, A., Magaud, V., Margni, M., McKone, T.., Posthuma, L., Rosenbaum, R.., van de Meent, D., van Zelm, R., 2017. USEtox® 2.0 Documentation (Version 1) [WWW Document]. URL http://usetox.org

Fantke, P., Arnot, J.A., Doucette, W.J., 2016. Improving plant bioaccumulation science through consistent reporting of experimental data. J. Environ. Manage. 181, 374–384. doi:10.1016/j.jenvman.2016.06.065

Fantke, P., Charles, R., Alencastro, L.F. de, Friedrich, R., Jolliet, O., 2011a. Plant uptake of pesticides and human health: Dynamic modeling of residues in wheat and ingestion intake. Chemosphere 85, 1639–1647. doi:10.1016/j.chemosphere.2011.08.030

Fantke, P., Juraske, R., Antón, A., Friedrich, R., Jolliet, O., 2011b. Dynamic multicrop model to characterize impacts of pesticides in food. Environ. Sci. Technol. 45, 8842–8849. doi:10.1021/es201989d

Fantke, P., Wieland, P., Juraske, R., Shaddick, G., Itoiz, E.S., Friedrich, R., Jolliet, O., 2012. Parameterization models for pesticide exposure via crop consumption. Environ. Sci. Technol. 46, 12864–12872. doi:10.1021/es301509u

Felsot, A.S., Unsworth, J.B., Linders, J.B.H.J., Roberts, G., Rautman, D., Harris, C., Carazo, E., 2010. Agrochemical spray drift; assessment and mitigation—A review*. J. Environ. Sci. Heal. Part B 46, 1–23. doi:10.1080/03601234.2010.515161

Gil, E., Gallart, M., Llorens, J., Llop, J., Bayer, T., Carvalho, C., 2014. Spray adjustments based on LWA concept in vineyard. Relationship between canopy and coverage for different application settings. Asp. Appl. Biol. 122, 25–32.

Gil, Y., Sinfort, C., 2005. Emission of pesticides to the air during sprayer application: A bibliographic review. Atmos. Environ. 39, 5183–5193. doi:10.1016/j.atmosenv.2005.05.019

Goglio, P., Smith, W.N., Grant, B.B., Desjardins, R.L., Gao, X., Hanis, K., Tenuta, M., Campbell, C.A., McConkey, B.G., Nemecek, T., Burgess, P.J., Williams, A.G., 2018. A comparison of methods to quantify greenhouse gas emissions of cropping systems in LCA. J. Clean. Prod. 172, 4010–4017. doi:10.1016/j.jclepro.2017.03.133

Gyldenkærne, S., Ravn, H.P., Halling-Sørensen, B., 2000. The effect of dimethoate and cypermethrin on soil-dwelling beetles under semi-field conditions. Chemosphere 41, 1045–1057. doi:10.1016/S0045-6535(99)00511-1

Gyldenkrne, S., Secher, B.J.M., Nordbo, E., 1999. Ground deposit of pesticides in relation to the cereal canopy density. Pestic. Sci. 55, 1210–1216. doi:10.1002/(SICI)1096-

9063(199912)55:12<1210::AID-PS76>3.0.CO;2-6

Hauschild, M.Z., Huijbregts, M.A.J., 2015. Introducing Life Cycle Impact Assessment, in: Hauschild, M., Huijbregts, M.A.J. (Eds.), The International Journal of Life Cycle Assessment. pp. 66–70. doi:10.1007/BF02978760

Henderson, 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.K., Jolliet, O., 2011. USEtox fate and ecotoxicity factors for comparative assessment of toxic emissions in life cycle analysis: Sensitivity to key chemical properties. Int. J. Life Cycle Assess. 16, 701–709. doi:10.1007/s11367-011-0294-6

Itoiz, E.S., Fantke, P., Juraske, R., Kounina, A., Anton, A., 2012. Deposition and residues of azoxystrobin and imidacloprid on greenhouse lettuce with implications for human consumption. Chemosphere 89, 1034–1041. doi:10.1016/j.chemosphere.2012.05.066

Jolliet, O., Müller-Wenk, R., Bare, J., Brent, A., Goedkoop, M., Heijungs, R., Itsubo, N., Peña, C., Pennington, D., Potting, J., Rebitzer, G., Stewart, M., Udo de Haes, H., Weidema, B., 2004. The LCIA Midpoint-damage Framework of the UNEP/SETAC Life Cycle Initiative. Int. J. Life Cycle Assess. 9, 394–404.

Juraske, R., Antón, A., Castells, F., Huijbregts, M.A.J., 2007. Human intake fractions of pesticides via greenhouse tomato consumption: Comparing model estimates with measurements for Captan. Chemosphere 67, 1102–1107. doi:10.1016/j.chemosphere.2006.11.047

Margni, M., Rossier, D., Crettaz, P., Jolliet, O., 2002. Life cycle impact assessment of pesticides on human health and ecosystems. Agric. Ecosyst. Environ. 93, 379–392. doi:10.1016/S0167-8809(01)00336-X

Nordborg, M., Cederberg, C., Berndes, G., 2014. Modeling potential freshwater ecotoxicity impacts due to pesticide use in biofuel feedstock production. Environ. Sci. Technol. 48, 111379–11388.

Notarnicola, B., Sala, S., Anton, A., McLaren, S.J., Saouter, E., Sonesson, U., 2017. The role of life cycle assessment in supporting sustainable agri-food systems: A review of the challenges. J. Clean. Prod. 140, 399–409. doi:10.1016/j.jclepro.2016.06.071

Olesen, M.H., Jensen, P.K., 2013. Collection and evaluation of relevant information on crop interception. EFSA Support. Publ. 10, 438E–n/a. doi:10.2903/sp.efsa.2013.EN-438

Ørum, J.E., Holtze, M.S., 2017. Bekæmpelsesmiddel- statistik 2015 Behandlingshyppighed og pesticidbelastning , baseret sprøjtejournaldata, Orientering fra Miljøstyrelsen.

Ørum, J.E., Hossy, H., 2015. Bekæmpelsesmiddelstatistik 2014. Orientering fra Miljøstyrelsen nr. 13.

Ørum, J.E., Samsøe-Petersen, L., 2014. Bekæmpelsesmiddelstatistik 2013. Orientering fra Miljøstyrelsen nr- 6. København.

Panagos, P., Borrelli, P., Meusburger, K., Alewell, C., Lugato, E., Montanarella, L., 2015. Estimating the soil erosion cover-management factor at the European scale. Land use policy 48, 38–50. doi:10.1016/j.landusepol.2015.05.021

Parajuli, R., Kristensen, I.S., Knudsen, M.T., Mogensen, L., Corona, A., Birkved, M., Peña, N., Graversgaard, M., Dalgaard, T., 2017. Environmental life cycle assessments of producing maize, grass-clover, ryegrass and winter wheat straw for biorefinery. J. Clean. Prod. 142, 3859–3871. doi:10.1016/j.jclepro.2016.10.076

Rosenbaum, R., Anton, A., Bengoa, X., Bjorn, A., Brain, R., Bulle, C., Cosme, N., Dijkman, T.J., Fantke, P., Felix, M., Geoghegan, T.S., Gottesburen, B., Hammer, C., Humbert, S., Jolliet, O., Juraske, R., Lewis, F., Maxime, D., Nemecek, T., Payet, J., Rasanen, K., Roux, P., Schau, E.M., Sourisseau, S., van Zelm, R., von Streit, B., Wallman, M., 2015. The Glasgow consensus on the delineation between pesticide emission inventory and impact assessment for LCA. Int. J. Life Cycle Assess. 20, 765–776. doi:10.1007/s11367-015-0871-1

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., Schuhmacher, M., Meent, D. van de, Hauschild, M.Z., 2008. USEtox—the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. Int J Life Cycle Assess 13, 532–546.

Schmidt Rivera, X.C., Bacenetti, J., Fusi, A., Niero, M., 2017. The influence of fertiliser and pesticide emissions model on life cycle assessment of agricultural products: The case of Danish and Italian barley. Sci. Total Environ. 592, 745–757. doi:10.1016/j.scitotenv.2016.11.183

Stockmarr, J., Thomsen, R., 2009. Water supply in Denmark. The Danish action plan for promotion of eco-efficient technologies, Danish Ministry of Environment.

van de Zande, J.C., Michielsen, J.M.G.P., Stallinga, H., 2007. Spray drift and off-field evaluation of agrochemicals in the Netherlands.

van Zelm, R., Larrey-Lassalle, P., Roux, P., 2014. Bridging the gap between life cycle inventory and impact assessment for toxicological assessments of pesticides used in crop production. Chemosphere 100, 175–181. doi:10.1016/j.chemosphere.2013.11.037

Webb, J., Hutchings, N., Amon, B., 2016. EMEP/EEA air pollutant emission inventory Guidebook.

Westh, T.B., Hauschild, M.Z., Birkved, M., Jørgensen, M.S., Rosenbaum, R.K., Fantke, P., 2015. The USEtox story: a survey of model developer visions and user requirements. Int. J. Life Cycle Assess. 20, 299–310. doi:10.1007/s11367-014-0829-8

Tables and table captions

Table 1. Comparison of pesticide emission fractions fem calculated by the BS (reference scenario), AS1 (Margni et al. 2002) and AS2 (application method and crop relation).

Emission scenarios	Average fraction emitted [kg kg^{-1}]	Standard deviation on fractions
BS		
f_{em_air}	$1.16\text{x}10^{-1}$	$2.03\text{x}10^{-1}$
f_{em_fw}	$1.60\text{x}10^{-3}$	0
$f_{em\_soil.agri}$	$3.75\text{x}10^{-1}$	$3.11\text{x}10^{-1}$
$f_{em\_soil.other}$	$8.70\text{x}10^{-2}$	$2.01\text{x}10^{-2}$
AS1		
f_{em_air}	$1.00\text{x}10^{-1}$	0
f_{em_fw}	$5.00\text{x}10^{-2}$	0
f_{em_soil}	$8.50\text{x}10^{-1}$	0
AS2		
f_{em_air}	$1.70\text{x}10^{-1}$	0
f_{em_fw}	$1.00\text{x}10^{-2}$	0
f_{em_soil}	$4.50\text{x}10^{-1}$	0

Table 2. Comparison of scenarios to test different emission modeling approaches. Results for potential freshwater ecotoxicity impact scores IS_{crop_ha} in [PAF m3 d ha^{-1}] in the base scenario (BS) and alternative scenarios AS1 and AS2

Crop	**BS**			**AS1**			**AS2**		
	2013	**2014**	**2015**	**2013**	**2014**	**2015**	**2013**	**2014**	**2015**
Maize	513	92	50	14370	2261	582	3041	475	138
Grass	17	11	13	219	141	169	51	31	37
Winter wheat	2210	434	551	58522	11790	14879	12410	2502	3154
Spring Barley	2086	458	631	64214	12888	18305	13514	2701	3808
Rape	1880	921	1394	56586	17682	33144	12244	4144	7267
Peas	3454	2928	6440	110166	69469	120016	23547	14653	26057

Table 3. Comparison of scenarios to test developments of LCIA characterization method. Results for potential freshwater ecotoxicity impact scores IS_{crop_ha} in [PAF m3 d ha^{-1}] in the base scenario (BS) and USEtox version 1.0 and 2.02

Crop	**BS - USEtox 1.0**			**BS - USEtox 2.02**		
	2013	**2014**	**2015**	**2013**	**2014**	**2015**
Maize	246	63	146	513	92	50
Grass	24	12	14	17	11	13
Winter wheat	1349	445	1223	2210	434	551
Spring Barley	758	267	390	2086	458	631
Rape	776	563	702	1880	921	1394
Peas	**1483**	**1893**	**6080**	**3454**	**2928**	**6440**
Glyphosate Agri-use	24	12	17	14	6	8

Figures and figure captions

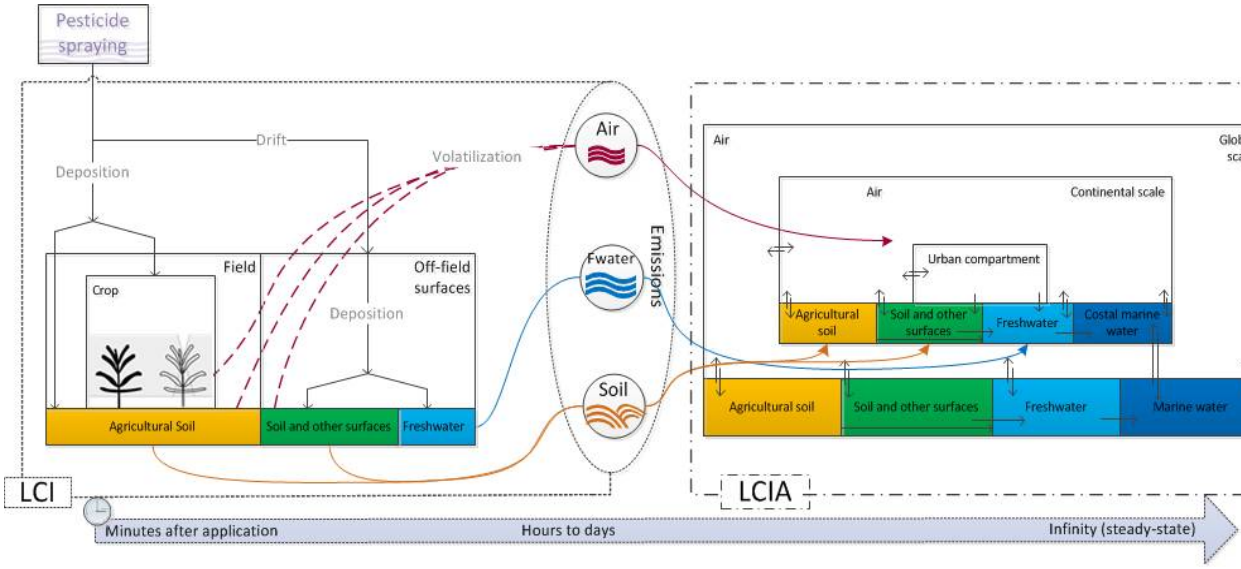

Figure 1. Interface between LCI and LCIA for pesticide application in crop production**.**

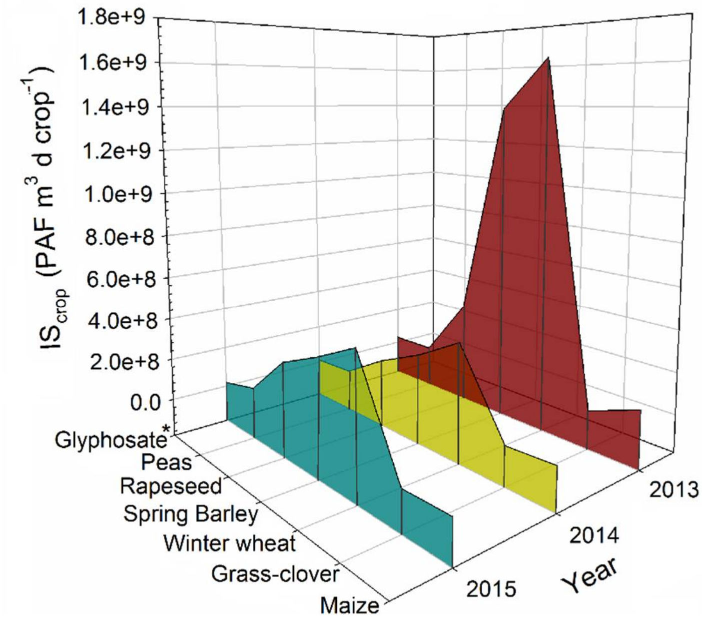

Figure 2. Freshwater ecotoxicity impact profiles for crop production (2013-2015), impact scores IS_{crop} in [PAF m^3 d $crop^{-1}$]. *Glyphosate (CAS107-83-6) assessed as the total agricultural use in Denmark.

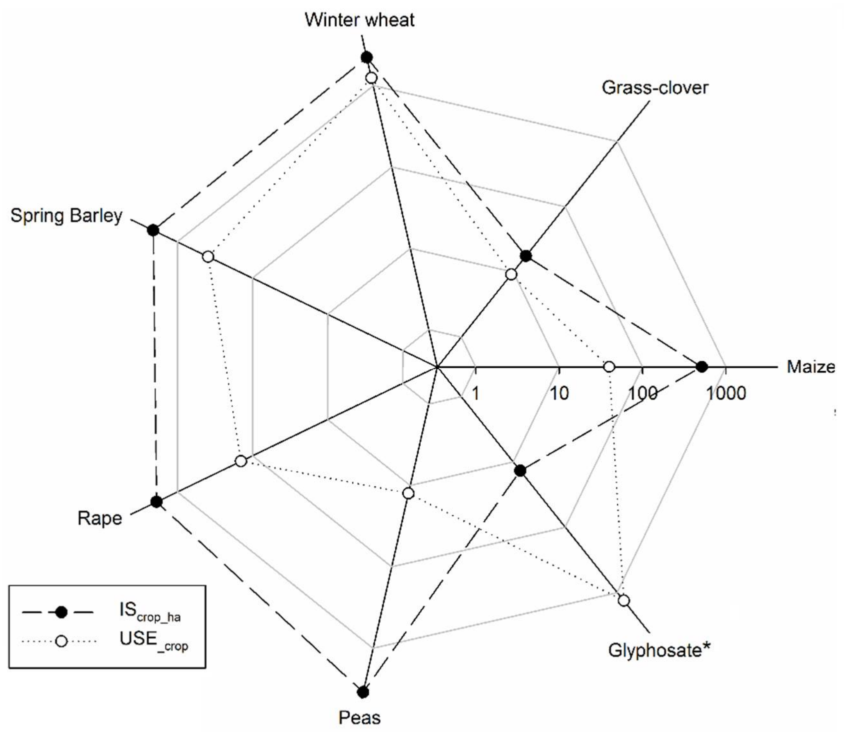

Figure 3. Comparison between use of pesticide active ingredient (USE_crop) [tones] and potential freshwater ecotoxicity impacts (IS_{crop_ha}) [PAF m3 d ha^{-1}] for 5 analyzed crops 2013 and *Glyphosate (CAS107-83-6) assessed as the total agricultural use in Denmark in logarithmic scale.

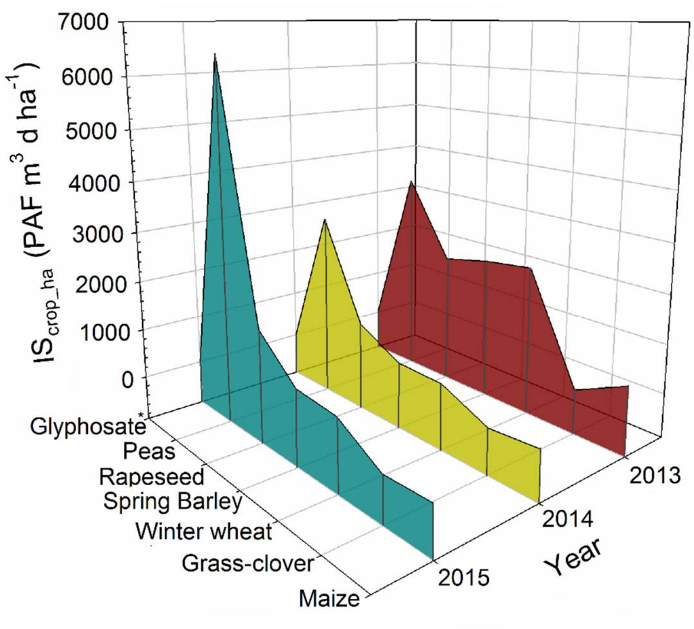

Figure 4. Pressure of pesticide impact scores by hectare of crop cultivated for Danish crop production (2013-2015), impact scores IS_{crop_ha} in [PAF m^3 d ha^{-1}]. *Glyphosate (CAS107-83-6) assessed as the total agricultural use in Denmark.

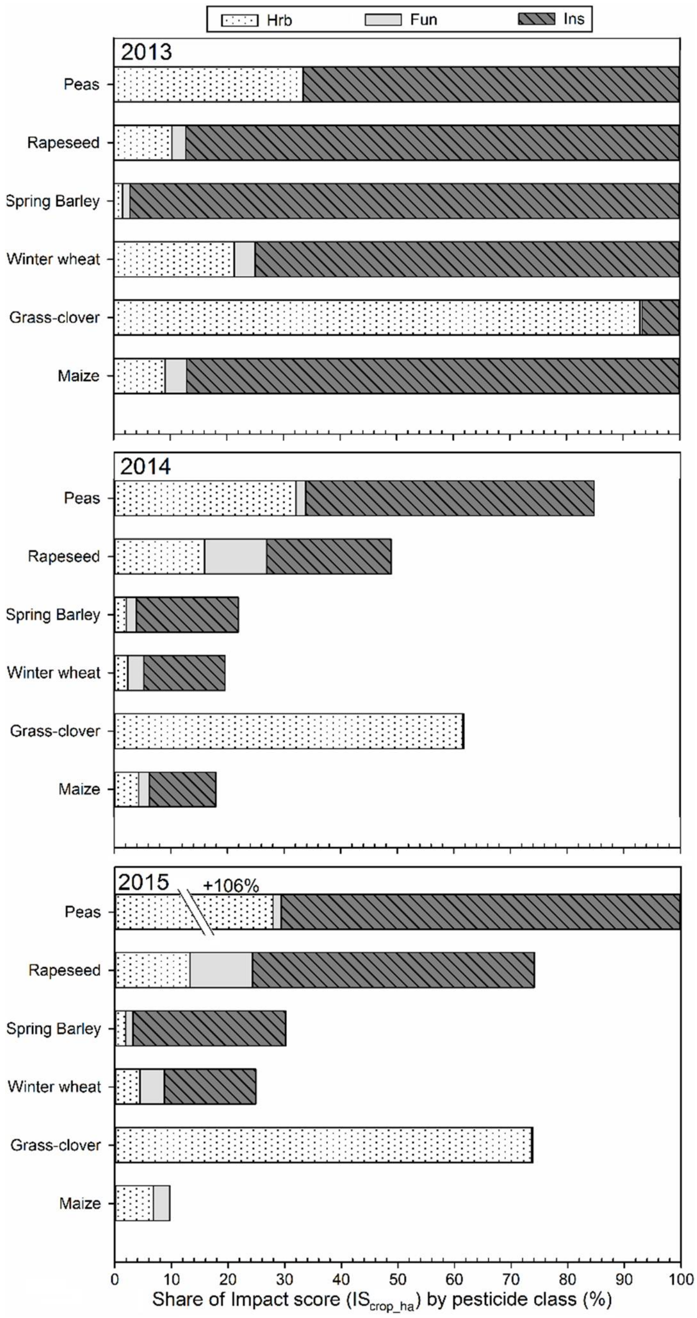

Figure 5. Share of freshwater ecotoxicity impact scores IS_{crop_ha} in [%] by pesticide class herbicides (Hrb), insecticides (Ins) and fungicides (Fun) taking as reference per crop IS_{crop_ha} - 2013 as reference year.

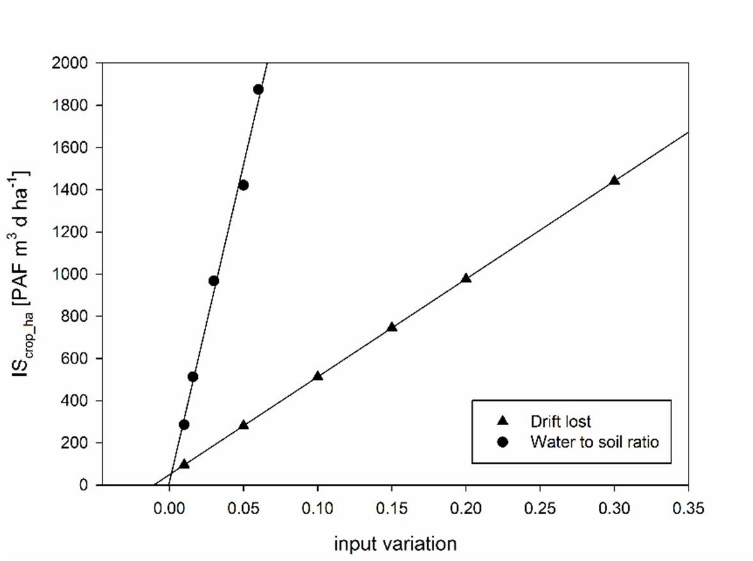

Figure 6. Sensitivity to model input parameters of BS. Variation for ecotoxicity impact scores (IS_{crop_ha}) in [PAF m^3 d ha^{-1}] of Maize in 2013 (Mz-13)