

PestLCI 2.0: a second generation model for estimating emissions of pesticides from arable land in LCA

T. J. Dijkman · M. Birkved · M. Z. Hauschild

Received: 23 December 2011 / Accepted: 4 May 2012 / Published online: 30 May 2012
© Springer-Verlag 2012

Abstract

Purpose The spatial dependency of pesticide emissions to air, surface water and groundwater is illustrated and quantified using PestLCI 2.0, an updated and expanded version of PestLCI 1.0.

Methods PestLCI is a model capable of estimating pesticide emissions to air, surface water and groundwater for use in life cycle inventory (LCI) modelling of field applications. After calculating the primary distribution of pesticides between crop and soil, specific modules calculate the pesticide's fate, thus determining the pesticide emission pattern for the application. PestLCI 2.0 was developed to overcome the limitations of the first model version, replacement of fate calculation equations and introducing new modules for macropore flow and effects of tillage. The accompanying pesticide database was expanded, the meteorological and soil databases were extended to include a range of European climatic zones and soil profiles. Environmental emissions calculated by PestLCI 2.0 were compared to results from the risk assessment models SWASH (surface water emissions), FOCUSPEARL (groundwater via matrix leaching) and MACRO (groundwater including macropore flow, only one scenario available) to partially validate the updated model. A case study was carried out to demonstrate the spatial variation of pesticide emission patterns due to dependency on meteorological and soil conditions.

Results Compared to PestLCI 1.0, PestLCI 2.0 calculated lower emissions to surface water and higher emissions to groundwater. Both changes were expected due to new pesticide fate calculation approaches and the inclusion of macropore flow. Differences between the SWASH and FOCUSPEARL and PestLCI 2.0 emission estimates were generally lower than 2 orders of magnitude, with PestLCI generally calculating lower emissions. This is attributed to the LCA approach to quantify average cases, contrasting with the worst-case risk assessment approach inherent to risk assessment. Compared to MACRO, the PestLCI 2.0 estimates for emissions to groundwater were higher, suggesting that PestLCI 2.0 estimates of fractions leached to groundwater may be slightly conservative as a consequence of the chosen macropore modelling approach. The case study showed that the distribution of pesticide emissions between environmental compartments strongly depends on local climate and soil characteristics.

Conclusions PestLCI 2.0 is partly validated in this paper. Judging from the validation data and case study, PestLCI 2.0 is a pesticide emission model in acceptable accordance with both state-of-the-art pesticide risk assessment models. The case study underlines that the common pesticide emission estimation practice in LCI may lead to misestimating the toxicity impacts of pesticide use in LCA.

Keywords Emission modelling · LCI · Life cycle inventory modelling · Pesticide · PestLCI

Responsible editor: Ivan Muñoz

Electronic supplementary material The online version of this article (doi:10.1007/s11367-012-0439-2) contains supplementary material, which is available to authorized users.

T. J. Dijkman (✉) · M. Birkved · M. Z. Hauschild
Department of Management Engineering,
Technical University of Denmark,
2800 Lyngby, Denmark
e-mail: tedi@dtu.dk

1 Introduction

Pesticides are designed to have a toxic effect on various organisms and hence have a high bioactivity. The bioactivity of pesticides is most active towards target organisms but still

highly active towards similar or even quite different organisms (see for example Thompson 1996; Oturan et al. 2008; Mitra et al. 2011). Pesticides are therefore likely to have an effect on a broad range of organisms, no matter whether these organisms are the intended target for the applied plant protection chemical or not. In order to assess the off-target toxicity impact potential caused by pesticide emissions in life cycle assessment (LCA), accurate estimates of the fraction of the applied pesticide emitted to the environment are required.

In the current life cycle inventory (LCI) practice, it is usually assumed that the full dose of applied pesticide is emitted to one environmental compartment. For example, in EcoInvent (Swiss Centre for Life Cycle Inventories 2011), it is assumed that the full pesticide dose is emitted to soil (Nemecek and Kägi 2007). Depending on the definition of the borders between technosphere and environment, these (simplifying) assumptions can be challenged. Assuming the field borders are defined as presented in Birkved and Hauschild (2006), where the field is considered to belong to the production system, the technosphere therefore includes the agricultural soil down to 1-m depth and the air column above it, only a fraction of the applied dose will be emitted from the technosphere to the environment due to pesticide loss processes such as degradation or uptake occurring within the technosphere. Assuming that the full applied dose is emitted to soil further neglects the pesticide distribution processes occurring in the field, such as deposition on plants, volatilization, runoff and soil leaching that determine the emissions to the environment, and are therefore part of the LCI.

In order to estimate pesticide emissions from an agricultural field, i.e. the technosphere, the first version of PestLCI was developed specifically for use in LCI (Birkved and Hauschild 2006). The model estimates emissions to three general environmental compartments: air, surface water and groundwater. As a consequence of the narrow sets of soil and climate data included in the model, PestLCI 1.0's applicability was limited to Denmark. In addition, the model neglected preferential flow of water through macropores that provide a quick path for pesticide leaching to groundwater (Kördel et al. 2008), i.e. facilitated leaching.

In order to overcome the limited data coverage of the model databases and the modelling gaps, a new version of the model was developed: PestLCI 2.0. Apart from extending the model applicability to the whole of Europe and including macropore flow, many of the fate modules present in PestLCI 1.0 were remodelled in order to include recent scientific developments. Together, these developments have led to an almost completely new model in PestLCI's framework.

The aim of this paper is to present the most recent PestLCI model, PestLCI 2.0, to compare results obtained with the new model to two dedicated pesticide risk assessment models, and to demonstrate the climate and soil specificity of the emission pattern of a pesticide across Europe,

both for the total emitted fraction and the distribution of the emissions over air, surface water and groundwater.

2 Methods

In this section, the overall model layout is presented together with a brief description of the updates, expansions and new modules of PestLCI 2.0. The supporting information provides a detailed documentation of the new equations used in the model.

2.1 Overall model structure and modelling platform

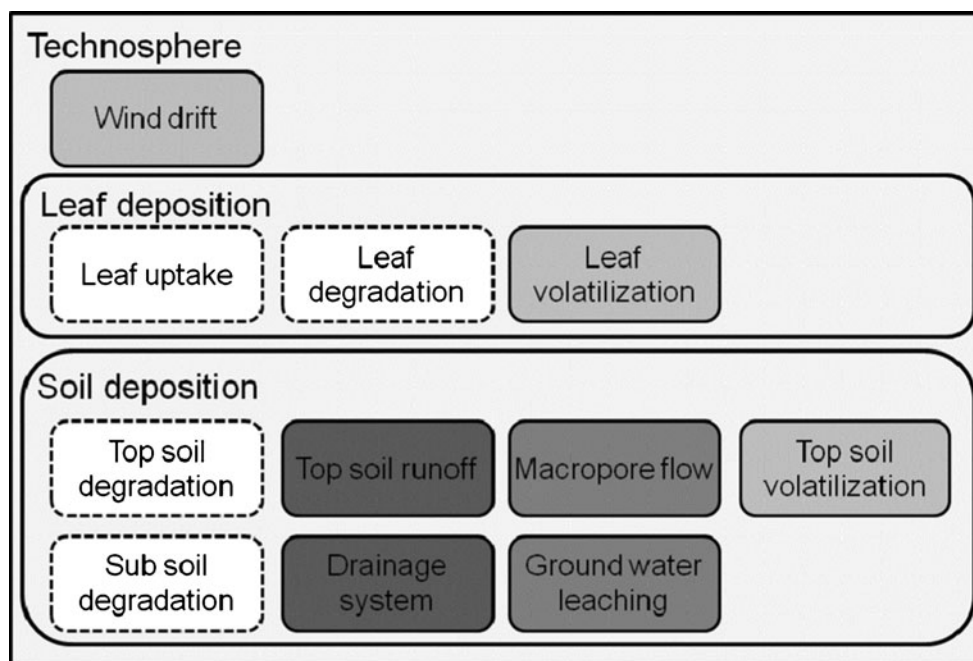
PestLCI 2.0 estimates the fraction of pesticide applied in the technosphere that crosses the technosphere-environment borders and thereby becomes an emission to the environment. The technosphere, which can be regarded as a 'field box', which follows the field borders of an arable field of user-determined dimensions reaches 1 m down in the soil column and extends 100 m up into the air column above the soil (i.e. a 101-m high box with a bottom area equal to the field area). The rationale of including the agricultural field in the technosphere is explained by Birkved and Hauschild (2006).

The model takes into account emissions to three environmental compartments: air, surface water and groundwater. Emissions to soils outside the technosphere are not included in the model, because emissions to soil compartments can only occur indirectly after emission of pesticide to air, surface water or groundwater: there is no direct path for transport of a pesticide from a crop or soil inside the technosphere to a soil outside the technosphere. PestLCI 2.0 calculates emissions from the technosphere for use in LCI and subsequently LCA. The final fate of the pesticide after emission to the environment is handled by characterization models as applied in life cycle impact assessment such as USEtox (Rosenbaum et al. 2008).

The PestLCI approach is based upon fate and exposure modelling principles as applied in relation to risk assessment of single chemical substances (as presented by, e.g. Mackay (2001), van Leeuwen and Hermens (1995) and EU (European Communities 2003)). The model is hence only valid for emission modelling of single substances. Pesticide products consists of a several single chemical compounds (solvents, active ingredients, wetting agents, dispersing agents, fillers, stickers etc.), PestLCI 2.0 has only been validated on the active ingredients of pesticide products, but PestLCI could in principle be applied for emission assessment of all pesticide product compounds (i.e. one substance at a time) as far as these compounds fall within chemical the ranges for which the model has been validated.

Figure 1 provides an overview of the model structure, distinguishing between primary and secondary distribution

Fig. 1 PestLCI 2.0 model structure. Primary distribution processes determine the fraction deposited on leaves and soil, and the fraction emitted by wind drift. After that, secondary distribution processes take place on leaves and in soil. Processes leading to emissions to air are marked *light grey*, emissions to surface water in *dark grey*, emissions to ground water in *medium grey*. Removal through degradation and uptake into leaves are marked in *white*



processes. Primary distribution processes are the initial distribution processes taking place in conjunction with the pesticide application. The primary processes determine the fractions of pesticide active ingredient deposited on leaves and on soil or emitted to air by wind drift. Thus, the primary distribution defines the starting conditions for further calculations. Secondary distribution processes account for the fate processes in the period after application.

From Fig. 1, it can be seen that after the primary distribution of pesticides over leaves and soil has taken place, PestLCI 2.0 takes into account three secondary fate processes on leaves: volatilization, degradation and uptake. These secondary processes take place in parallel, starting immediately after application and ending at the start of the first precipitation event after pesticide application. In PestLCI 2.0, it is assumed that any pesticide residue present on leaves at the beginning of the first precipitation event after pesticide application washes off to the soil, independent of the amount of precipitation.

PestLCI 2.0 includes seven secondary fate processes in the soil (see Fig. 1). The topsoil is defined as the upper 1 cm of the soil column. Degradation and volatilization in topsoil are processes that start immediately after application and are assumed to terminate at the start of the first precipitation event. At this point, the pesticide fractions available for runoff, leaching and macropore flow are calculated based on the fraction left in the topsoil plus the fraction being washed off from the leaves. The fraction of pesticide in the top soil after the first precipitation event after pesticide application is assumed to start leaching deeper into the subsoil towards the groundwater. Whilst leaching, the pesticide is subject to biodegradation in soil and may be

intercepted by the drainage system in the field if such a system is installed.

Whilst the modular structure of PestLCI 1.0 has not been changed, the modelling platform of PestLCI 2.0 has been shifted from MS Excel to Analytica 4.2 (Lumina Decision Support 2010). This platform change allows for a more user-friendly interface and increased transparency of the calculations. In addition, the Analytica platform is ideal for the more complex and iterative calculations applied in PestLCI 2.0.

2.2 Primary distribution

The primary distribution processes are pesticide emissions by wind drift (f_d), pesticide deposition on leaves (f_l) and pesticide deposition on soil (f_s). The sum of these three fractions is always 1. The distribution between leaves and soil after wind drift emissions have been taken into account is determined by the leaf interception fraction (Linders et al. 2000), which depends on crop type and the development stage of the crop. Only deposition on leaf surfaces and top soil are included in the primary distribution modelling in PestLCI 2.0. Other surfaces possibly present in the field are not taken into account in the initial distribution step.

For wind drift emissions, seven different loss functions have been added, based on the IMAG Drift Calculator (Holterman and Van de Zande 2003). These additional wind drift loss curves allow the user to select a more accurate representation of the field situation. The loss curves are available for four different crop morphologies (potato, flower bulb, sugar beet and cereals) and bare soil using conventional spray equipment, as well as for cross-flow sprayers used in orchards for leaved and leafless trees. All curves

have been empirically validated up to wind speeds of 4.5 m s^{-1} (Holterman and Van de Zande 2003). Since it is expected that a farmer will seek to minimize application emissions of the costly pesticides due to wind drift, this maximum wind speed is assumed to be valid for use in PestLCI 2.0.

The calculation method for wind drift emissions in PestLCI 2.0 has been further detailed compared to PestLCI 1.0. Instead of basing calculations on the average distance represented by the distance between the middle of the spray boom and the field edge, the distance between field edge and each spray nozzle is now used. Given the shape of the loss curves, with emissions rapidly falling as the distance to field edge increases, this method results in a more accurate calculation of the pesticide emissions across the technosphere border, especially from pesticide sprayed close to the field border. The distance between the sprayer nozzles is by default set to 10 cm; however, this distance can be changed by the user according to preferences.

2.3 Secondary distribution on plants

The secondary distribution processes that are modelled for pesticide deposited on plants are volatilization, uptake and degradation (see Fig. 1). The modelling of each of these three processes in PestLCI 2.0 has, to various degrees, been modified compared to PestLCI 1.0. The individual module changes are summarized in the following paragraphs.

2.3.1 Volatilization from leaves

PestLCI calculates the volatilization from leaves using first-order kinetics. In PestLCI 1.0, each pesticide was assigned one out of the possible three rate constants present in the database, based on the pesticide's air–water distribution coefficient. In order to improve this simplification, a new approach was introduced based on the work of Van Wesenbeeck et al. (2008), who regressed the evaporation rate as a function of a chemical's vapour pressure for chemicals with vapour pressures varying between $1.0 \cdot 10^{-4}$ and $2.2 \cdot 10^4$ Pa. From the evaporation rate of chemicals, the vaporization rate constant at a fixed temperature is calculated, which is then corrected according to the average atmospheric temperature in the month of application. This temperature-corrected vaporization rate constant is used to calculate the fraction of pesticide evaporated from the plant leaves. Electronic supplementary material (ESM) 1 contains the equation set used for this calculation.

2.3.2 Uptake by leaves

The PestLCI approach for pesticide uptake in leaves was based on the assumption that due to the fact that most pesticides are lipophilic molecules (i.e. more soluble in fat

than in water and thus having $\log K_{ow} > 0$), leaf uptake occurs dominantly by diffusion through the cuticle (Korte et al. 2000). The first-order uptake rate of pesticides can then be calculated from the Arrhenius function (Baur and Schönherr 1995). This approach is unchanged, but a new regression was made to establish the rate constant parameters. The new leaf uptake parameters used are found in ESM 1.

2.3.3 Degradation on leaves

Pesticides deposited on the crop leaves are exposed to sunlight and can hence be degraded by either photochemical degradation or by direct photolysis if deposited on the upper side of the leaves. Because little data is available regarding the latter reaction pathway, PestLCI only considers photochemical degradation, through reaction with $\text{OH}\cdot$ radicals as a surrogate for the overall degradation process on leaves. The atmospheric concentration of these radicals depends on the light intensity, and therefore has a strong temporal and spatial variation.

Whilst the modelling approach was not altered for PestLCI 2.0, a new regression was made of the $\text{OH}\cdot$ radical concentration as a function of light intensity, which is used to determine the rate constant, because the regression used in PestLCI 1.0 was found to be inaccurate at high light intensities and therefore inaccurate for southern Europe. As a consequence of the expanded spatial coverage of PestLCI 2.0, the dependency of daylight length on the latitude was included. The new regression as well as the calculation of the daylight length is elaborated in ESM 1.

2.4 Secondary distribution in topsoil and subsoil

Modelling of volatilization, degradation and runoff processes in PestLCI 2.0 has been altered with varying degrees compared to PestLCI 1.0. Since macropores form a quick (i.e. facilitated) leaching path into the subsoil (Kördel et al. 2008), potentially resulting in a dramatic increase of the fraction of pesticides emitted to groundwater, PestLCI 2.0 was expanded to include preferential soil flow in the form of macropore flow. The modelling of conventional pesticide leaching via the soil matrix (piston flow) is unchanged compared to PestLCI 1.0, and therefore we refer to Birkved and Hauschild (2006) for these processes.

2.4.1 Topsoil volatilization

In PestLCI 1.0, the fraction of pesticides emitted by volatilization from soil was calculated through an approach relying on fugacity to calculate a pesticide flux. In contrast, PestLCI 2.0 applies a simplified method requiring fewer input data in which fugacity is used to calculate the rate constant for volatilization, assuming first-order kinetics. The volatilization is

quantified using a fugacity level 3 model, based on the ‘Surface soil model’ by Mackay (2001). In this model, pesticide molecules diffuse through the interstitial air and water in soil, after which they cross the air boundary layer before being considered volatilized. The details of this approach are found in ESM 1.

An improvement included in the current approach is that the organic carbon–water partitioning coefficient required for the calculation of the fugacity capacity of pesticides in soil solids is now dependent on the pH in the topsoil. For ionic pesticides, partitioning can change by several orders of magnitude, depending on the topsoil's pH, and is therefore important to include.

2.4.2 Topsoil biodegradation

The approach used here to calculate the biodegradation rate in the topsoil was not changed, and remains based on the method given by Larsbo and Jarvis (2003): a first-order rate constant for biodegradation in soil is corrected for the soil temperature and moisture content.

For PestLCI 2.0, the method for determining the soil temperature correction factor was modified by introducing a new, simpler equation based on Boesten et al. (1996) for calculation of the correction factor relying on one equation that is valid for the range of top soil temperatures considered in the model. As a second modification, the top soil temperature is no longer assumed to be identical to the temperature of the air. The new equation set used for top soil biodegradation can be found in ESM 1.

2.4.3 Topsoil runoff

The approach applied to quantify runoff in PestLCI 1.0 was valid only when the average monthly maximum daily rainfall was equal to or larger than 17 mm. Since many European regions experience periods with less precipitation, a new approach based on Berenzen et al. (2005) has been introduced in PestLCI 2.0. This approach relies on the ratio of runoff water to precipitation and the fraction of pesticide being present in top soil water. Corrections are done for the field slope and the pesticide-specific buffer zone where pesticide application is prohibited; increasing the distance that runoff water has to cover in order to cross the technosphere border. Details of this new topsoil runoff approach are found in ESM 1.

2.4.4 Macropore flow and tillage

In structured soils such as clays or silty soils, the downward movement of water not only takes place through the soil matrix: often macropores provide a facilitated leaching pathway that bypasses the slow matrix flow (i.e. piston flow).

Macropores may be formed by cracking of a drying soil or by various activities, such as rain worm migration in the soil. As a consequence of the elevated leaching rate caused by the presence of macropores, pesticide emissions to groundwater may be considerably higher than what should be expected from soil matrix flow only (Kördel et al. 2008).

The modelling approach used in PestLCI 2.0 focused on macropore volume and the rate at which water flows through these macropores. Following the approach presented by Hall (1993), the water in soil pores is divided in an immobile and a mobile part. Water does not flow in the ‘immobile’ pores. The ‘mobile’ water is divided in a slow-flowing and a fast-flowing domain. The fast-flowing domain represents the macropores. The volume of water flowing through macropores in PestLCI 2.0 is calculated from the volume of water precipitated during a rainfall event and the water storage capacity of the topsoil. If the storage capacity is exceeded, water starts flowing into macropores. It is assumed that the fraction of pesticide ingredients dissolved in the water flowing through the macropores will quickly reach the groundwater (Villholth et al. 1998) and it is hence considered to be emitted to groundwater without undergoing degradation. For more details on the equations used in the calculation for macropore flow, we refer to ESM 1.

So far, the quantification of macropore flow assumed an undisturbed field in which pores develop through natural processes. Tillage, defined as ‘any mechanical operation on the soil and crop residues that aims at providing a suitable seedbed where crop seeds are sown’ (Alletto et al. 2010), disturbs the soil, thus affecting macropore development and structure. Based on the literature overview presented by Alletto et al. (2010), it was concluded that macropore leaching of pesticides is reduced by a factor 7.5 when the soil is tilled by means of conventional tillage practice. When applying conservation tillage, defined by Alletto et al. (2010) as ‘any tillage and planting system that leaves at least 30 % of the soil surface covered by crop residue after planting to reduce soil erosion by water, or at least 1.1 tons of crop residue/ha to reduce soil erosion by wind’, the leaching is reduced by a factor 3.5. Given the small data foundation for the latter number, conservation tillage leaching estimates have to be applied with care.

2.5 Databases

PestLCI 1.0's applicability was limited to Danish circumstances, because the soil and climate databases only comprised data for one Danish soil and one Danish set of climate data. PestLCI 2.0 aims at application in a European context. For that reason, the climate and soil databases were expanded.

A total of 25 climate sets was included in the expanded database, covering the 16 European climate zones distinguished

in the FOOTPRINT project (see Centofanti et al. 2008). For each of these climate zones, up to three sets of climate data from randomly chosen weather stations within each climate zone were included. Each climate set consists of 10-year averages of monthly average minimum, maximum and average temperatures, monthly average precipitation and number of rain days (Klein Tank et al. 2002), monthly solar irradiation (European Communities 2007) and the potential water balance, calculated from the approach presented by Linacre (1977).

The expanded soil database now contains seven European soil profiles with different compositions, selected from the Spade Database (Hiederer et al. 2006) on basis of varying clay, silt and sand content in order to cover a wide range of likely soil compositions.

Also the pesticide ingredient database was extended by adding the required substance property data for 20 active ingredients of pesticides frequently used in Europe on top of the 70 active ingredients already contained in the PestLCI 1.0 ingredient database.

2.6 Comparison with PestLCI 1.0

Selected scenarios presented by Birkved and Hauschild (2006) were remodelled in PestLCI 2.0 and the results obtained in the two versions of the model were compared. This comparative validation was carried out for two scenarios, summarized in Table 1: 1 kg ha⁻¹ of Bentazone applied in May and August to maize in different growth stages on a 1 ha field using PestLCI 1.0 default settings. The soil profile data and climate data used in PestLCI 1.0 were inserted in PestLCI 2.0. Because monthly minimum and maximum rainfall data were not included in PestLCI 1.0, these were therefore calculated as 10-year averages for the climate station Roskilde-Tune (Geodata 2011). In addition, new solar irradiation data sources were used (European Communities 2007). For the parameters included in PestLCI 2.0 that are not used in PestLCI 1.0, default PestLCI 2.0 settings were applied. A sensitivity analysis performed showed that the sensitivity of these default modelling parameters was at least 2 orders of

magnitude lower than the most sensitive model parameters. Therefore, it can be assumed that the use of these default parameters did not affect the accuracy of the comparison to any considerable extent.

2.7 Comparison of PestLCI with pesticide risk assessment models

Compartment-specific emissions calculated by PestLCI 2.0 were compared with compartment-specific emissions calculated by the pesticide risk assessment models SWASH 3.1 for emissions to surface water (Alterra 2009) and FOCUSPEARL 4.4.4 (RIVM, PBL and Alterra 2011) and MACRO 4.3 (Jarvis 2001) for emissions to groundwater. FOCUSPEARL uses chromatographic flow to estimate emissions to groundwater, which is comparable to the approach to calculate leaching in PestLCI 2.0, but FOCUSPEARL does not take macroporous flow into account. In order to compare the macropore flow, MACRO was applied. This model is a model to calculate 1-dimensional water flows in macroporous soils based on a dual porosity approach.

In SWASH, surface water emissions by drainage and runoff were quantified by application of sub-model, MACRO 4.3 (Jarvis 2001). For this comparison, the compartment-specific emission patterns of the pesticide MCPA, a phenoxy herbicide, were quantified in both risk assessment models and PestLCI 2.0. The properties of MCPA required by the individual models are listed in Table S1 in ESM 2. For all MCPA scenarios, the assumption of one annual application of 1 kg ha⁻¹ applied to cereals was used. The risk assessment models were run mainly using default settings and scenarios (i.e. scenarios provided with the models).

The PestLCI 2.0 settings in this step were chosen to resemble the default settings in SWASH and FOCUSPEARL as closely as possible. With regard to geographical settings, the comparison of MACRO applied in SWASH was done using the four data sets for locations as close as possible to the locations applied in MACRO. The comparison FOCUSPEARL-PestLCI 2.0 was performed using six locations in the same climatic zone, as close as possible to the six locations modelled in FOCUSPEARL.

The months of application modelled in PestLCI 2.0 were June to August for the comparison with SWASH, since the scenarios in SWASH are based on pesticide applications in one of these months, the exact moment depends on the scenario. For the comparison with FOCUSPEARL, the month of application used in the FOCUSPEARL scenarios was also used in PestLCI 2.0.

Since FOCUSPEARL lacks macropore flow, an additional comparison was done using MACRO which includes both matrix flow and macropore flow. Unfortunately, the FOCUS scenarios include only one groundwater scenario

Table 1 Scenarios used for the comparison of PestLCI 1.0 and PestLCI 2.0

Parameter	Scenario 1	Scenario 2
Soil	Tune (DK)	Tune (DK)
Climate	Roskilde-Tune (DK)	Roskilde-Tune (DK)
Crop type	Maize	Maize
Month	May	August
Application type	Field crops	Tall crops
Development stage	Stem elongation	Development of fruit/ripening

for MACRO. Therefore this comparison is a limited validation of the model.

The PestLCI 2.0 soil profile applied in the soil comparison calculations was the ‘average’ profile, which has clay, silt and sand fractions close to the average of the fractions of these constituents found in the Spade database (Hiederer et al. 2010). This average soil profile was applied since it fitted well to the majority of the soil textures used in the SWASH surface water scenarios (FOCUS 2001). The characteristics of the average soil profile are listed in Table S2 in ESM 2.

2.8 Case study

A case study in which PestLCI 2.0 was carried out to quantify the emissions of MCPA applied to potatoes in development stage 2 (formation of basal side shoots/main stem elongation) which is comparable to BBCH codes 20–39 (Linders et al. 2000), in order to illustrate the climate and soil specificity of pesticide emissions. Thus, the influence of climatic conditions and soil properties on the compartment-specific pesticide emissions to air, surface water and groundwater as well as the variation in the aggregated emissions to all compartments was illustrated.

In order to illustrate the influence of the climatic conditions on pesticide emission patterns, three climate data sets corresponding to specific climate zones were applied in the case study: ‘Temperate Maritime’ (Tranebjerg, Denmark; DK), ‘Continental 2’ (Gyor, Hungary; HU) and ‘Mediterranean 1’ (Tessaloniki, Greece; GR). These climate sets are in the following referred to as DK, HU and GR, respectively. These sets are described in Table S3 in ESM 2. In order to quantify the influence of the climatic conditions on the emission patterns, the soil properties had to be kept constant across all climate scenarios. For this purpose, the average soil profile was applied, all other PestLCI 2.0 settings were likewise kept constant across the three climate scenarios.

To demonstrate the effect of soil characteristics on pesticide emission patterns, three soil sets were included in the case study: high sand, average and high clay, all having quite different fractions of organic carbon and soil pHs. These soils will in the following simply be referred to as sand, average and clay, respectively. The climate data set applied in the soil comparison was the DK set. All other PestLCI 2.0 settings were kept constant across the three soil scenarios. The soil characteristics are given in Table S2 in ESM 2.

In order to illustrate the combined climate and soil influence, i.e. the influence of different field locations, on pesticide emission patterns, the model was run for the three climate data sets combined with the three soil samples. From these in total nine model scenarios, in emissions to air, surface water and groundwater was determined.

3 Results

3.1 Comparison PestLCI 1.0 and PestLCI 2.0

Table 2 presents the emissions of bentazone calculated by both PestLCI 1.0 and PestLCI 2.0 by application to maize in May and August. The emission data from PestLCI 1.0 originate from Birkved and Hauschild (2006). The results indicate that the emissions to air are more or less independent of model version. The largest difference between the air emissions calculated by two model versions is observed for the May scenario (scenario 1). The emissions to surface water calculated by PestLCI 2.0 are 2 orders of magnitude lower than those calculated by PestLCI 1.0. Also, here the largest difference between the surface water emissions calculated by two model versions is observed for the May scenario (scenario 1). The fractions emitted to groundwater as calculated by PestLCI 2.0 are up to approximately five to seven times larger compared to the emissions calculated by PestLCI 1.0. The highest ratio between the groundwater emissions calculated by two model versions is observed for the August scenario (scenario 2). Comparing the total emission fractions for both scenarios in the two model versions reveals no large differences between the aggregated emissions calculated by PestLCI 1.0 and PestLCI 2.0. Moreover the aggregated emissions are lower than 6 % of the applied amount for both models.

3.2 Comparison of PestLCI with pesticide risk assessment models

The results obtained from applying SWASH for quantification of emissions of MCPA to surface water are presented in Table 3. This table also lists the emissions

Table 2 Comparison of results obtained from PestLCI 1.0 and PestLCI 2.0 on bentazone emissions applied in May (scenario 1) and August (scenario 2)

		PestLCI 1.0	PestLCI 2.0	Ratio PestLCI 2.0/PestLCI 1.0
Scenario 1	f_{air}	$1.60 \cdot 10^{-2}$	$1.05 \cdot 10^{-2}$	0.66
	f_{sw}	$7.60 \cdot 10^{-3}$	$3.73 \cdot 10^{-5}$	$4.91 \cdot 10^{-3}$
	f_{gw}	$1.50 \cdot 10^{-3}$	$6.84 \cdot 10^{-3}$	4.56
	Aggregated emissions	0.025	0.017	0.69
Scenario 2	f_{air}	$4.60 \cdot 10^{-2}$	$5.41 \cdot 10^{-2}$	1.18
	f_{sw}	$1.50 \cdot 10^{-3}$	$1.07 \cdot 10^{-5}$	$7.13 \cdot 10^{-3}$
	f_{gw}	$3.00 \cdot 10^{-4}$	$2.21 \cdot 10^{-3}$	7.3
	Aggregated emissions	0.048	0.056	1.18

Table 3 Comparison SWASH and PestLCI 2.0 results for surface water emission (as fraction of applied pesticide)

Scenario	Month	SWASH emissions			PestLCI 2.0 emissions	Ratio SWASH/PestLCI 2.0
		Drainage	Runoff	Total		
D1	August	$3.06 \cdot 10^{-2}$	0	$3.06 \cdot 10^{-2}$	$2.20 \cdot 10^{-4}$	139
D3	July	$1.00 \cdot 10^{-4}$	0	$1.00 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$	0.50
D4	August	$2.10 \cdot 10^{-3}$	$6.35 \cdot 10^{-4}$	$2.74 \cdot 10^{-3}$	$1.60 \cdot 10^{-4}$	17
D5	June	$1.00 \cdot 10^{-3}$	$2.55 \cdot 10^{-5}$	$1.03 \cdot 10^{-3}$	$9.30 \cdot 10^{-5}$	11

calculated by PestLCI 2.0 for comparable scenarios. The SWASH results showed higher emissions to surface water from drainage systems than from surface runoff. Summing the runoff and drainage fractions showed that the total emissions to surface water modelled by SWASH are on average 0.86 % of the applied dose, the average emission calculated by PestLCI 2.0 was 0.017 % of the applied dose.

Table 4 presents the results for emissions of MCPA to groundwater, calculated by FOCUSPEARL and PestLCI 2.0. The 20-years average emissions found by FOCUSPEARL for the six different locations were on average 0.12 % of the applied dose. For PestLCI 2.0, an average of 0.019 % was found to reach the groundwater via leaching. Including macropore flow, which FOCUSPEARL does not include the average emissions calculated by PestLCI were 0.29 %. All data obtained from FOCUSPEARL 4.4 can be found in Table S4 in *ESM 2*.

The FOCUS groundwater scenario included in MACRO, which includes macropore flow, resulted in a groundwater emission fraction of $3.7 \cdot 10^{-4}$. The emission fraction of the most similar PestLCI 2.0 scenario (Tours, see Table 4) was $2.1 \cdot 10^{-3}$, hence 7.7 times higher than MACRO.

3.3 Results from case study

3.3.1 Climatic influence on emission patterns

The PestLCI 2.0 results obtained for MCPA emission patterns under three different sets of climate conditions are summarized in Fig. 2. The data shown in Fig. 2 indicated

that the emission patterns differ according to location and hence climate. The emissions to air increase in the order $DK < HU < GR$. In contrast, the emissions to surface and groundwater increase in the order $DK < GR < HU$. The variability in emissions, calculated as the ratio between the maximum and minimum compartment-specific emission fractions are listed in Table 5 for both the emissions to the environmental compartments and the total emissions.

3.3.2 Soil profile influence on emission patterns

Figure 3 illustrates how the soil profiles influence the pesticide emissions patterns. As was the case for climate specificity, Fig. 3 reveals not only that most emissions occurred to air, but that the emissions to surface water and groundwater showed a clear soil dependency. The emissions to these compartments increased in the order $sand < average < clay$. Table 5 lists the variability in emissions to the different compartments as well as the variability in the total emissions.

3.3.3 Combined influence of climatic conditions and soil profile on emission patterns

The rightmost column in Table 5 reveals how the combined effect of varying soils and climatic circumstances leads to an even larger variability in pesticide emissions, illustrating the relevance of using both soil- and climate-specific data when calculating the life cycle inventory. Table 5 shows an undisputable site dependency of the emissions to all compartments considered, except for the emissions to air for the soil-specific

Table 4 Comparison FOCUSPEARL and PestLCI 2.0 (leaching results only) for groundwater emissions (as fraction of applied pesticide)

Scenario	FOCUSPEARL		PestLCI 2.0 emissions			Ratio FOCUSPEARL/PestLCI 2.0	
	Location	Emissions	Location	Total	Leaching		Macropore flow
1	Chateaudun	$4.35 \cdot 10^{-5}$	Tours	$2.13 \cdot 10^{-3}$	$1.17 \cdot 10^{-6}$	$2.13 \cdot 10^{-3}$	37
2	Hamburg	$2.08 \cdot 10^{-3}$	De Bilt	$2.07 \cdot 10^{-3}$	$1.16 \cdot 10^{-4}$	$1.96 \cdot 10^{-3}$	18
3	Joikionen	$2.47 \cdot 10^{-4}$	Birzai	$2.55 \cdot 10^{-3}$	$3.13 \cdot 10^{-6}$	$2.54 \cdot 10^{-3}$	79
4	Kremsmünster	$1.53 \cdot 10^{-3}$	Kremsmünster	$3.93 \cdot 10^{-3}$	$2.26 \cdot 10^{-4}$	$3.71 \cdot 10^{-3}$	6.8
5	Okehampton	$2.72 \cdot 10^{-3}$	Gogerddan	$2.60 \cdot 10^{-3}$	$5.16 \cdot 10^{-4}$	$2.08 \cdot 10^{-3}$	5.3
6	Porto	$5.80 \cdot 10^{-4}$	La Coruna	$3.90 \cdot 10^{-3}$	$2.95 \cdot 10^{-4}$	$3.61 \cdot 10^{-3}$	2.0

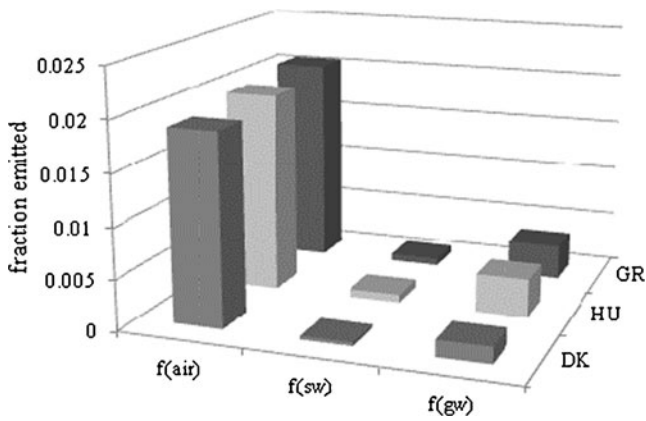


Fig. 2 Results PestLCI 2.0 for climate specificity

scenario. The largest variations are observed when both climate and soil data are varied.

3.4 Sensitivity analysis

A sensitivity analysis was carried out, based on a scenario of MCPA application in May, using the climate scenario DK and the average soil. For this analysis, not only the model parameters, but also the pesticide, climate and soil input data were varied with +10 % to determine the corresponding change in emissions. The three parameters towards which the emissions to each of the environmental compartments show the highest sensitivity are listed in Table 6. The numbers given in this table are the relative sensitivities: the ratio of change in outputs relative to the change in inputs. The results indicate that emissions to air are relatively insensitive. The distance to the field border and hence technosphere border is the most sensitive parameter for emissions to air. Emissions to surface and groundwater are mainly sensitive towards soil properties.

4 Discussion

4.1 Comparison of PestLCI 1.0 and PestLCI 2.0

Comparing the emission fractions calculated by PestLCI 1.0 and PestLCI 2.0 reveals noticeable differences, mainly

concerning the emissions to surface water and to groundwater. The emissions to air have changed slightly as a consequence of changes in the equations applied for quantification of volatilization from leaves and soil: volatilization from plant surfaces is in the 2.0 version based on a simpler, regression-based equation based on Van Weesenbeeck et al. (2008) and volatilization from top soil is calculated based on a rate constant, replacing PestLCI 1.0's mass flux approach. The emissions to air are however mainly caused by wind drift losses, so the changes are relatively small. Focusing on surface water emissions, the observed differences can be explained by a combination of two factors. Firstly, the approach to calculate surface runoff has been altered. As a consequence of the inclusion of correction factors for the slope of the field and the width of the buffer zone, both lower than 1, runoff is predicted to lead to lower emissions. Secondly, and most importantly, the inclusion of macropore flow in the model is assumed to result in facilitated transport of pesticides directly to the groundwater leaving less pesticide residues available for leaching through the soil matrix, a process during which it can be intercepted by the drainage system. The surface water emissions calculated by PestLCI 2.0 fall in the same orders of magnitude as the emissions for a number of pesticides given by Berenzen et al. (2005), though in the lower end. The updated version of PestLCI calculates higher emissions to groundwater compared to PestLCI 1.0. This is a consequence of including macropore flow. A second reason for the increase in the groundwater emissions is a change in the calculation of the filter velocity of the soil. By applying the actual evaporation instead of potential evaporation, a higher filter velocity is found. This results in a higher rate of downward movement of water-dissolved pesticide molecules through the soil, consequently lowering the fraction of pesticide degraded before the residues reach 1-m depth where pesticide degradation is assumed to cease, according to Larsbo and Jarvis (2003). Concluding, the main difference between PestLCI 1.0 and PestLCI 2.0 is found in the emissions to surface water. The main reason for this difference is the inclusion of macropore flow in PestLCI 2.0.

Table 5 Variability of pesticide emissions: for the climate-dependent, soil-dependent and both climate- and soil-dependent scenarios

	Climate-dependent scenarios (soil: average)	Soil-dependent scenarios (climate: DK)	All scenarios (combined climate- and soil-dependent scenarios)
<i>f</i> (air)	1.1 ^a GR:DK ^b	1.0 Clay:average	1.1 GR, clay; DK, sand
<i>f</i> (sw)	2.3 HU:DK	29 Clay:sand	68 HU, clay; DK, sand
<i>f</i> (gw)	2.3 HU:DK	3.4 Clay:sand	7.8 HU, clay; DK, sand
Total emissions	1.2 GR:DK	1.2 Clay:sand	1.5 HU, clay; DK, sand

^a This number is the ratio between maximum and minimum emissions are listed per environmental compartment and for the total emissions

^b The scenario giving the highest and lowest emission to the given environmental compartment, denoted as max:min

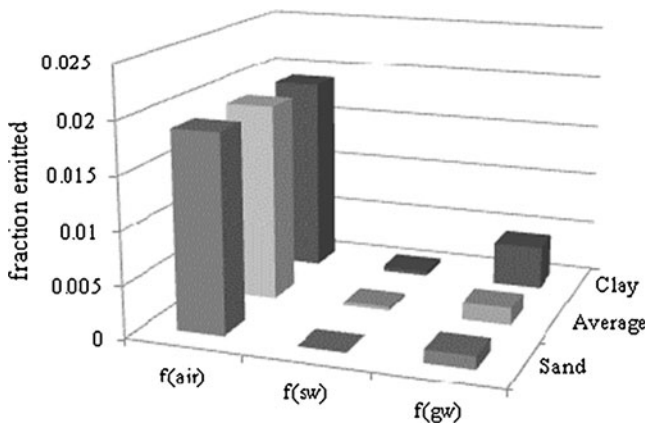


Fig. 3 Results PestLCI 2.0 for soil specificity

4.2 Comparison of emission estimates from PestLCI and risk assessment models

Comparing the results obtained for emissions to surface water from SWASH and PestLCI 2.0 revealed that the sum of surface water emissions calculated by PestLCI 2.0 are up to 2 orders of magnitude lower than those calculated by SWASH. This difference is accounted for by a combination of two factors. Firstly, the compared models differ in inputs and calculation methods. Even though SWASH was parameterized to operate with as many PestLCI input data as possible, the parameterizations of the two models were not fully identical. For example, the drainage depth applied in PestLCI 2.0 was 0.5 m with a drained fraction of 0.5 in all scenarios, whilst the three scenarios included in MACRO module applied in SWASH had different and varying drainage depths and distances between drainage pipes. Secondly, the models incorporated in SWASH were developed for risk assessment purposes. PestLCI 2.0 was developed for use in LCA, which aims at assessing average scenarios. Risk assessment on the other hand most often aims at providing realistic worst-case scenario estimates. The scenarios applied in this study to run the risk assessment models are no exception from this principle

Table 6 Relative sensitivities of the emissions to air, surface water and groundwater towards their three most sensitive parameters

f_{air}	Field width	-0.80
	Solar irradiation	-0.28
	Average temperature	0.23
f_{sw}	Soil pH	18.0
	Fractions sand, silt, clay	14.4
	Potential evaporation	14.4
f_{gw}	Soil pH	27.1
	Fractions sand, silt, clay	14.9
	Potential evaporation	14.0

(FOCUS 2000). A difference between the model results should therefore not come as a surprise but merely underline the generally acknowledged differences in the two assessment methodologies. The lower emissions to surface water calculated by PestLCI 2.0 were considered acceptable due to the differences in the assessment methodologies.

Comparing the FOCUSPEARL and PestLCI 2.0 results for similar scenarios showed that the calculated emissions to groundwater by leaching generally differ up to 1 order of magnitude. The groundwater emissions calculated with FOCUSPEARL are all higher than those found by PestLCI 2.0, again reflecting the difference between the conservative realistic worst-case approach applied in risk assessment models and the average assessment approach applied in LCA. A second reason for the observed differences is that the soil samples used in the comparison were not matching 100 %, because PestLCI 2.0's database does not have the FOCUS soil samples, and vice versa.

As FOCUSPEARL did not include groundwater emissions via macropore flow, a comparison of PestLCI 2.0 and MACRO was done for the only groundwater scenario present in the MACRO version developed for the FOCUS project. The result revealed that groundwater emissions calculated by PestLCI were higher than those found by MACRO. This is contrasting with the general perception of differences in approach between environmental risk assessment and LCA. Even though the differences in soil profile may play a role here, it may also suggest that PestLCI tends to overestimate emissions to groundwater via macropores for some soils.

Looking at all data given in Table 4, MCPA emissions to groundwater via macropore flow calculated by PestLCI 2.0 are in the order of 0.2–0.4 % of the applied dose. The literature overview presented by Kördel et al. (2008) covers ten measured leaching results, of which three studies involved macropore flow. The group of studies involving macropore flow showed groundwater emissions between 0.01 and 0.117 % of the applied dose. This suggests that the groundwater emissions estimated with PestLCI 2.0 are noticeable higher, and hence that the approach taken in PestLCI 2.0 to model macropore flow might result in slightly overestimated groundwater emission estimates for some soils. However, more scenarios are needed to conclude on this.

Finally, the model comparisons for both surface water and groundwater have been carried out with one pesticide active ingredient, and hence can only be regarded as a partial validation.

4.3 Case study

The case studies illustrate that there is a spatial dependency of pesticide emissions, mediated through differences in terms of climate and soil. Analysing the emissions to air reveals an increase in emissions with increasing average ambient

temperature, reflecting the higher volatilization rate of chemicals at higher temperatures. The trends in emissions to surface water and groundwater observed from Fig. 2 emissions are the result of two factors: the intensity and frequency of rain events. The rain intensities (in millimeters per day) of the scenarios are related according to $HU \approx GR > DK$, whilst the rain frequency (time between rain events) are related $GR > HU \approx DK$. The scenarios with higher rain intensity are expected to have more runoff, more macropore flow and hence increased leaching of dissolved pesticide to groundwater, whilst a longer dry period between rain events results in more pesticide degradation and evaporation, thus lowering the fraction available for emission to surface water and groundwater. The sequence observed in Fig. 2 is the result of the interplay of these two effects.

Figure 3 and Table 5 illustrate that there are clear differences in pesticide emissions between the different soil types. The effect of including the dependence of pesticide sorption on soil pH had a negligible effect on pesticide emissions to air, because this emission route is dominated by wind drift emissions. The explanation for the observed pattern in emissions to surface water is found in the equations used to calculate runoff emissions: in order to take differences in soil structure into account, the calculation of the fraction of precipitation that runs off from the field is based on the sand content of the soil. Another equation is used for soils with low (i.e. less than 50 %) sand content than for soils with high sand content. For emissions to groundwater, this difference is explained in terms of soil pH. MCPA is a dissociating pesticide. Because the pH of the pore water in the clay soil is higher than pore water pH of the other soils (sand and average soils which have comparable pHs—see Table S2 in the ESM 2), the sorption in the clay soil is lower. Thus, the pore water of the clay soil will contain more dissolved MCPA which results in a higher leaching rate to groundwater. For emissions to groundwater, the pH-dependent sorption behaviour is therefore part of the explanation of the differences between the soil scenarios.

Table 5 shows that the largest ratio between highest and lowest emissions to an environmental compartment occurred for emissions to surface water, whilst emissions to air were relatively invariable. Since the emissions to air constitute a dominating part of the total emissions (see Figs. 2 and 3), the variation in the total emissions was relatively low: at most a factor 1.2. However, these results were obtained by combining three sets of climate data with three sets of soil data, so including more data might result in a larger variation in the total emissions, in particular for pesticides with a lower volatility, where emissions to surface water and groundwater with their dependency on soil and climate properties will play a more dominant role.

The aggregated emissions patterns indicate that between 2 and 3 % of the applied pesticide was emitted from the technosphere. The results sets shown in Figs. 2 and 3 indicate that pesticide emissions have spatial variability;

especially due to climatic dependency and soil characteristic dependency, less so in the total emissions as a fraction of the total application dose. This observation is in sharp contrast to the way pesticide emission inventories are calculated in current LCA practice. Commercial available inventory datasets such as for example Ecoinvent (Swiss Centre for Life Cycle Inventories 2011) assume that the full dose applied is emitted (i.e., 100 % emission), and that the emissions are to one environmental compartment only, namely soil. Following this approach, we consider the total emissions overestimated. As a consequence, the environmental impact potential resulting from the use of pesticides may be overestimated as well, depending on the (emission compartment specific) characterization factors. In contrast to the current approach to calculate the LCI data on pesticide emissions, we consider the approach presented here more accurate and realistic and therefore capable of delivering realistic pesticide emission inventories.

4.4 Sensitivity and uncertainty analysis

The results of the sensitivity analysis (Table 6) showed that the emissions to air were relatively insensitive towards changes in the input parameters. The highest sensitivity for emissions to air was observed for the field width. This was expected, because the emissions to this environmental compartment are dominated by wind drift. The wind drift emissions in turn depend on the distance between the spray boom nozzle and the field border. In the sensitivity analysis of PestLCI 1.0, the size of the field which is dependent on the field width was given as one of the most influential parameters in the emissions to air (Birkved and Hauschild 2006). The other sensitive parameters found, both for PestLCI 1.0 (Birkved and Hauschild 2006) and PestLCI 2.0 are mainly related to emissions from plant surfaces. This is explained by the fact that, after wind drift, volatilization from plants is the most important source of emissions to air.

Emissions to surface and groundwater are more sensitive than the emissions to air. From Table 6, it can be seen that the same parameters contribute most to the sensitivity of both emissions. The emission estimates are most sensitive towards soil pH, which intuitively makes sense: the soil pH determines the fraction of pesticide dissolved in the pore water, i.e. the fraction that is available for runoff, macropore flow or leaching. The soil constituents are included in the algorithms to determine the fraction of rainwater that will run off and furthermore they influence the structure of the soil and hence the formation of macropores. Finally, the potential evaporation is used in the calculation of the rate of downward movement of pesticides through the soil, thus affecting leaching rate and hence drainage fraction and groundwater emissions. Comparing the sensitivities of surface water and groundwater emissions found in Table 6 to the sensitivity analysis done for PestLCI 1.0 (Birkved and

Hauschild 2006) shows that soil pH is not mentioned as a sensitive parameter for PestLCI 1.0. The reason why it appears as a sensitive parameter for the new model version in Table 6 is the fact that the sorption of pesticides is pH dependent in PestLCI 2.0, making surface water emissions and macropore flow pH dependent.

Given that the soil pH, soil constituents and potential evaporation are the parameters contributing most to the sensitivity, data availability and quality for these parameters are important to include these in emission assessment. Both soil pH and composition are taken from measured soil samples included in the SPADE 2.0 database (Hiederer et al. 2006), which was developed for pesticide fate modelling for use in risk assessment. The data validation is described in Hollis et al. (2006). The first version of the SPADE database, which includes soil samples from nine EU countries, is freely available and can be used to incorporate more soil samples in PestLCI 2.0. Calculation of the potential evaporation is done on basis of a simplified equation proposed by Linacre (1977) in which the potential evaporation is a function of latitude, elevation and temperature, thus simplifying the assessment by leaving out the physical property data of water and air. Even though the validation done by Linacre (1977) shows a good agreement between calculated and measured data, it can be expected that the uncertainty in pesticide emissions caused by the potential evaporation is higher than the uncertainty in the results as a consequence of the soil properties.

A number of modules in PestLCI 2.0 require more input data compared to the input data required for PestLCI 1.0, thereby inducing more uncertainty. The sensitivity of the results towards these additional parameters was taken into account in the sensitivity analysis, revealing that the outcomes were not sensitive towards the inputs added to version 2.0. Assuming that representative default values have been used for these inputs, it can be concluded that the uncertainty in the results probably has not increased considerably from version 1.0 to 2.0. In addition, for other modules the data demand was reduced.

Despite the improvements, there are some limitations in the current model. Firstly, the modelling approach of the macropore flow is relatively simple, resulting in some additional uncertainty in the model results. The extent of this uncertainty could not be quantified. A more complex approach would have resulted in a considerable increase in the input data demand and was therefore avoided. Secondly, PestLCI 2.0 currently only takes pesticide active ingredients into account. Many active pesticide ingredients are known to have toxic and/or persistent metabolites, such as, e.g. diuron (Oturán et al. 2008). If these metabolites could also be modelled, the quality of LCIs would increase further. Both limitations will have to be considered when a next version of the model is prepared.

4.5 Application and availability of the model

The results obtained with PestLCI 2.0 can be applied in combination with characterization factors (CF) obtained from emission route-specific impact assessment models, such as USEtox (Rosenbaum et al. 2008), where the product of the emission and the CF gives the characterized impact potential. So far, little work has been done on development of toxicity CFs for groundwater. It would be interesting to see if characterization factors for this compartment appear in the future characterization models. PestLCI 2.0 results cannot be used to quantify emissions to agricultural soils, as the model developers do not regard pesticide application to agricultural soil as an emission to the environment, as was explained in the model description.

PestLCI 2.0 was modelled in Analytica and is available for download from <http://www.man.dtu.dk/PestLCI>. In order to run the model, the Analytica Player is needed. The Analytica Player is available for free from the website of Lumina Decision Support. The player allows the user to operate the model and design scenarios using the included pesticide, climate, crop development and soil databases, as well as changing a number of field and crop management parameters. The player does not allow for data to be added to the database or equations to be modified, but the authors of this paper are open for including new data in future updates of PestLCI 2.0.

5 Conclusions

In this paper, an expanded and updated version of the PestLCI model has been presented. Macropore flow and the effect of tillage have been introduced as new pesticide fate influencing mechanisms in PestLCI 2.0. In addition new calculation methods have been introduced for a considerable number of the fate modules in order to improve the accuracy of emission modelling from arable land. Furthermore, expanded climate, soil and active ingredient databases were introduced, thereby widening the scope and applicability of this version of the model to Europe. The model platform was changed from Excel to Analytica.

PestLCI 2.0 results have been compared to the results of PestLCI 1.0 for the same pesticide application scenarios. Air emissions were comparable for both models, PestLCI 2.0 groundwater emission estimates were slightly higher than PestLCI 1.0 due to the inclusion of macropore flow and improved calculation of the water infiltration rate, whilst introduction of new algorithms and macropore flow led to considerably lower PestLCI 2.0 emission estimates to surface water compared to PestLCI 1.0.

By comparing emissions to surface water and groundwater calculated by PestLCI 2.0 to results for the same

compartments obtained by risk assessment models, the model was partially validated.

The MACRO module in SWASH was used to compare emissions to surface water, FOCUSPEARL was used for groundwater emissions via matrix leaching. Because this model does not include macropore flow, the only MACRO groundwater scenario available in FOCUS was used to compare groundwater emissions including emissions caused by macropore flow. For the comparisons with SWASH and FOCUSPEARL, the majority of the results were within less than 2 orders of magnitude, where the emission estimates of PestLCI 2.0 in general were lower than those found by the risk assessment models, indicating that the results are in acceptable accordance. The differences in the results are explained partly by the differences in input parameters and the generally conservative approach applied in risk modelling as opposed to the average approach applied in LCA, and partly by the fact that the soil samples compared were not identical.

The comparison of groundwater emissions including macropore flow applying MACRO revealed that the emissions calculated by PestLCI 2.0 were higher than those obtained from MACRO, which suggests that macropore flow might be modelled slightly conservative in the PestLCI model. However, due to the limited data availability, no definitive conclusions can be drawn on this modelling aspect.

Finally, the results of the case study showed that emissions of pesticide to air, surface water and groundwater are variable, depending on climatic circumstances and soil type. Total emissions from the technosphere are only a small fraction of the applied pesticide dose. Both results call for a change in the way LCIs for pesticides are currently handled.

Acknowledgments The authors would like to thank the project ‘Development of genetically modified cereals adapted to the increased CO₂ levels of the future’ funded by the Danish Ministry of Food, Agriculture and Fisheries for funding of the research supporting this paper.

References

- Alletto L, Coquet Y, Benoit P, Heddad D, Barriuso E (2010) Tillage management effects on pesticide fate in soils. A review. *Agron Sustain Dev* 30:367–400
- Alterra (2009). SWASH 3.1.1: Surface Water Scenarios Help. Alterra, Wageningen
- Baur P, Schönherr J (1995) Temperature dependence of organic compounds across plant cuticles. *Chemosphere* 30:1331–1340
- Berzen N, Lentzen-Godding A, Probst M, Schulz H, Schulz R, Liess M (2005) A comparison of predicted and measured levels of runoff-related pesticide concentrations in small lowland streams on a landscape level. *Chemosphere* 58:683–691
- Birkved M, Hauschild MZ (2006) PestLCI: a model for estimating field emissions of pesticides in agricultural LCA. *Ecol Model* 198:433–451
- Boesten J, Helweg A, Businelli M, Bergstrom L, Schäfer H, Delmas A, Kloskowski R, Walker A, Travis K, Smeets L, Jones R, Vanderbroeck V, Van der Linden A, Broerse S, Klein M, Layton R, Jacobsen O-S, Yon D (1996) FOCUS report—soil persistence and EU registration—EU document 7617/VI/96, EU, Brussels
- Centofanti T, Hollis JM, Blenkinsop S, Fowler HJ, Truckell I, Dubus IG, Reichenberger S (2008) Development of agro-environmental scenarios to support pesticide risk assessment in Europe. *Sci Total Environ* 407:574–588
- Communities E (2003) Technical guidance document on risk assessment. Part II. European Commission Joint Research Centre, Ispra
- European Communities (2007) PV-GIS estimation utility. <http://sunbird.jrc.it/pvgis/apps/pvest.php?europe>. Accessed 29 July 2011
- FOCUS (2000) FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document reference Sanco/321/2000 rev.2, 202 pp
- FOCUS (2001) FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC—report of the FOCUS working group on surface water scenarios, EU, Brussels
- Geodata (2011) Daily weather climate data statistics—Tune/Roskilde: <http://www.geodata.us/weather/place.php?usaf=061700&tuban=99999&c=Denmark&y=2011>. Accessed 29 July 2011
- Hall DGM (1993) An amended functional leaching model applicable to structured soils. I. Model description. *J Soil Sci* 44:579–588
- Hiederer R, Jones RJA, Daroussin J (2006) Soil Profile Analytical Database for Europe (SPADE): Reconstruction and validation of the measured data (SPADE/M). *Geografisk Tidsskrift, Danish Journal of Geography* 106(1):71–85
- Hollis JM, Jones RJA, Marshall, CJ, Holden A, Van de Veen JR, Montanarella L (2006) SPADE-2: The soil profile analytical database for Europe, version 1.0. Office for official publications of the European Communities, Luxembourg
- Holterman HJ, Van de Zande JC (2003) IMAG drift calculator v1.1: User manual. <http://www.toxswa.pesticidemodels.eu/download/IDCmanual.pdf>. Accessed 29 July 2011
- Jarvis N (2001) The MACRO model, version 4.3 (Technical description). SLU, Uppsala
- Klein Tank AMG, Wijngaard JB, Können GP, Böhm R, Demarée G, Gocheva A, Mileta M, Pahiardis S, Jędrklic L, Kern-Hansen C, Heino R, Bessemoulin P, Müller-Westermeier G, Tzanakou M, Szalai S, Pálsdóttir T, Fitzgerald D, Rubin S, Capaldo M, Maugeri M, Leitass A, Bukantis A, Aberfeld R, Van Engelen AFV, Forland E, Mietus M, Coelho F, Mares C, Razuvaev V, Nieplova E, Cegnar T, Antonio López J, Dahlström B, Moberg A, Kirchner W, Ceylan A, Pachaliuk O, Alexander LV, Petrovic P (2002) Daily dataset of 20th-century surface air temperature and precipitation series for the European Climate Assessment. *Int J Climatol* 22:1441–1453
- Kördel W, Egli H, Klein M (2008) Transport of pesticides via macropores (IUPAC technical report). *Pure Appl Chem* 80:105–160
- Korte F, Kvesitadze G, Ugrehelidze D, Gordeziani M, Khatishvili G, Buadze O, Zaalishvili G, Coulston F (2000) Organic toxicants and plants. *Ecotoxicol Environ Saf* 47:1–47
- Larsbo M, Jarvis N (2003) MACRO 5.0 Model of water flow and solute transport in macroporous soil. Technical description. Uppsala, Swedish University of Agricultural Sciences
- Linacre ET (1977) A simple formula for estimating evaporation rates in various climates, using temperature data alone. *Agric Meteorol* 18:409–424
- Linders J, Mensink H, Stephenson G, Wascope D, Racke K (2000) Foliar interception and retention values after pesticide application.

- A proposal for standardized values for environmental risk assessment. *Pure Appl Chem* 72:2199–2218
- Lumina Decision Support (2010) Analytica user guide. Lumina Decision Support, Inc, Los Gatos
- Mackay D (2001) Multimedia environmental models: the fugacity approach, 2nd edn. Taylor and Francis, Boca Raton
- Mitra A, Chatterjee C, Mandal FB (2011) Synthetic chemical pesticides and their effects on birds. *Res J Environ Toxicol* 5:81–96
- Nemecek T, Kägi T (2007) Life cycle inventories of Swiss and European agricultural production systems. Final report ecoinvent v2.0 No 15a. Zürich and Dübendorf, Agroscope Reckenholz-Taenikon Research Station. www.ecoinvent.ch Accessed 16 December 2011
- Oturan N, Traikovska S, Oturan MA, Couderchet M, Aaron JJ (2008) Study of the toxicity of diuron and its metabolites formed in aqueous medium during application of the electrochemical advanced oxidation process ‘electro-Fenton’. *Chemosphere* 73:1550–1556
- RIVM, PBL, Alterra (2011) FOCUSPEARL 4.4.4. RIVM, Bilthoven, PBL, Bilthoven, Alterra, Wageningen
- Rosenbaum RK, Bachmann TK, Gold LS, Huijbregts MAJ, Jolliet O, Juraske R, Koehler A, Larsen HF, MacLeod M, Margni M, McKone TE, Payet J, Schuhmacher M, Van de Meent D, Hauschild MZ (2008) USEtox: The UNEP/SETAC-consensus model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *Int J Life Cycle Assess* 13 (7):532–546
- Swiss Centre for Life Cycle Inventories (2011) ecoinvent v. 2.2. Swiss Centre for Life Cycle Inventories, St-Gallen
- Thompson HM (1996) Interactions between pesticides: a review of reported effects and their implications for wildlife risk assessment. *Ecotoxicol* 5:59–81
- Van Leeuwen CJ, Hermens JLM (eds) (1995) Risk assessment of chemicals: an introduction, 1st edn. Kluwer Academic Publishers, Dordrecht
- Van Wesenbeeck I, Driver J, Ross J (2008) Relationship between the evaporation rate and vapour pressure of moderately and highly volatile chemicals. *Bull Environ Contam Toxicol* 80:315–318
- Villholth KG, Jensen KH, Fredericia J (1998) Flow and transport processes in a macroporous subsurface-drained glacial till soil I: field investigations. *J Hydrol* 207:98–120