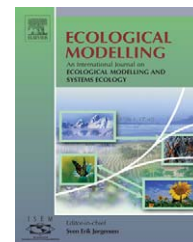


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PestLCI—A model for estimating field emissions of pesticides in agricultural LCA

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ABSTRACT

Life cycle assessment (LCA) involves assessment of resource consumption and emissions caused by the provision of a given service over the whole life cycle of the products it involves, from the cradle to the grave. The quantification of exchanges with the environment during the life cycle of a product or service is a specific element of LCA termed life cycle inventory (LCI). Estimation of chemical emissions in agricultural LCA is typically based on standard emission factors which at best are determined by a few physical–chemical substance properties and the use scenario of the chemical compound. Dynamic and realistic models capable of predicting compartment specific mode of entry fractions for various chemicals and uses under specific temporal and use circumstances are scarce. This lack of appropriate models to estimate emission fractions results in a lower accuracy when accounting for one of the major corner stones in any LCA, chemical emissions, and it inevitably influences the outcome of the impact assessment, where the environmental impacts are normally assumed proportional to the emissions in LCA.

PestLCI is a modular model for estimation of pesticide emissions from field application to the different environmental compartments. It estimates the fractions of the applied quantity which is emitted to the air, surface water, and groundwater compartment based on information which will normally be available to the model user about: type and time of application, crop species and development stage, geological and meteorological conditions and the area of application, and properties of the active ingredients of the pesticide. The use and capability of the model is illustrated through two realistic Danish case studies, but the modular structure of the model will allow adaptation to conditions valid for other regions of the world.

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1. Introduction

A well performed life cycle assessment can comprise several hundred different chemical emissions, taking place at different locations in time and space (the time scope of LCA is infinite, and the geographical scope is global). Since the toxicological impacts only represent one aspect of their

potential environmental impacts, the assessors in LCA are typically not experts in the fields of environmental chemistry and fate modeling, and are therefore not potential users of most of the existing environmental fate and exposure models. Due to the number of chemicals typically included in a LCA study, chemical data compilation quickly becomes an overwhelming and expensive task. Chemical fate, exposure

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and emission models intended for use in LCA, must therefore be as simple and precise as possible.

Life cycle assessment comprises an inventory phase and an impact assessment phase. In the inventory phase (LCI) information is gathered about input and emissions for all processes in the studied system (see Fig. 1). The impact assessment phase (LCIA) follows the LCI and performs an assessment of all relevant environmental impacts associated with the input and emissions mapped in the LCI. LCIA thus also covers other chemical-related impacts like global warming and tropospheric ozone formation, as well as physical impacts on land and input-related impacts on the availability of resources (Wenzel et al., 1997; Hauschild and Wenzel, 1998).

In an LCA, the agricultural field may be considered as part of the technosphere (unit process in Fig. 1), and the emissions of pesticides from this unit process are then only those fractions of the applied dose which reach the environment surrounding the field, including the groundwater under it. Considering the field to be part of the technosphere entails that environmental impacts on ecosystems in the field are not considered in the later impact assessment. This is consistent with the motivation for applying pesticides in the field: to reduce populations of unwanted organisms (be it plants, insects or fungi), and indeed, the ecotoxic impacts occurring in the field would be dramatic (as intended) if they were included in the LCA and would probably dominate all the other environmental impacts determined in the agricultural LCA.

Modeling emissions from this kind of unit processes corresponds to traditional fate and exposure modeling as known from environmental risk assessment (ERA); however the final goal of LCI is not to predict an environmental concentration (PEC) but to model the fractions of pesticides emitted from the field to the different compartments of the surrounding environment.

Many of the existing pesticide fate and exposure models have been developed to support ERA and do therefore typically provide conservative estimates, traditionally termed realistic worst cases. An example is MACRO DB (Jarvis et al., 1997), which estimates the 80th percentile of the percolate concentration of pesticides. The combination of worst case estimates and aggregation over time and space used in

LCA can result in environmental impacts far beyond the reasonable.

Given that LCA assesses all environmental impacts, a conservative estimate of toxic impacts from pesticides is unwanted since this will bias the assessment against the other types of impacts for which a best estimate is generally provided (Hauschild, 2005).

Most of the existing pesticide models developed for ERA also tend to focus on one of the possible emission compartments by providing estimates on, e.g. the leachate or runoff concentrations of pesticides. No single model provides simultaneous estimates on emissions to all emission compartments, air, surface water and ground water. The use of separate models for estimation of emissions to the different compartments is impractical because the total mass balance for the field needs to be correct.

PestLCI has been developed in order to overcome the restrictions and data requirements of ERA models as a model capable of predicting the emission fractions of pesticides to air, surface water and ground water to be used in the LCI to calculate emissions which serve as input to the LCIA phase. PestLCI is partially based on an earlier pesticide emission model for LCI (Hauschild, 2000). In its present form, the model provides data on one soil type (a characteristic Danish Hapludalf soil) and substance data on active ingredients in 69 pesticides approved for use in Denmark (corresponding to 99.99% of the applied quantity of approved herbicides, 100.00% of the approved growth regulator, 93.39% of the approved fungicides and 96.53% of the approved insecticides in Denmark (based on DEPA, 2003)). Furthermore, data on one (Danish) meteorological station (Roskilde) is included in the model. The model is prepared for data on other regions than the Danish. Where relevant, the model may also predict emissions of other ingredients present in the pesticide formulation, provided the required substance data for these are entered into the model's substance database.

The model in combination with its databases allows the users to assess emission fractions of the 69 pesticides based only on knowledge of the application time, crop being treated, and location of the field, pedological and meteorological conditions. If the time of pesticide application and/or national

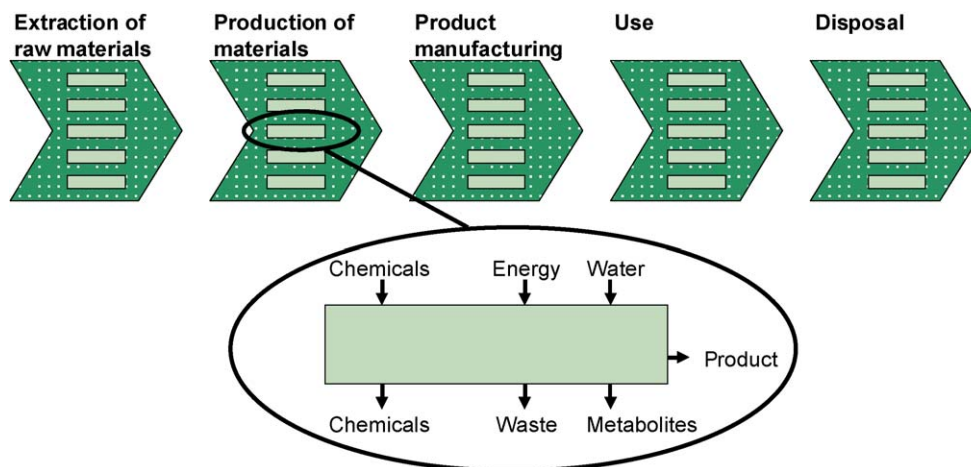


Fig. 1 – Life cycle or product system. Each life cycle stage comprises a number of processes, typically modeled as unit processes. The exchanges with the environment occurring in each unit process are quantified in LCI. Based on DEPA (2002).

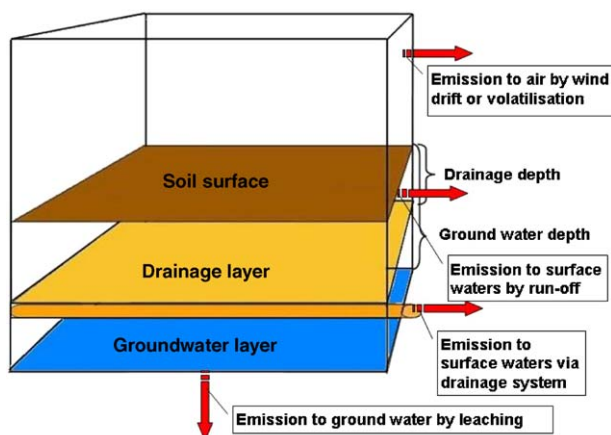


Fig. 2 – System boundaries of PestLCI. Vertically a 50 m air column is simulated. Below the soil surface, a 1 m soil column is simulated. Horizontally the field borders constitute the boundaries. Emissions can occur vertically (by evaporation or leaching with infiltrating water) or horizontally (by advection with wind, surface runoff or advection with drainage water).

location of the field are unknown, which is often the case in LCA, the assessment can be performed based on averaged default data.

2. Model development

2.1. Overall structure of the emission model

The overall aim of the model is to estimate the total fractions of a pesticide applied to a field, which reach the surrounding environment by crossing the boundaries of the technosphere (see Fig. 2). The estimated fractions are intended to represent best estimate for an average situation.

PestLCI has been given a modular structure where each major fate process in the field has its own module. The individual modules calculate the fractions of the incoming pesticide amount undergoing a specific fate process, and mass conservation is observed throughout the model. Fig. 3 gives an overview of all the field processes which are modeled in PestLCI.

The modular structure has several advantages:

- It allows the different modules to represent state-of-the-art for that specific fate process and makes partial updates easy as long as the new modules, which are introduced, respect the interface requirements to the rest of the model (i.e. calculates fractions undergoing the fate they cover).
- It allows adaptations of PestLCI to specific (geographical) conditions which influence some of the fate processes.
- In cases where monitoring data are available for a specific process, these may also be used to calculate fate fractions which can replace the relevant module of the model.

The emission of pesticide from the field is modeled in two sequential steps:

1. Emission during application (primary distribution).
- 2a. Post-application emission from leaves (secondary distribution on leaves).
- 2b. Post-application emission from soil (secondary distribution on soil).

The total emission fraction of pesticide is quantified according to Fig. 3 as the sum of the fraction emitted to air, fraction emitted to surface water and fraction emitted to ground water:

$$f_{em} = \frac{m_{em}}{m_{appl}} = f_{air} + f_{sw} + f_{gw} \quad (1)$$

where f_{em} is the fraction of the applied mass of pesticide which becomes emitted to the surrounding environment, m_{em} the mass emitted, m_{appl} the mass of pesticide applied to the field, f_{air} the fraction of applied mass emitted to air, f_{sw} the fraction of applied pesticide emitted to surface waters and f_{gw} is the fraction of applied mass emitted to groundwater.

2.2. Primary distribution

The primary distribution is the process occurring immediately after application. When applied, the pesticide can distribute in the following way, as presented in Fig. 4:

1. Loss by wind drift f_d .
2. Deposition on leaves or other parts of the crop f_l .
3. Deposition on soil surface f_s .

2.2.1. Fraction lost by wind drift (f_d)

Depending on the type of application technique, e.g. the height of spray equipment above ground, and the wind speed, a varying fraction of the pesticide will be lost by wind drift.

Four different application techniques are included in PestLCI:

1. Application by aircraft.
2. Application using conventional (e.g. tractor pulled) spray equipment on tall crops (bushes and trees taller than 1 m).
3. Application using conventional spray equipment on field crops (lower than 1 m).
4. Soil incorporation.

Loss by wind drift is only considered for the first three types of application, as soil incorporation is assumed not to result in any loss by wind drift.

Based on data from EPPO (1996) functions for the loss by wind drift were established for the three relevant types of application. The data from EPPO (1996) are valid for wind speeds up to 5.6 m/s, which is considered appropriate, since the farmer is assumed to seek to optimize the efficiency of the pesticide by maximizing the fraction reaching the compartment that needs treatment (plant or soil). The farmer will therefore seek to minimize losses by for instance wind drift, by applying pesticides at reasonable wind speeds.

Based on the extrapolated data from EPPO (1996) it was found that wind drift is only relevant in distances of up to 110 m from the field edge. Above this distance the loss frac-

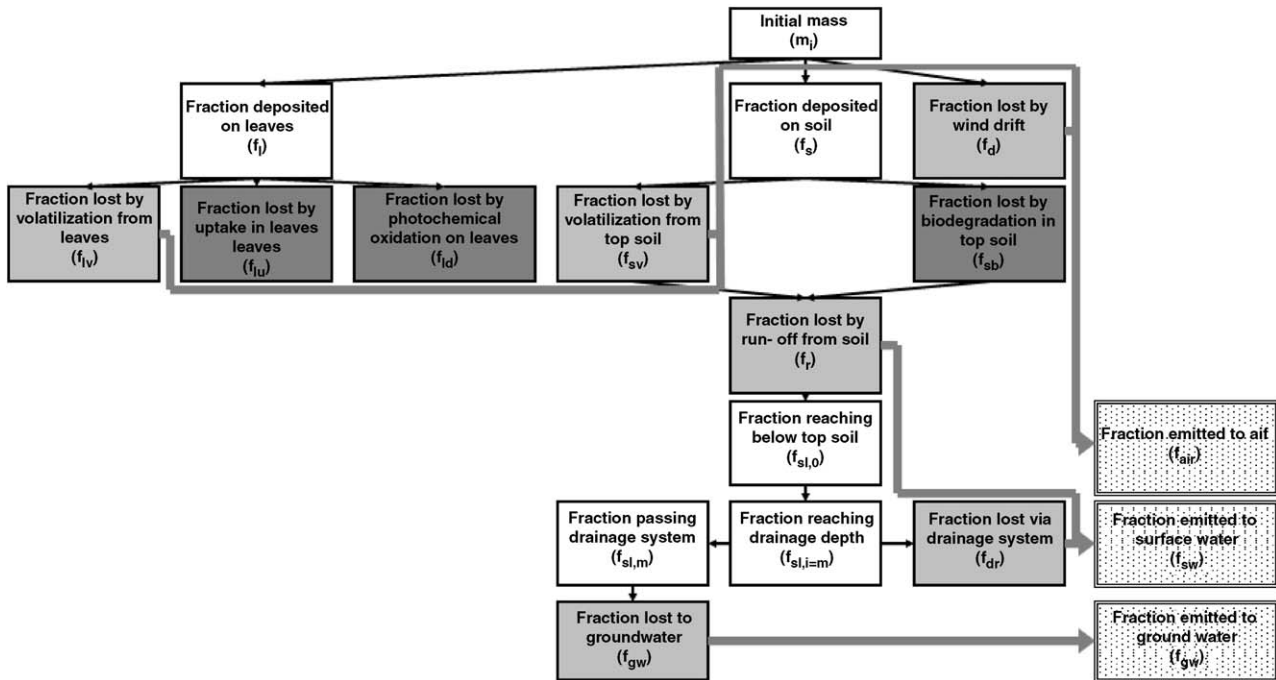


Fig. 3 – Overall model structure and mass flows. Black arrows indicate flows, thick grey arrows indicate emissions. Dark grey boxes are terminal processes not leading to emissions from the field. Light grey boxes are terminal processes leading to emissions. Dotted boxes indicate emissions to receiving compartments outside the field.

tions representing the wind drift of pesticide ingredients to areas outside the field are less than 0.01 for all three types of application techniques. Based on the data from EPPO (1996) the losses by wind drift at an application distance below 110 m from the field edge are calculated as:

- Application to field crops:

$$f_{dx} = 0.1707 e^{-0.0958X} \tag{2a}$$

- Application to tall crops:

$$f_{dx} = 0.2927 e^{-0.0443X} \tag{2b}$$

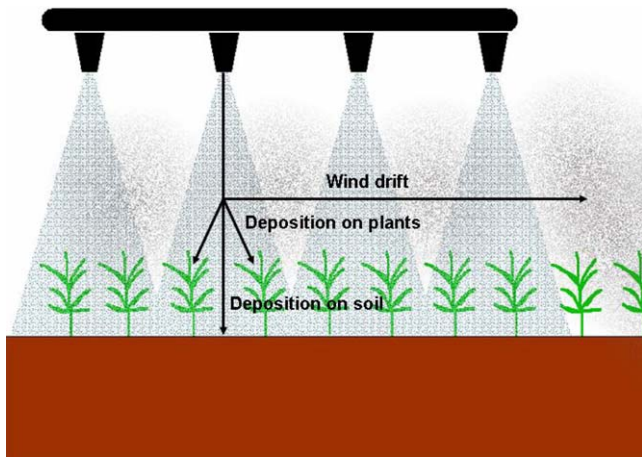


Fig. 4 – Primary distribution of pesticide immediately after spraying. The pesticide distributes between deposition on plants, deposition on soil and loss by wind drift.

- Application by air craft:

$$f_{dx} = 0.4976 e^{-0.0441X} \tag{2c}$$

- Soil incorporation:

$$f_{dx} = 0 \tag{2d}$$

where f_{dx} is the fraction leaving the field by wind drift for application in the distance X (m) from the field edge (max 110 m).

Assuming square fields with one side parallel to the prevailing wind direction, for each pass of the spray boom in a distance below 110 m, the fraction lost to wind drift is calculated. The number of passes needed to cover the area exposed to wind drift is calculated as

$$n_{pass} = \frac{110 - P}{W_{boom}} \tag{3}$$

where n_{pass} is the number of times the spray boom has to pass to cover the area exposed to wind drift, P the width (m) of the legally required protective no-spray zone surrounding the field and W_{boom} is the width (m) of the spray boom.

The distance to the field edge (X_{pass}) in each pass is calculated as

$$\begin{aligned} X_{pass} &= ((Pass - 1)W_{boom}) + P + 0.5W_{boom} \\ &= ((Pass - 0.5)W_{boom}) + P \end{aligned} \tag{4}$$

where $Pass$ is the pass number.

Table 1 – Fractions of applied pesticides deposited on leaves of cereals (f_l) following application at four different development stages

Crop	Development stage	f_l
Cereals I	Leaf development	0.25
Cereals II	Tillering	0.50
Cereals III	Stem elongation	0.70
Cereals IV	Booting/senescence	0.90

Data from Linders et al. (2000).

In Eq. (4) X_{pass} is considered to be the distance from the center of the spraying boom to the field edge, and the protective no-spray zone is assumed to be included in the field area.

The fraction of the total applied mass lost in each pass (f_{dpass}) is subsequently calculated, setting the first pass to occur in a distance equal to half the width of the spray boom plus the width of the protective border surrounding the field. Assuming square fields and equal dosing over the whole field the f_{dpass} in each pass is calculated as

$$f_{dpass} = \frac{W_{boom} \sqrt{A}}{A} f_{dX_{pass}} = \frac{W_{boom}}{\sqrt{A}} f_{dX_{pass}} \quad (5)$$

where A is the area of the field sprayed, $W_{boom} \sqrt{A}$ is the area sprayed in each pass, and $f_{dX_{pass}}$ is the fraction lost in a given pass at a given distance from the field border.

For a given number of passes of the spray boom over the area exposed to wind drift, the total fraction lost by wind drift (f_d) is calculated as

$$f_d = \sum_{Pass=1}^{Pass=n_{pass}} f_{dpass} \quad (6)$$

2.2.2. Fraction deposited on leaves (f_l)

The fraction deposited on leaves is modeled applying the interception fractions compiled by Linders et al. (2000). Interception fractions are provided for 28 different types of crops at three to four development stages. As an example, the fractions intercepted by cereals at four different development stages are presented in Table 1.

2.2.3. Fraction deposited on soil surface (f_s)

Since the pesticide in the primary distribution phase can only undergo wind drift, deposition on leaves or deposition on soil, the fraction deposited on soil (f_s) is calculated as

$$1 = f_d + f_l + f_s \Leftrightarrow f_s = 1 - (f_d + f_l) \quad (7)$$

2.3. Secondary distribution on plants

The fraction intercepted by the crop is assumed primarily to be deposited on the upper side of the crop leaves. This fraction can undergo the following secondary distribution:

1. Volatilization from leaves (f_{lv}).
2. Abiotic degradation on leaves (f_{ld}).
3. Uptake in leaves (f_{lu}).

Table 2 – Adjusted Henry's law constants (unit less) and the associated volatilization half-lives and dependent first order volatilization rate constants

K'_H	$t_{1/2,lv}$ (h)	k_{lv} (h^{-1})
$>10^{-3}$	24	2.01×10^{-2}
10^{-6} to 10^{-3}	66.5	1.04×10^{-2}
$<10^{-5}$	166.4	4.17×10^{-3}

Data from EPPO (1996).

The fraction deposited on leaves is therefore equal to the sum of the fractions distributed via these processes:

$$f_l = f_{lv} + f_{ld} + f_{lu} \quad (8)$$

2.3.1. Fraction lost by volatilization from leaves (f_{lv})

Vapour emissions of pesticides following foliar deposition can be modeled in various ways. The most transparent method is presented by EPPO (1996). According to air/water distribution coefficient the pesticide is assigned a half life with respect to foliar volatilization (see Table 2).

For volatilization as an isolated process, assuming constant solute volume, the fraction of pesticide deposited on the leaves lost by volatilization (f_{lv}) can be calculated according to the integrated form of the reaction rate equations as

$$f_{lv} = f_l \left(1 - \frac{[P]_t}{[P]_0} \right) = f_l \left(1 - \frac{m_{leaf,t}}{m_{leaf,t=0}} \right) = e^{-k_{lv}t} \quad (9)$$

where $[P]_t$ and $[P]_0$ are the time dependent area concentrations of pesticide on leaf surface (mol/m^2), $m_{leaf,t}$ and $m_{leaf,t=0}$ the time dependent masses on leaves (g/m^2), k_{lv} the volatilization rate constant (h^{-1}) and t is the time (h) considered.

2.3.2. Fraction taken up by leaves (f_{lu})

The relative importance of the adsorption of foliarly applied pesticides depends on pesticide properties, plant properties and application technique (or rather dispersant used in the pesticide formulation) as discussed by Satchivi et al. (2000a,b) who report leaf absorption ranges from 17.4% (after 192 h) for Bentazon to 99% (after 96 h) for Haloxyfop-methyl. Plant-uptake may thus be significant for the overall distribution of the applied pesticide in the field system.

Xenobiotic compounds can enter the leaves in vapour form through the stomata or by diffusion through the waxy cuticle layer. Entrance through the stomata seems the most important way for inorganic gases, whereas diffusion through the cuticle seems to be the most important way for lipophilic organic compounds (Korte et al., 2000). Stomata are located on the lower side of the leaves, and assuming that deposition occurs exclusively on the upper side of the leaves, the leaf uptake of pesticides is therefore simulated in PestLCI as the uptake through the waxy cuticle layer.

The first order rate constant of the uptake process of lipophilic organic compounds by cuticular diffusion can, following Baur and Schönherr (1995), be described according to the Arrhenius function as

$$\log k_{lu} = a - bV - \frac{-E_D}{R \times 2.3(T + 273.15)} \times 10^3 \quad (10)$$

Table 3 – Species-dependent constants a and b used in Eq. (10) calculated from Baur and Schönherr (1995)

Species	a	b
Pear	3.231	6.341×10^{-2}
Orange	0.8000	-0.1167

where k_{lu} (s^{-1}) is the first order rate constant of cuticular leaf absorption, a and b the plant species-dependent constants, V the characteristic volume (cm^3/mol) of a molecule calculated according to Abraham and McGowan (1987), E_D the activation energy of diffusion (kJ/mol), T the temperature ($^{\circ}C$) and R is the gas constant ($J/(K \cdot mol)$).

From four absorption experiments on pear (*Pyrus communis*) and orange leaves (*Citrus aurantium*), presented in Baur and Schönherr (1995), a and b were derived, see Table 3.

Since the molecular volume is used later in relation to diffusion, it was decided to base Eq. (10) on molecular volumes instead of characteristic volumes as proposed by Baur and Schönherr (1995). The characteristic volume and the molecular volume are highly correlated (see Fig. 5), and estimation of the characteristic volume based on the molecular volume is therefore straight forward.

The activation energy of diffusion is exponentially correlated to the characteristic volume. Based on the data presented by Baur and Schönherr (1995) the following two expressions for estimation of E_D from the molecular volume (MV in cm^3/mol) were obtained:

- Citrus:

$$E_D = 78.875 e^{3.470 \times MV/1000} \quad (11)$$

- Pear:

$$E_D = 63.6 e^{2.874 \times MV/1000} \quad (12)$$

Using the a and b values presented in Table 3, the correlation between V and MV of Fig. 5 and inserting Eqs. (11) and (12) in Eq. (10), the following expressions are obtained for k_{lu} for citrus and pear:

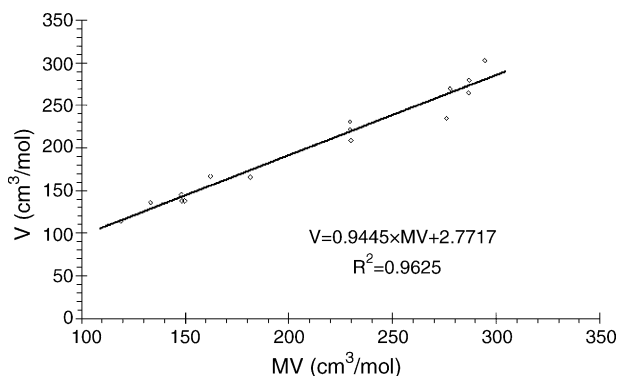


Fig. 5 – Correlation between characteristic volume (V) of a molecule calculated according to Abraham and McGowan (1987) and molecular volume (MV) estimated using ACD Labs (2003). Data on characteristic volumes from Satchivi et al. (2000b).

- Citrus:

$$\text{Log } k_{lu} = (0.800 - 0.117(0.945 \times MV + 2.772) - \frac{78.875 e^{3.470 \times MV/1000}}{R \times 2.303 \times T_1} \times 10^3) \times 3600 \quad (13)$$

- Pear:

$$\text{Log } k_{lu} = (3.231 + 0.063(0.945 \times MV + 2.772) - \frac{63.222 e^{2.874 \times MV/1000}}{R \times 2.303 \times T_1} \times 10^3) \times 3600 \quad (14)$$

where k_{lu} is the first order rate constant for leaf uptake (h) and T_1 is average air temperature of the application month.

The fraction of pesticide deposited on the leaves and later lost by leaf uptake (f_{lu}) can now be calculated as an isolated fate process, assuming constant solvent volume:

$$f_{lu} = f_l \left(1 - \frac{m_{leaf,t}}{m_{leaf,t=0}} \right) = f_l (1 - e^{-k_{lu}t}) \quad (15)$$

Citrus and pear are two plant species with different cuticle thickness and composition. In PestLCI these two species are used to represent other crop species. Each species is evaluated and assigned to one of the expressions according to the characteristics of its cuticle layer—Eq. (13) is applied for crops with thick cuticle layers and waxy leaves and Eq. (14) is applied for other crops. Regardless the temperature, the leaf uptake rate is predicted to be considerably lower for the citrus-like leaves (Eq. (13)) than for other leaves (Eq. (14)), particularly for large molecules, so the characterization of a crop as having a citrus-like cuticle or a pear-like cuticle is a source of uncertainty to consider.

2.3.3. Fraction lost by photodegradation on leaves (f_{id})

Pesticides mainly deposited on the upper side of the leaves are subjected to sunlight and may therefore undergo photochemical transformation either by direct photolysis or photochemical degradation.

Given the scarcity of photolysis rate constants, the photodegradation in PestLCI is modeled as photochemical degradation alone, hence using reaction rates with OH radicals (OH^*) as surrogate values for the overall photodegradation processes on the leaves.

The concentration of OH^* can vary greatly within a very narrow spatial (and temporal) scope due to the numerous processes removing the radicals. The processes consuming OH radicals are partially related to human activity and resulting emissions of volatile organic carbon compounds capable of reacting with the OH^* and thereby removing these. PestLCI is designed to model pesticide emissions in farming areas, where human activity and emission of organic compound compounds is considered low. It is therefore reasonable to assume that the OH^* concentration in the countryside is close to the natural background level of these radicals.

Given a location around 56° northern latitude, the intensity of the solar irradiation varies dramatically over the year in Denmark from approximately 42 MJ/m^2 in January to approx-

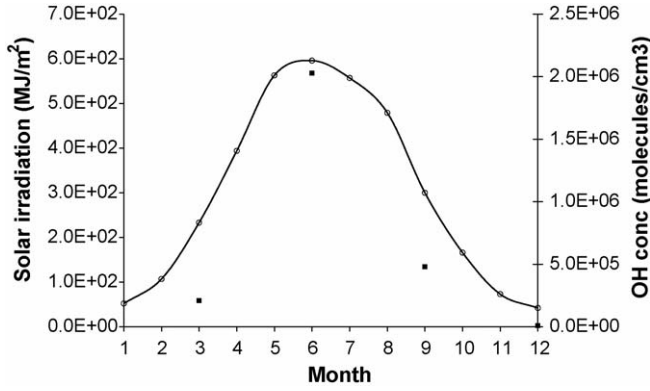


Fig. 6 – Average (1961–1999) daily light intensity in MJ/m² (open circles) variation in Denmark (Roskilde) and OH concentrations during day hours (closed squares) at a latitude of 55°N. Data on light intensity from Planteinfo (2004), data on OH[•] concentration from Bahm and Khalil (2004).

imately 596 MJ/m² in June (see Fig. 6). The formation of OH radicals in the troposphere depends on activation by light, and their concentration therefore varies with the light intensity. According to Bahm and Khalil (2004), the OH concentration in a height of 0.5 km varies by more than a factor 200 over the year at a latitude of 55°N from 0.1×10^5 molecules/cm³ in March to 20.3×10^5 molecules/cm³ in June closely following the solar irradiation intensity as illustrated in Fig. 6. The concentration of OH radicals in a height of 0.5 km is assumed to represent the natural background level of OH[•].

Assuming a linear correlation between light intensity and the latitude-specific Log[OH[•]] the following equation was derived:

$$\text{Log}[\text{OH}^{\bullet}]_l = 3.994 \times 10^{-3} \times I_l + 4.158 \quad (R^2 = 0.89) \quad (16)$$

where I_l is the latitude-specific daily average light intensity in MJ/m² of the application month.

The oxidation by OH[•] is a pseudo-first order process (depending on the concentration of OH[•]). The reaction rate constant is given as

$$k_{l_{o,l}} = k_{\text{OH}}[\text{OH}^{\bullet}]_l \quad (17)$$

where $k_{l_{o,l}}$ is the latitude-specific pseudo-first order leaf oxidation rate constant (h⁻¹) of the application month, k_{OH} is the overall OH[•] oxidation rate constant (cm³/(molecules × h)) and $[\text{OH}^{\bullet}]_l$ is the latitude-specific concentration of OH radicals of the application month in the troposphere in molecules/cm³.

To generate the light intensity-dependent leaf oxidation rate constant, Eq. (16) is inserted into Eq. (17), giving:

$$k_{l_{o,l}} = k_{\text{OH}} \times 10^{3.994 \times 10^{-3} \times I_l + 4.158} \quad (18)$$

The fraction of pesticide deposited on the leaves, which is lost by oxidation by reaction with OH[•] radicals on the leaves,

can now be calculated as an isolated process as

$$\begin{aligned} f_{ld} &= f_l \left(1 - \frac{m_{l_{\text{leaf}, t_{\text{rain}}}}}{m_{l_{\text{leaf}, t=0}}} \right) \\ &= f_l (1 - e^{-k_{\text{OH}} \times 10^{(3.994 \times 10^{-3} \times I_l + 4.158) \times t_{\text{rain}} \times dl/24}}) \end{aligned} \quad (19)$$

where dl is the day length (time with sun light) in h of the application month and t_{rain} is the monthly mean time (h) to the next precipitation event larger than 1 mm.

2.3.4. Fraction lost by fate processes on leaves

Evaporation, uptake and photochemical oxidation are competing processes. The overall rate constant of the combined fate processes equals the sum of rate constants for each process and is thus calculated as

$$k_{lp} = k_{lv} + k_{lu} + k_{l_{o,l}} \quad (20)$$

where k_{lp} (h⁻¹) is the overall rate constant of the processes removing pesticide from the leaves.

Each of the fractions lost by the individual processes equals the fraction of pesticide deposited on the leaves multiplied by the ratio of the rate constant of that process to the rate constant of the overall removal from the leaf surface:

$$f_{lv} = f_l \frac{k_{lv}}{k_{lp}} \quad (21a)$$

$$f_{lu} = f_l \frac{k_{lu}}{k_{lp}} \quad (21b)$$

$$f_{ld} = f_l \frac{k_{l_{o,l}}}{k_{lp}} \quad (21c)$$

2.4. Secondary distribution on topsoil

The fate processes in the top layer of the soil all influence the fraction penetrating the topsoil layer and thereby the fraction that is available for leaching. The topsoil layer in PestLCI is the upper 1 cm of the soil. The processes considered in this soil layer are

1. Volatilization from soil (f_{sv}).
2. Biodegradation (f_{sb}).
3. Runoff (f_r).

All three processes are competing in the removal of pesticide from the topsoil. The sequence of the processes used in PestLCI is: volatilization and biodegradation compete to remove pesticide from the topsoil. After a given time precipitation sets in resulting in runoff and leaching of the pesticide below the topsoil (see also Fig. 3).

The assumption made to establish this sequence is that the farmer seeks to optimize the use of the pesticide by spraying when rainfall is not forecast for the coming days. The residence time in topsoil (t_{rts}) in PestLCI is modeled as the time to the next precipitation event larger than 1 mm which corresponds well with the assumption made by Reus et al. (1999) who assume that the precipitation event

causing runoff occurs 3 days after application of the pesticide. In Denmark, there is little difference between the annual average time between precipitation events larger than 1 mm and the average for the growth season. Since data for the former is readily and freely available for Denmark, the annual average time of 4.4 days (Roskilde) is applied (Planteinfo, 2004). For other regions, the precipitation pattern of the growth season may differ significantly from the annual pattern, and here, the former should be considered when determining the average time between precipitation events.

2.4.1. Fraction lost by volatilization from topsoil (f_{sv})

The evaporation of pesticides from soil is dependent on a number of factors, including physical–chemical properties of the pesticide, composition and texture of the soil, local meteorological conditions and application technique.

Reus et al. (1999) present a simple fugacity model for volatilization from soil, which is adopted for this module of PestLCI. The base assumption of this fugacity model is that the evaporation from soil can be described by Fick's first law of diffusion, assuming that the primary driving force behind the evaporation is the concentration difference between soil air and free air over the soil. The latter is assumed to be zero due to the high dilution speed in free air, and interactions between the soil and the pesticide, like adsorption in the soil gas phase, are neglected. The model is concentration-dependent, due to the concentration dependency of the diffusion. This means that to model the fraction lost by volatilization, the dose (g/ha) used in the application of the pesticide has to be known. This information will normally be available for pesticide applications, and for Danish conditions, normal dosing of all pesticides approved for use is given in DEPA (2003).

The dose reaching the ground ($d_{0,s}$) (g/ha) is calculated from the soil deposition fraction (f_s) and the applied dose (d_a) (g/ha) as

$$d_{0,s} = f_s d_a \quad (22)$$

where $d_{0,s}$ is the dose reaching the soil (g/ha) and d_a is the applied dose (g/ha).

The fugacity capacity of the soil, Z_s (mol/(Pa K)) is calculated in analogy to the method presented by Reus et al. (1999) as

$$Z_s = \frac{K_{oc} f_{oc} \rho_b Z_w}{1 - \phi_s} \quad (23)$$

where K_{oc} is the organic carbon–water distribution coefficient (l/kg) of the pesticide ingredient, f_{oc} is the fraction of organic carbon in topsoil (dimensionless), ρ_b is the soil bulk density (kg/l), Z_w is the fugacity capacity of water (mol/(Pa K)), calculated from the water solubility and the vapour pressure of the pesticide as presented by Mackay (2001), and ϕ_s is the soil porosity (dimensionless).

The initial (immediately after application) soil air pesticide concentration, $C_{sa,t=0}$ (g/l) is calculated as

$$C_{sa,t=0} = \frac{PEC_{s,t=0} f_{ma}}{\rho_b V_a} \quad (24a)$$

and

$$C_{sa,t} = \frac{PEC_{s,t} f_{ma}}{\rho_b V_a} \quad (24b)$$

where $PEC_{s,t=0}$ and $PEC_{s,t}$ (g/kg) are the predicted soil concentration after a single application at $t=0$ and t h, respectively, V_a the volume fraction of air in soil, and f_{ma} is the mass fraction of pesticide in soil (pore) air.

The dose reaching the soil is assumed to distribute equally in the topsoil layer. The $PEC_{s,t=0}$ (g (pesticide)/kg (soil)) of pesticide in the topsoil layer is hence calculated as

$$PEC_{s,t=0} = \frac{d_{0,s} \times 10^{-4} \text{ ha/m}^2}{IPD \times \rho_b \times 10001/\text{m}^3} \quad (25a)$$

and

$$PEC_{s,t} = \frac{(1 - f_{tsl,tn}) d_{0,s} \times 10^{-4} \text{ ha/m}^2}{IPD \times \rho_b \times 10001/\text{m}^3} \quad (25b)$$

where IPD is the initial soil penetration depth (m) of the pesticide and $f_{tsl,tn}$ is the total fraction lost from the top soil by evaporation and biodegradation in the time step from t_{n-1} to t_n .

The mass fraction in the soil air used in Eqs. (24a) and (24b) is calculated as

$$f_{ma} = \frac{Z_a V_a}{Z_a V_a + Z_w V_w + Z_s V_s} \quad (26)$$

where Z_a is the fugacity capacity of air (mol/(Pa K)) calculated from the gas constant and the temperature as presented by Mackay (2001), V_w the volume fraction of water in soil, and V_s is the volume fraction of soil (solid matter) in bulk soil.

From the soil air concentration $C_{sa,t}$ the boundary flux resulting from initial conditions is estimated to account for the mass escaping from the soil air into the free air and thereby escaping the system. Assuming infinitesimally small time steps, and thereby very small changes in the soil air concentration, the boundary flux is estimated as

$$J_{0,t=0} = \frac{D_a C_{sa,t=0}}{d} \quad (27a)$$

and

$$J_{0,\Delta t} = \frac{D_a C_{sa,t}}{d} \quad (27b)$$

where, $J_{0,t=0}$ is the boundary flux (g/m² h) resulting from initial dosing, D_a the default dilution velocity in air (here the default value of the EPRIP model (Reus et al., 1999) 32,455 m/h is used), d the thickness of the boundary layer (m) and C_{sa,t_1} is the soil air concentration at the beginning of a time step.

In each time step ($\Delta t = t_2 - t_1$) of the numerical integration, the soil air concentrations (C_{sa,t_1} and C_{sa,t_2}) are calculated following Eqs. (24a) and (24b) as

$$C_{sa,t_1} = \frac{PEC_{s,t_1} f_{ma}}{\rho_b V_a} \quad (28a)$$

$$C_{sa,t_2} = \frac{PEC_{s,t_2} f_{ma}}{\rho_b V_a} \quad (28b)$$

where PEC_{s,t_1} and PEC_{s,t_2} are the bulk soil concentration of pesticide (g/kg) of the individual time steps.

The flux is calculated by numerical integration for an appropriate time step. The soil concentration in the next time (t_2) step is then

$$\begin{aligned}
 & PEC_{s,t_2} \\
 &= PEC_{s,t_1} - \left(\frac{J_{0,t} \times 1 \text{ m}^2 \times \Delta t}{0.01 \text{ m} \times 1 \text{ m}^2 \times \rho_b \times 10^3 \text{ l/m}^3} + PEC_{s,t_1} f_{sb,\Delta t} \right) \\
 &\Leftrightarrow PEC_{s,t_2} = PEC_{s,t_1} - \left(\frac{J_{0,t} \times \Delta t}{101/\text{m}^2 \times \rho_b} + PEC_{s,t_1} f_{sb,\Delta t} \right) \quad (29)
 \end{aligned}$$

where $f_{sb,\Delta t}$ is the fraction lost by biodegradation in the time step and Δt is the time step considered (h).

For each small time step the boundary mass flux is calculated as

$$\text{Mass flux}_{\Delta t} = \frac{D_a C_{sa,t_1} \Delta t}{d} = J_{0,t} \Delta t \quad (30)$$

The fraction lost by volatilization in each time step is calculated accordingly as

$$f_{sv,\Delta t} = \frac{J_{0,t} \Delta t}{d_{0,s} \times 10^4 \text{ ha/m}^2} \quad (31)$$

The individual time step evaporation losses can be aggregated from $t=0$ to t_{rain} giving the total fraction lost by evaporation:

$$f_{sv,t_{\text{rain}}} = \sum_0^{t_{\text{rain}}} \left(\frac{J_{0,t} \Delta t}{d_{0,s} \times 10^4 \text{ ha/m}^2} \right) \quad (32)$$

where $f_{vs,t_{\text{rain}}}$ is the fraction lost by volatilization from the topsoil at the time of the next precipitation event.

2.4.2. Fraction lost by biodegradation in topsoil (f_{sb})

The fraction lost by biodegradation in the topsoil (f_{sb}) appearing in Eq. (29) is calculated by adjusting the biodegradation rate constant according to soil temperature and soil moisture content.

The temperature (T_{topsoil}) in the top (upper 1 cm) soil is assumed to follow the variations of the air temperature exactly. The temperature variations used in the model for Roskilde are presented in Fig. 7.

The biodegradation rate constant is adjusted according to the topsoil temperature applying a correction factor ($F_{ts,T}$) which is calculated as

$$F_{ts,T} = F_{s,T}(T_{\text{topsoil}}) \quad (33)$$

where T_{topsoil} is measured in °C and the soil temperature biodegradation correction factor $F_{s,t}$ is estimated according to Larsbo and Jarvis (2003) for three different temperature ranges as

$$F_{s,T} = e^{\alpha(T-T_{\text{ref}})}, \quad T > 5^\circ\text{C} \quad (34a)$$

$$F_{s,T} = \left(\frac{T}{5} \right) e^{\alpha(5-T_{\text{ref}})}, \quad 0^\circ\text{C} \leq T \leq 5^\circ\text{C} \quad (34b)$$

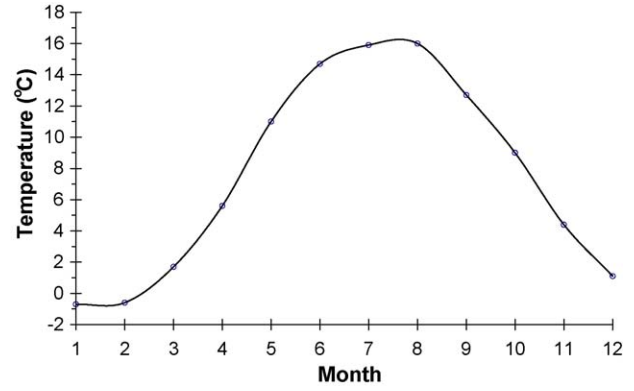


Fig. 7 – Average (1961–1999) monthly air temperature (°C) in Denmark (Roskilde). Data from Planteinfo (2004).

$$F_{s,T} = 0, \quad T < 0^\circ\text{C} \quad (34c)$$

where T_{ref} is the reference temperature (°C) for the biodegradation rate constant and α is the temperature response factor, which according to Jarvis and Stenemo (2001) equals 0.08°C^{-1} .

The biodegradation rate constant is also adjusted according to the soil moisture. The soil humidity biodegradation correction factor $F_{s,m}$ is estimated according to Larsbo and Jarvis (2003) as

$$F_{s,m} = \left(\frac{\theta}{\theta_{\text{ref}}} \right)^\beta \quad (35)$$

where β is the exponential response factor for soil moisture content, θ the volumetric soil moisture content and θ_{ref} is the volumetric moisture content of the reference soil used in the determination of the biodegradation rate constant, which Larsbo and Jarvis (2003) in MACRO 5.0 assumes equal to the saturated micropore water content. As indicated by Jarvis and Stenemo (2001), the reference soil moisture content is most likely 40–50% as recommended by the EU guidelines on soil biodegradation tests. In PestLCI this fraction is therefore by default 50%.

The topsoil moisture biodegradation correction factor $F_{ts,m}$ is calculated applying this topsoil moisture content in Eq. (35):

$$F_{ts,m} = F_{s,m}(\theta_{ts}) \quad (36)$$

where θ_{ts} is the volumetric moisture content of the topsoil.

The fraction lost by biodegradation in the topsoil is for a given time step now calculated as

$$f_{sb,\Delta t} = f_s(1 - e^{-F_{ts,m} F_{ts,t} k_{sb} \Delta t}) \quad (37)$$

where k_{sb} is the pseudo-first order biodegradation rate constant (h^{-1}) and Δt is the time step considered (h).

Since volatilization and biodegradation are competing processes, the fraction lost by each process is calculated for each time step using numerical integration.

Table 4 – Soil type factor used in Eq. (39) as determined by the sand content of the top soil. Data from Reus et al. (1999)

Sand content (%)	F_{st}
>85	0.01
85–45	0.5
<45	1

The fraction left after $t = t_{rain}$ h is calculated as

$$f_{s,t_{rain}} = f_s - \sum_{t=0}^{t=t_{rain}} (f_{sb,\Delta t} + f_{sv,\Delta t}) \quad (38)$$

where f_s is the fraction of pesticide originally deposited on the soil.

2.4.3. Fraction lost by runoff (f_r)

Using the approach described for the EPRIP method (Reus et al., 1999), the fraction lost by runoff can be calculated from the porosity as determined by the sand content of the soil, from the slope of the field, a rain fall factor and the K_{oc} of the pesticide as

$$f_r = f_{s,t_{rain}} F_{st} F_s F_r (0.55 \log K_{oc} + 1.47) \quad (39)$$

where F_{st} is a soil type factor accounting for the porosity of the soil, F_s is a slope factor, and F_r is a rainfall factor.

The soil type factor F_{st} is assigned based on the sand content of the topsoil according to Table 4.

The slope factor is, according to Reus et al. (1999), calculated as

$$F_s = 0.124 \times SL + 0.0082 \times SL^2 \quad (40)$$

where SL is the average slope of the field (%).

The rainfall factor F_r used in Eq. (39) is calculated as

$$F_r = 0.0208 \times RE + 0.00011 \times RE^2 \quad (41)$$

where RE is the excess rain (mm), calculated according to Reus et al. (1999) as

$$RE = R_{max} - 17 \quad (42)$$

where R_{max} is the monthly maximum daily rainfall (mm/day).

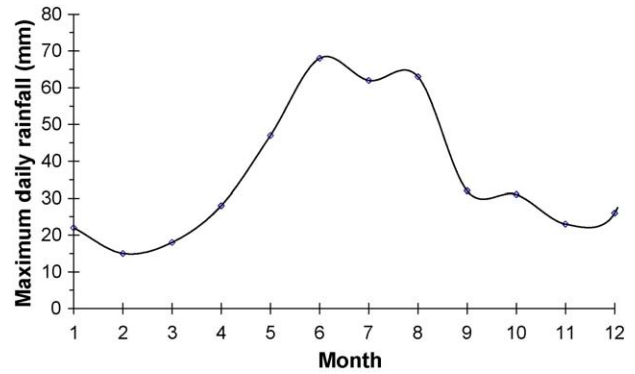


Fig. 8 – Average (1961–1999) maximum rainfall in 1 day (mm/day) in Denmark (Roskilde). Data from Planteinfo (2004).

As observed from Fig. 8, the maximum daily rainfall in Denmark in some months lies below the 17 mm/day used as correction in Eq. (42). These months are however not assumed to lie in the period where pesticides are applied in Denmark, since the low temperatures (see Fig. 7) in these months avoid growth of fungal and herbal pests and insect activity.

2.5. Secondary distribution below topsoil layer

The fraction reaching below the topsoil layer is the fraction available for leaching. Through leaching pesticides can, if the conditions are appropriate, reach the ground water. However, on their way to the groundwater layer, the pesticides may be removed from the soil by biodegradation.

2.5.1. Overall soil model

In pesticide models which include leaching (e.g. MACRO 5.0, Larsbo and Jarvis, 2003), the characterization of the stratification of the soil is extremely important for the precision of the leaching modeling. In PestLCI, the soil is therefore divided into a number of horizons each with their unique characteristics affecting leaching velocity and degradation. An example of a Danish soil and the characteristics used to describe each horizon in PestLCI is presented in Table 5.

The leaching module of PestLCI relies on calculation of the horizon specific retention times by unidirectional downward movement. During the calculated retention time, the

Table 5 – Danish soil profile (Tune located near Roskilde)

Horizon name	Depth (cm)	% Clay (<2 μ m)	% Silt (2–50 μ m)	Sand (>50 μ m)	pH	Dry bulk density (g/cm ³)	f_{om}	f_{oc}^a
Ap	0–25	18	35	47	7.1	1.56	2.86	1.43
Bt	25–43	25	30	45	7.2	1.64	0.48	0.24
Bt(g)	43–66	20	27	53	7.6	1.69	0.37	0.19
Cc(g) 1	66–95	20	27	53	8.3	1.83	0.55	0.28
Cc(g)2	95–116	18	32	50	8.3	1.76	0.52 ^a	0.26
Ccg	116–155	19	31	50	8.3	1.77	0.48	0.24

Data calculated from DJF (2003).

^a Calculated according to Schwarzenbach et al. (2003) as: $0.5 \times f_{om} = f_{oc}$.

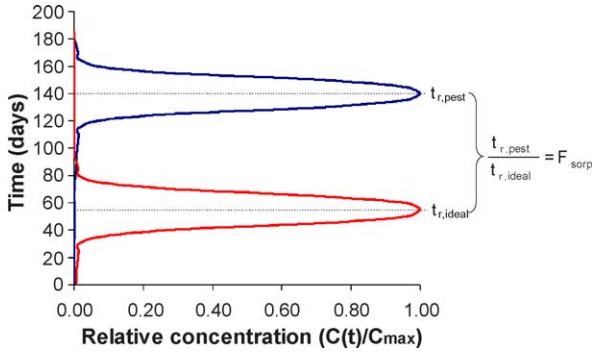


Fig. 9 – Illustration of the relation between retention factor (F_{sorp}) and retention time of an ideal tracer ($t_{r,ideal}$, lower curve) and the retention time of a pesticide ($t_{r,pest}$, upper curve) in soil. The difference in retardation time is due to sorption of the pesticide, which is accounted for by the retardation factor (F_{sorp}).

depth- and temperature-corrected biodegradation removes pesticide.

2.5.2. Soil horizon retardation

The retardation in each soil horizon is calculated based on the ideal retardation time ($t_{r,ideal}$) which corresponds to the retardation time of substances which are not retained by sorption. $t_{r,ideal}$ is thus equal to the retardation time of an ideal tracer having the same diffusion and dispersion coefficients as the pesticide.

The retardation time of the ideal tracer is the time it takes to achieve maximum concentration of the tracer in the percolate of the soil horizon.

The retardation time of the pesticide ($t_{r,pest}$) is the product of the retardation time of the ideal tracer and the retardation factor (F_{sorp}) of the pesticide which corrects the retardation time of the ideal tracer for sorption (see Fig. 9).

It is assumed that the time to maximum concentration in the percolate ($t_{r,pest}$) corresponds to the average time it takes the pesticide to reach the bottom of a horizon.

The retardation time ($t_{r,ideal,i}$ in h) of a narrow pulse of an ideal tracer in horizon i is calculated according to Borggaard et al. (1996) as

$$t_{r,ideal,i} = \frac{L_i}{v_i} \left(\sqrt{1 + \left(\frac{D_{w,a,i}}{v_i L_i} \right)^2} - \frac{D_{w,a,i}}{v_i L_i} \right) \times 24 \text{ h/d} \quad (43)$$

where L is the thickness of horizon i (m), v_i the average pore water velocity (m/d) and $D_{w,a,i}$ is the apparent dispersion/diffusion coefficient (m^2/d) in horizon i .

As 0.01 m of the first soil horizon is included in the topsoil model module:

$$L_i = L_1 - 0.01, \quad i = 1 \quad (44)$$

v_i in Eq. (43) is the average pore water velocity (m/d), which is estimated here as

$$v_i \approx \frac{q}{\phi_i} \quad (45)$$

where q is the filter velocity (m/d) and ϕ_i is the volumetric water content of the soil (%).

The filter velocity is estimated from the average annual hydraulic flow in the soil:

$$q = \frac{((P_{ann,av} + I_{ann,av}) - PE_{ann,av}) \times 10^{-3} \text{ m/mm}}{365 \text{ d}} \quad (46)$$

where $P_{ann,av}$ is the annual average precipitation (mm) in 0 m height at the soil surface, $I_{ann,av}$ is annual average irrigation (mm) and $PE_{ann,av}$ annual average potential evaporation.

The apparent dispersion/diffusion coefficient ($D_{w,a,i}$) used in Eq. (43) is the sum of the effective diffusion coefficient in water ($D_{w,diff,i}$) and the dispersion coefficient (D_{disp}):

$$D_{w,a,i} = D_{w,diff,i} + D_{disp} \quad (47)$$

The apparent diffusion coefficient can, according to Trapp and Matthies (1998), be estimated as

$$D_{w,diff,i} = \frac{D_w \theta_i^{10/3}}{\phi_i^2} \quad (48)$$

where D_w is the diffusion coefficient in water, θ_i is the volumetric water content of soil horizon i , and ϕ_i is the porosity of horizon i .

The diffusion coefficient in water is estimated according to Schwarzenbach (2003) as

$$D_w = \frac{13.26 \times 10^{-5}}{\eta^{1.14} MV^{0.589}} \times 8.64 \frac{\text{m}^2 \text{ s}}{\text{cm}^2 \text{ d}} \quad (49)$$

where η is the water viscosity in centipoises ($10^{-2} \text{ g}/(\text{cm s})$) based on annual soil temperature average and MV is the molecular volume of the pesticide in cm^3/mol (here estimated using ACD Labs, 2003).

The dispersion coefficient used in Eq. (47) can, in accordance with Trapp and Matthies (1998), be estimated as

$$D_{disp,i} \approx v_i \quad (50)$$

The retardation factor of a pesticide in soil can, according to Stumm (1992), be calculated as

$$F_{sorp,i} = 1 + \frac{\rho_{b,i}}{\theta_i} K_{dpH,i} \quad (51)$$

where $\rho_{b,i}$ is the bulk density (kg/l), θ_i the volumetric water content, and $K_{dpH,i}$ is the pH dependent sorption coefficient (l/kg), all specific for horizon i .

For organic acids it is assumed that only the non-dissociated fraction sorbs, the rest behaves like an ideal tracer. The pH corrected sorption coefficient is calculated as

$$K_{dpH,i} = \alpha_{HA,i} K_{d,i} = \frac{1}{1 + 10^{\text{pH}_i - \text{pK}_a}} K_{d,i} \quad (52)$$

where α_{HA} is the fraction of pesticide on the non-dissociated form at the horizon specific pH (pH_i) and $K_{d,i}$ is the horizon specific sorption coefficient (l/kg).

$K_{d,i}$ can, according to Schwarzenbach (2003), be calculated as

$$K_{d,i} = f_{oc,i} K_{oc} \quad (53)$$

The retardation time ($t_{r,pest,i}$) of a pesticide in horizon i is now calculated as

$$t_{r,pest,i} = F_{sorp,i} t_{r,ideal,i} \quad (54)$$

2.5.3. Soil horizon biodegradation reducing factors

The horizon specific biodegradation rate constant is based on the soil biodegradation rate constant corrected according to temperature, soil moisture content, depth and bioavailability.

The temperature correction is calculated from the soil temperature in 10 cm depth, using Eqs. (34a)–(34c).

The soil temperature in 10 cm depth is estimated from the air temperature above the soil according to Fig. 10.

The temperature correction factor for biodegradation in deeper soil layers ($F_{ds,t}$) is calculated as

$$F_{ds,t} = F_{s,t}(T_{soil,10\text{ cm}}) \quad (55)$$

where $F_{ds,t}$ is calculated based on the soil temperature in 10 cm depth (Fig. 10) according to Eqs. (34a)–(34c).

The horizon specific soil moisture correction factor for biodegradation in deeper soil layers ($F_{ds,m,i}$) is calculated according to Eq. (36) as

$$F_{ds,m,i} = F_{s,m}(\theta_i) \quad (56)$$

where θ_i is the soil moisture content of horizon i .

The soil depth biodegradation correction factor ($F_{ds,d,i}$) is calculated based on a weighted average of the soil depth using the factors presented by FOCUS (2000) as

$$F_{ds,d,i} = f_{1-30} \times 1 + f_{30-60} \times 0.5 + f_{60-100} \times 0.3 + f_{100} \times 0 \quad (57)$$

where f_{1-30} is the fraction of soil horizon in the depth range (1–30 cm), f_{30-60} the fraction of the soil horizon in the depth range (30–60 cm), f_{60-100} the fraction of the soil horizon in the

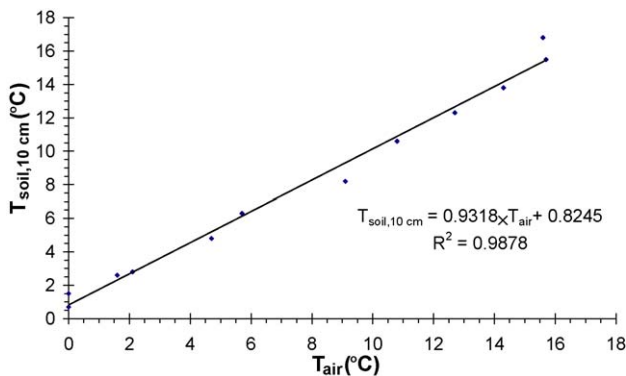


Fig. 10 – Correlation between air temperature above soil (measured at 1.5 m height) and soil temperature in 10 cm depth. Data on soil temperature from DEPA (1999a,b), data on air temperature from Planteinfo (2004).

depth range (60–100 cm) and f_{100} is the fraction of the soil horizon in the depth range (100–∞ cm).

Following Larsbo and Jarvis (2003), for practical purposes, biodegradation ceases in 1 m depth, and the fraction reaching groundwater is therefore in PestLCI equal to the fraction reaching 1 m.

The factor correcting the soil biodegradation with respect to bioavailability ($F_{ds,b,i}$) is calculated according to Schwarzenbach (2003) as

$$F_{ds,b,i} = \frac{1}{1 + K_{dpH,i} \rho_s \frac{1-\phi_i}{\phi_i}} \quad (58)$$

where ρ_s is the density of the solid material in soil (default 2.65 kg/l according to Borggaard et al., 1996), and ϕ_i is the porosity of the soil horizon i .

2.5.4. Soil horizon biodegradation

The horizon specific soil biodegradation rate constant corrected according to temperature, soil moisture content, depth and bioavailability is now calculated as

$$k_{bs,ds,i} = F_{ds,t} F_{ds,m,i} F_{ds,d,i} F_{ds,b,i} k_{bs} \quad (59)$$

The fraction of applied pesticide left for leaching ($f_{sl,0}$) after runoff has occurred is calculated as

$$f_{sl,0} = f_{s,t,rain} - f_r \quad (60)$$

The fraction of applied pesticide ($f_{sl,i}$) leaching through any horizon is calculated as

$$f_{sl,i} = f_{sl,i-1} e^{t_{r,pest,i} k_{bs,ds,i}} \quad (61)$$

2.5.5. Drainage interception

When drainage systems are present in the soil, a fraction of the water and the pesticide dissolved in it will be intercepted and lost through the drainage system. Here the fraction intercepted is assumed to be equal to the drainage system frequency (here the national fraction of drained arable land is used).

The soil horizon where the drainage system is present is simply split in two separate soil horizons: one above the drainage system and one below.

The fraction leaching through upper soil horizon is subsequently split by the drainage system into a fraction which is intercepted by the drainage system and a fraction which is leaching through the drainage layer and on to the next horizon. The fraction leaching through the soil horizon ($i = m$) just above the drainage system and escaping the drainage system is calculated as

$$f_{sl,m} = f_{sl,i} (1 - \delta) \quad (62)$$

where δ is the drainage frequency. If the field is known to be drained, $\delta = 1$. If no specific field is assumed, the average drainage frequency of the region or country is assumed, determined as the fraction of the agricultural land which is drained.

Table 6 – Physical–chemical properties, fate parameters and typical use of Bentazone, MCPA and Pendimethalin

Parameter	Bentazone	MCPA	Pendimethalin
Normal dosing (g/ha)	500	1500	1600
Crop	Corn	Spring sown cereals	Winter cereals
Temporal use ^a	Before 1 September	Before 1 August	None
Border zone ^b	10 m	None	10 m
Product example ^c	Basagran 480	NF-M 750	Stomp
CAS no.	25057-89-0	94-74-6	40487-42-1
MV (cm ³ /mol)	178.5	152.7	231.5
Ws (g/l)	0.5	0.6	0.3
V _p (Pa)	4.6 × 10 ⁻⁴	0.8	4.0
pK _a	2.9	3.1	N/A
K _{om} (l/kg)	0.4	29	111
K _{oc} (l/kg) ^d	0.8	58	222
K _H	9.19 × 10 ⁻¹⁴	5.70 × 10 ⁻¹⁴	8.56 × 10 ⁻⁷
t _{1/2,soil} (days)	48	15	171
k _{sb} (h ⁻¹) ^e	6.02 × 10 ⁻⁴	1.93 × 10 ⁻³	1.69 × 10 ⁻⁴

References: DEPA (2003, 2004), ACD Labs (2003), USDA (2004) and Linders et al. (1994).

^a Temporal restriction on use.

^b Width of the required no-spray zone.

^c Example of product containing pesticide as only active ingredient.

^d K_{oc} calculated from K_{om} (l/kg) assuming f_{om} = 2 × f_{oc} according to Schwarzenbach et al. (2003).

^e k_{sb} calculated from t_{1/2,soil}.

The fraction lost to the drainage system (f_{dr}) is calculated as

$$f_{dr} = f_{sl,m}^{\delta} \tag{63}$$

The fraction avoiding the drainage is further depleted by biodegradation in the same manner as in the horizons above the drainage system. The final fraction reaching the groundwater in horizon g is calculated as

$$f_{sl,i} = f_{dr}, \quad (f_{100} = 1.00) \tag{64}$$

3. Results

The total load of pesticides (herbicides, insecticides and fungicides) sold in Denmark in 2002 was approximately 2722 tonnes of which approximately 2105 tonnes were herbicides (DEPA, 2003). Some of the most frequently used herbicides were MCPA (approximately 145 tonnes), Pendimethalin (99 tonnes) and Bentazone (56 tonnes). The physical–chemical properties, fate parameters and use of these three pesticides are presented in Table 6.

To illustrate the applicability of PestLCI, two different comparisons of model results were carried out. The first comparison regards the emission fractions resulting from the application of Bentazone at four different times over the year. The second comparison regards the variations in emissions result-

ing from the application of Bentazone on maize, MCPA on spring sown cereals and Pendimethalin on winter cereals in May.

3.1. Example 1: temporal variation of emission fractions of the same pesticide

To compare the temporal variation in emission patterns, four Bentazone application scenarios on maize were set up. The scenarios are presented in Table 7.

Tune (field) and Roskilde (meteorological station) are located approximately 10 km apart and using the data from these two sites in combination to create realistic scenarios is therefore considered reasonable. The data presented in Figs. 6–8 were therefore used to characterize the meteorological conditions at Tune.

A number of crucial parameters needed in addition to substance characteristics and field system defaults to perform the simulations in PestLCI are presented in Table 8.

To compare the variations in emission fractions caused by temporal variation in the application of Bentazone, the three overall emissions fraction (see Fig. 2) were calculated for the emission to surface water (f_{sw}), to groundwater (f_{gw}) and to air (f_{air}) as

$$f_{sw} = f_{dr} + f_r, \quad f_{gw} = f_{sl,i=g}, \quad f_{air} = f_d + f_{lv} + f_{sv} \tag{65}$$

Table 7 – Time of application, height and development stage for maize crop used in the Bentazone scenarios

Scenario	Month	Crop height	Crop development stage
1	April	Field crops	Leaf development
2	May	Field crops	Stem elongation
3	June	Tall crops	Inflorescence emergence/flowering
4	August	Tall crops	Development of fruits/ripening

Table 8 – Parameters used to parameterize PestLCI

Parameter	Units	Value
Reference water content for biodegradation rate constant (MWHC) (θ_{ref})	%	50
Temperature response factor for biodegradation rate constant (α)	$^{\circ}\text{C}^{-1}$	0.08
Soil moisture content response factor for biodegradation constant (β)		0.7
Field area (ha) (A)	ha	10
Field slope (SL)	%	1.00
Width of spray boom (W_{boom})	m	8
Width of protected border zone included in field area (P)	m	10
Mean particle density (default value) (ρ_s)	g/cm^3	2.65
Soil air content (v/v) (V_a)	%	0.25
Soil water content (v/v) (V_w)	%	0.25
Soil solid matter content (v/v) (V_s)	%	0.5
Primary penetration depth of pesticide (IPD)	m	0.010
Drainage depth	m	0.600
Soil-air boundary layer, d	m	0.005
Drainage frequency	–	0.55

The results of the comparison of the temporal variation of the emission patterns of Bentazone are presented in Fig. 11.

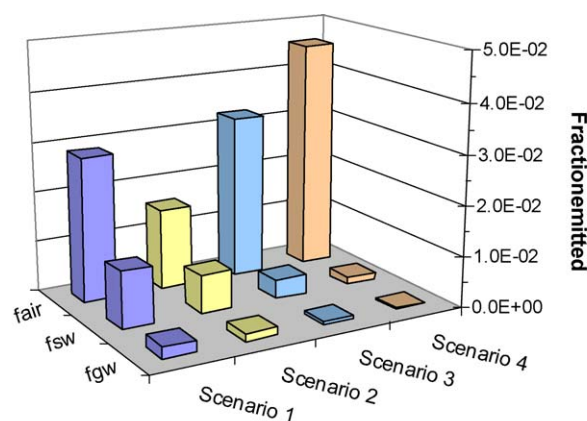
According to Linders et al. (1994), the realistic worst case fraction leaching by spring application of Bentazone is 1–13% with a mean of 8% depending on soil type, meteorological conditions and application form and time. The corresponding Bentazone fractions leaching in the two spring PestLCI scenarios are 0.23% (April) and 0.15% (May).

The fractions lost to surface water could not be validated; however runoff fractions for spring application of Mechlorprop and autumn application of Dichlorprop under Danish conditions are reported in the range 0.0002% (Dichlorprop) to 0.008% (Mechlorprop) (Felding et al., 1997). The minimum and maximum percentage lost by runoff in the two PestLCI spring scenarios with Bentazone are in the range 0.006% (August) to 0.032% (May).

The fractions emitted to air range from 1.6 to 4.6%. These fractions could not be validated by comparison with measured data. However, according to the standard air emission factors for pesticides presented by USEPA (1995), the standard emission factor (disregarding loss by wind drift) for pesticides like Bentazone ($1.3 \times 10^{-4} \text{ Pa} < V_p < 1.3 \times 10^{-2} \text{ Pa}$) is 3.5%.

3.2. Example 2: variation of emission fractions caused by differences in crop type and development stage

To compare the influence of the type and development stage of the crop, applications in May of the three pesticides presented in Table 6 are simulated using the pesticide specific normal



	fair	fsw	fgw
Scenario 1	2.9E-02	1.1E-02	2.3E-03
Scenario 2	1.6E-02	7.6E-03	1.5E-03
Scenario 3	3.3E-02	3.8E-03	7.5E-04
Scenario 4	4.6E-02	1.5E-03	3.0E-04

Fig. 11 – Bentazone emission fractions to surface water (f_{sw}), groundwater (f_{gw}) and air (f_{air}) resulting from the four temporal scenarios.

dosings to a 10 ha field parameterized in the same way as in the Bentazone scenarios in example 1. The three scenarios are presented in Table 9.

The resulting emission fractions of the three pesticides are presented in Fig. 12. The percentages of Pendimethalin and MCPA emitted to ground water are 0.64 and 0.0018%, respectively. Corresponding realistic worst case leaching percentages for the two pesticides by spring application can be found in Linders et al. (1994). Depending on soil type, meteorological conditions and application form and time they are <0.001–9% (mean 1.8) and <0.001–0.2% (mean 0.003), respectively.

The fractions lost by runoff in the three scenarios range from 0.0063 to 0.15%. The only runoff validation data available for similar conditions are those presented by Felding et al. (1997) for Mechlorprop and Dichlorprop and used in example 1, ranging from 0.0002 to 0.008%.

The fractions lost by air emission are as presented in Fig. 12: Bentazone (1.6%), MCPA (3.7) and Pendimethalin (16%). The corresponding standard emission fractions presented by USEPA (1995) disregarding wind drift are: Bentazone (3.8%), MCPA (5.8%) and Pendimethalin (5.8%). Except for Pendimethalin, the emission fractions are therefore comparable to standard emission factors for pesticides.

Table 9 – Crop type, crop height and crop development stage used in the scenarios for comparison of emission fractions by application to different crops in different development stages

Scenario	Pesticide	Crop	Crop height	Crop development stage
1	Bentazone	Maize	Field crops	Stem elongation
2	MCPA	Spring sown cereals	Field crops	Tillering
3	Pendimethalin	Winter cereals	Tall crops	Stem elongation

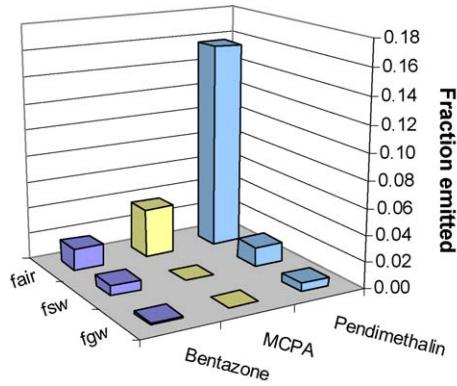


Fig. 12 – Emission fractions of Bentazone, MCPA and Pendimethalin to surface water (f_{sw}), groundwater (f_{gw}) and air (f_{air}) resulting from application in May using normal dosing.

3.3. Sensitivity analysis

A sensitivity analysis was performed varying all input parameters to PestLCI—substance-related as well as system-related to reveal their influence on the modeled emission fractions. The results are reported as sensitivity ratios for each combination of input parameter and emission fraction. A sensitivity ratio is the ratio between the percentage change in model output and the percentage change in model input. The parameters showing the highest sensitivity ratios for each of the emission fractions to air, surface water and ground water are presented in Table 10.

4. Discussion

The aim of PestLCI is to provide estimates on the emission fractions and modes of entry to the surrounding environment of pesticides being applied to fields using readily available data about substances and field system.

As presented in this paper, it is possible to account for this variation in a reasonably simple and transparent way using existing knowledge on the processes determining the fate of pesticides in the environment.

The applied characterization of the soil is in LCA terms quite data demanding, but it is considered very unlikely to be able to account for the complex processes occurring in soils (see Fig. 13), if the characterization of the soil is dealt with in a more general way, like assuming average conditions through all horizons. As presented in Fig. 13, the half life and residence time in the individual horizons varies in an unsystematic pattern which can hardly be described by applying a uniform average soil horizon from the top soil to 1 m depth. Biodegradation in deeper soil layers is a significant process removing large fractions of the pesticides applied. In the Bentazone case (example 1) the fractions of the applied

Table 10 – Sensitivity analysis results for the fractions emitted to air, surface water and ground water given for the five most influential parameters for each emission fraction

Parameter	Sensitivity ratio
f_{air}	
Solar irradiation in application month (MJ/m^2)	-1.32
Atmospheric $t_{1/2}$ (days) assuming 15 h day	6.64×10^{-1}
OH radical concentration (molecules/ cm^3)	-4.63×10^{-1}
Length of light period (h/day)	-4.63×10^{-1}
Field area (m^2)	-8.83×10^{-2}
Groundwater recharge (mm/y)	2.17
f_{sw}	
Soil, $t_{1/2}$ (days)	2.13
Sand content (top layer) (%)	-1.96
Maximum rainfall in 1 day (mm)	1.91
Field slope (%)	1.10
f_{gw}	
Groundwater recharge (mm/y)	9.32×10^2
Soil, $t_{1/2}$ (days)	7.44×10^2
Soil solid matter content (v/v)	-2.00
Reference water content of biodeg. constant (%)	2.00
Drainage frequency, δ	-1.70

A negative ratio indicates that input and output are inversely related.

amount which is removed by biodegradation in the deeper soil layers thus range from 0.7 to 0.09. Applying Pendimethalin on maize instead of Bentazone (substituting Bentazone with Pendimethalin in example 1), the same fractions range from 0.3 to 0.05. It is thus important to ensure an adequate modelling of this process.

The intended application within LCA has led to some fundamental choices in the development of PestLCI:

- (1) A modular structure was chosen to give a flexible and transparent model. The flexibility lies in the ease with which individual modules can be:
 - exchanged with other modules which have a more appropriate data requirement;
 - tuned to accommodate local conditions at the agricultural site;

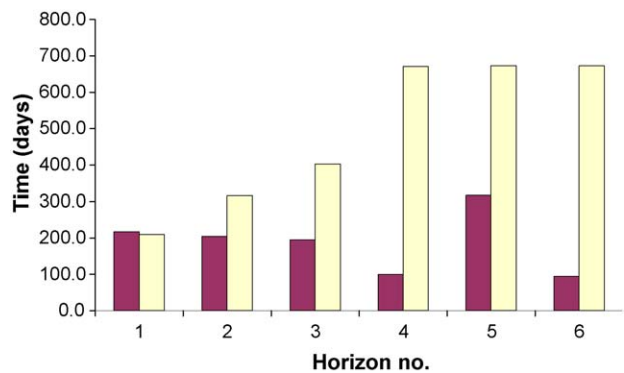


Fig. 13 – Horizon specific retention times in days (dark columns) and half lives in days for Bentazone (light columns) according to scenario 2 of Table 7.

- updated to be better in accordance with state of the art for the processes which are modeled, without having to re-program the whole model;
- superseded by measured data if such are available.

Furthermore, the modular structure increases transparency, meeting a key requirement in life cycle assessment where the overall analysed systems are often so complex that it is very difficult for outsiders to identify the key elements of the assessment unless it is very transparently reported.

- (2) The individual modules for PestLCI have been chosen as a compromise between environmental realism and feasibility in terms of data need. The use in LCA means that many substances must be modeled and that the field system may just be a minor part of the product system. Furthermore, the field and its surroundings will often be modeled as generic averages. Aspects like calculation time and ease of implementation are therefore more relevant for LCA models than for ERA models. Using monthly and annual data for PestLCI reduces the resources needed to provide external data and thereby to perform the evaluations. For instance soil leaching is a process which typically takes years, and the overall leaching velocity is therefore determined by the precipitation pattern of several years and not precipitations patterns of a given month. The meteorological, pesticide and geological data used in PestLCI are readily available at least for Denmark and provided for free (Planteinfo, 2004), and monthly and annual averaged meteorological data for any country is typically available in book form. It could be argued that the precision could be improved using better resolved data than monthly annual averages. The answer would be that the precision could be improved using such data, but the costs and benefits are not proportional, at least not for LCI where the aim is to provide the most likely (median) estimate contrary to ERA where the aim is to provide the most realistic worst case estimate. For PestLCI it is thus considered reasonable to estimate the median case from average data.
- (3) The ease of use is another important aspect which is more relevant for LCA than ERA. The evaluation time of one single pesticide using MACRO DB (Jarvis et al., 1997) is typically in the order of hours. Evaluation times of this magnitude are far beyond reasonable in the overall iterative framework of LCA, where evaluations may need to be performed on large numbers of chemicals several times as the key data are improved in the iterative process. Furthermore, the typical LCA practitioner and model user is a generalist, not an expert in the field of pesticide modeling. The choices necessary to achieve valid emission fractions should therefore be of general nature.

These choices are made as a compromise between meeting the boundary conditions of life cycle assessment (site-generic assessment, low data requirements, and mass flows—not concentrations) and providing modeling results which do give a best estimate of average emissions. With its modular structure, PestLCI is well geared to model average field and meteorological conditions for a larger area as well as specific field conditions for a given application, thereby meeting the boundary conditions and at the same time allowing site-

specific assessment in the cases where this is needed. As regards the latter goal, this is validated comparing the results obtained by PestLCI and by well renowned ERA models for pesticides.

The results for the fractions leaching to groundwater are in good accordance with the general estimated leaching fractions presented by Linders et al. (1994). It should be noted that results presented by Linders et al. (1994) are realistic worst case estimates obtained from the leaching model PESTLA (Boesten and van den Linden, 1991). These validation points should be interpreted with caution, since comparison of a later version of PESTLA (PEARL, Tiktak et al., 2000) and three other leaching models as presented by FOCUS (2000), has shown differences of up to three orders of magnitude in the worst case groundwater percolate concentration among the models investigated. The validation of the leaching module of PestLCI could also partially have been performed using other existing leaching models like MACRO (Larsbo and Jarvis, 2003), PRZM (Carsel et al., 1998) or PELMO (Klein et al., 1997). Depending on soil, pesticide and meteorological conditions or for the same combination of these, the predictions of the leaching concentration and thereby the leaching fractions vary up 3 decades between the models for the same soil, meteorological conditions and pesticides (FOCUS, 2000). Despite the simple and LCA applicable approach applied in PestLCI, the model seems to be able to reflect the observed variations in leaching fractions of the pesticides included in the examples.

The fraction lost by runoff was validated using data for different pesticides. The fraction lost by runoff is primarily dependent on the vapour pressure and K_d of the pesticide, since the fraction available for runoff, when a precipitation event occurs, is inversely proportional to the vapour pressure and the capability of the soil to retain the pesticide by sorption. The estimated fractions lost by runoff are however in acceptable accordance with measured data on Dichlorprop and Mechlchlorprop.

Except for Pendimethalin, the fractions lost by air emission are in good accordance with the standard emission fractions presented by USEPA (1995), which however do not include loss by wind drift. The Danish meteorological conditions are very different from the prevailing North American conditions and especially the soil temperatures are generally low, which in general lowers the significance of the fraction lost by volatilization. For pesticides like Pendimethalin, having as high a vapour pressure as 4.0 Pa, loss by volatilization will despite the lower temperature play a significant role in the emission pattern. Due to the high vapour pressure the standard emission factors are potentially underestimating the fractions lost by volatilization. Since the standard emission fractions are disregarding loss by wind drift, the question is if the model results for Bentazone and MCPA are credible. Both pesticides have a vapour pressure in the lower end of the both validity range for the standard emission factors. The fact the fractions lost by air emission in examples 1 and 2 including wind drift actually are of comparable magnitude to the standard emission factors, is potentially caused by the fact that both pesticides have vapour pressures in the lower end of the validity of the respective standard emission factors, further indicating the fractions lost by air emission are overestimated for Bentazone and MCPA, when applying standard emission fac-

tors, but that the inclusion of the fraction lost by wind drift in examples 1 and 3 compensates for this. Pendimethalin on the other hand has a vapour pressure more than 3.7×10^4 times larger than the lower end of the standard emission factor validity range. The fractions lost through air emission in example 2 exceed the standard emission factors by approximately a factor 3. This discrepancy is potentially caused by the fact that the standard emission factors are disregarding the fraction lost by wind drift and potentially also under estimating the fraction lost by volatilization.

The variations of the emission fractions, obtained by using PestLCI in the four Bentazone scenarios, are ranging from approximately a factor 3 (fraction emitted to air) to approximately a factor 8 (fraction emitted to groundwater). The variations of the emission fractions observed from the three scenarios on different land uses are ranging from a factor 9 (emission to air) to approximately a factor 36,000 (emission to groundwater). These variations indicate the magnitude of the error that could be associated with the use of static emission fractions instead of a model like PestLCI. The data on the fractions leaching to groundwater indicate that the pest management practice in terms of crop development stage at application and the applied pest management technique is a key factor determining the likelihood of groundwater contamination. Further, the data indicate that the emission fractions just for one field are very dynamic and the use of static emission factors and possibly pseudo-static emission factors cannot, with an acceptable accuracy, account for the variations resulting from different agricultural practices.

Due to its relatively simple structure, PestLCI has a number of limitations:

1. Uptake by crops through roots is not dealt with in the present version of the model but considered for inclusions in later updates of the model. The rationale behind including leaf uptake and not root uptake is that the existing models for root uptake are based on a purely lipophilicity-based equilibrium approach leading to total stem concentration factors (TSCF) as presented by Trapp and Matthies (1998). This approach has been criticized (Trapp and Schwartz, 2000) due to its narrow validity range, applicability only to persistent non-dissociating pesticides and its lack of plant species specificity. Further studies presented by Trapp et al. (2003) indicate that for trees, compounds with a $\text{Log}K_{ow} > 5.0$ do not bioaccumulate significantly by root uptake due to their strong adsorption onto soil lowering their availability to bioaccumulation by root uptake. Approximately 13% of the pesticides approved for use in Denmark has $\text{Log}K_{ow} > 5$ and approximately 47% dissociate at realistic ambient pH. This means that the TSCF approach is only applicable to approximately 40% of the pesticides approved for use in Denmark. When accounting for uptake by crops, some plant species differentiation thus seems needed to reflect the morphological variation observed between crops like trees and grasses.
2. Even though the leaf uptake model included in PestLCI is only based upon two different plant species, these are rather different in their leaf morphology and considered able to reflect the major variations in leaf uptake in a reasonable and valid way. Furthermore, the driving forces of the leaf uptake model are temperature, molecular volume and plant species and not only the octanol–water partition coefficient (K_{ow}) as is the case for the TSCF approach.
3. The model methodology assumes that the farmer follows the recommended use (time of application, dosing, etc.) of the pesticides. Significant groundwater contamination can, however, be caused by few farmers not following the recommendations, and this would not be shown by PestLCI.
4. Other models like MACRO DB (Jarvis et al., 1997) include a leaf wash off fraction which corresponds to the fraction of pesticide deposited on leaves, which is washed off per millimeter rain. Assuming that the farmer seeks to optimize the efficiency of the pesticide and hence avoids applying pesticide just before a known precipitation event, the applied pesticide will typically reside on the leaves for one to several days before a precipitation event occurs. As the half life of pesticide on the leaf, just with respect to oxidation by OH^\bullet , is typically in the order of hours, the fraction which will be left when a precipitation event occurs will be very small, and the wash off is therefore disregarded in PestLCI.

4.1. Sensitivity analysis

The sensitivity analysis reveals that the parameters with the largest influence on all emission fractions are parameters which depend on the location of the field and the time of application.

As seen from Table 10, groundwater recharge is the most sensitive parameter in general. The sensitivity of this parameter is positively correlated to f_{sw} and f_{gw} which is in good accordance with the general perception of the relation between the ground water recharge and ground water and surface water emission patterns.

The fraction emitted to air is most sensitive to changes relating to solar irradiation, since atmospheric fate of the pesticides is the process having the most influence on the air emission results.

In general, only two pesticide properties were identified as having significant influence on the emissions patterns, relating either to persistence in air or soil.

The majority among the most sensitive parameters are related to soil properties, geological conditions and meteorological conditions or combinations hereof, which is unfortunate, since these parameters are not generally collected in LCA rendering the application of default values necessary. This will inevitably lead to a higher uncertainty of the model's emission mass estimation.

5. Conclusion and outlook

PestLCI in the presented form represents an alternative to the application of static or pseudo-static (based on one or two properties) emission fractions in LCI. The model is considered capable to account for the variation in emission patterns caused by substance properties, geological and meteorological conditions, and pest management strategies applied by the farmer, and it is applicable to the use in life cycle assessment of agricultural product systems.

Realistic scenarios of pesticide application to field crops reveal more than four orders of magnitude variation in emission fractions to groundwater. This variation would be ignored by the use of static emission fractions and illustrates the need for a pesticide emission model like PestLCI in LCA of agricultural food and non-food products.

The model has already shown its usefulness in the Danish LCA-FOOD project (LCA-FOOD, 2004) where a database on agricultural unit processes has been established.

PestLCI is prepared to incorporate variations in all the system parameters but there is a need to establish the relevant data for other countries than Denmark where the model has been developed.

The model can be adapted to the conditions in any country if the needed data are available. National meteorological and agricultural authorities typically compile the meteorological and soil data needed to run PestLCI. It is therefore considered very likely that within most countries site dependent assessment of emission fractions should be possible. The simple databases included in the model are easily updated.

PestLCI has been programmed as an Excel spreadsheet model incorporating a database with the physical chemical data of the 69 pesticides which are allowed for field use in Denmark and providing (Danish) default values for all other parameters needed to run the model. The authors are interested in collaboration on the adaptation of the PestLCI model to other regions of the world, and the spreadsheet model is available from the corresponding author upon request.

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