Method and documentation of harmonized plant uptake and residue modelling of organic and inorganic pesticides

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Abstract

The main objective of work package 4 (WP4) is to apply, improve and align state-of-the-art LCIA models in a way that model input data and results can consistently be aligned with LCI model data and results and that characterization results can be operationally incorporated in current LCA databases and software. A document providing guidance on plant uptake and residue modelling of organic and inorganic pesticides is provided in the present deliverable.

1. Coupling emissions with USEtox

Before describing in detail the process of coupling emission model results with crop residue models, we introduce briefly how generally emission and impact models are coupled for pesticides in LCA. As starting point, the impact score for human toxicity and ecotoxicity impacts of pesticide emissions, IS (impact/functional unit), is calculated as:

\[
IS = \sum_{p,c} \left( m_{emi,p,c} \times CF_{p,c} \right)
\]

(1)

where \(m_{emi,p,c}\) (kg\(_{emitted}/FU\)) is the total emitted mass of pesticide \(p\) into a given environmental compartment \(c\), and \(CF_{p,c}\) (impact/kg\(_{emitted}\)) is the corresponding characterization factor for a given impact category (i.e. human toxicity or ecotoxicity).

Emission mass is usually not known to LCA practitioners (Rosenbaum et al. 2015), but can be obtained from the pesticide mass applied to crop fields, \(m_{app,p}\) (kg\(_{applied}/FU\)) and the related mass fraction that is emitted into different environmental compartments, \(mf_{p,c}\) (kg\(_{emitted}/kg_{applied}\)):

\[
m_{emi,p,c} = m_{app,p} \times mf_{p,c}
\]

(2)

When pesticides contain metal ions, they cannot be characterized as organic substances, since characterizing metals requires to consider speciation and other metal-relevant characteristics (Dong et al. 2014). Emission fractions for pesticides, which need to be characterized as metal ions, hence require a correction factor that accounts for the mass contribution of the metal ion to the overall mass of the emitted pesticide molecule:

\[
m_{emi,p,c} = m_{app,p} \times mf_{p,c} \times \frac{MW_{iEP} \times n_i}{MW_p}
\]

(3)

where \(MW_{iEP}\) (g/mol) is the molecular weight of the metal ion \(i\) found in pesticide \(p\), \(n_i\) is the number of metal ions apparent in the pesticide molecule, and \(MW_p\) (g/mol) is the molecular weight of the pesticide. An example is basic copper chloride used as fungicide (CAS: 1332-40-7, molecular formula: Cl\(_2\)Cu\(_4\)H\(_6\)O\(_6\), \(MW_p = 427.14\) g/mol), which contains \(n_i = 4\) molecules of Cu(II) (CAS:...
15158-11-9, \( MW_{i\epsilon p} = 63.55 \text{ g/mol} \). This gives a mass contribution of Cu(II) on basic copper chloride emission of \((63.55 \text{ g/mol} \times 4)/427.14 \text{ g/mol} = 0.6\).

In most LCAs, applied mass is derived from reported doses applied to a certain crop area, summed over different treatments, and is assumed to reach only field soil, i.e. \( mf_{p,c} = 1 \) for \( c = \text{ field soil} \), and \( mf_{p,c} = 0 \) for all other compartments across pesticides (Nemecek & Schnetzer 2011). This approach, however, is too simplistic and can be misleading, since relevant emission fractions might reach other compartments and field crop surfaces. Instead, a mass-balance model should be applied that accounts for pesticide distribution processes after field application, considering crop and field characteristics (e.g. crop growth stage and field width) along with agricultural practices (e.g. application method). Such a model is PestLCI 2.0 (Dijkman et al. 2012), which was further adapted and implemented as a web-based PestLCI Consensus tool (Fantke et al. 2017). Using this adapted PestLCI Consensus model, we can estimate initial distribution (first minutes after application) and secondary emission (until first rain event) fractions. Emission distribution fractions sum up to \( \sum_c mf_{p,c} = 1 \) for any given pesticide.

Characterization factors, \( CF_{p,c} \) (impact/kg emitted), use the pesticide mass emitted into a given environmental compartment as starting point to evaluate related impacts (either on humans or on ecosystems) based on characterizing for each pesticide its environmental fate, exposure and (eco-)toxicity effects. We recommend the scientific consensus model USEtox (Rosenbaum et al. 2008), to obtain human toxicity- and ecotoxicity-related characterization factors as:

\[
CF_{p,c} = FF_{p,c} \times XF_{p,c} \times EF_p = If_{p,c} \times EF_p
\]  

(4)

where \( FF_{p,c} \) (kg in compartment per kg emitted/d) is the fate factor denoting the increase in pesticide mass in compartment \( c \) for an emission into any compartment, \( XF_{p,c} \) (kg intake/d per kg in compartment or kg dissolved/kg in compartment) is the exposure factor relating population intake (for human exposure) or dissolved pesticide mass (for ecosystem exposure) to total mass in the given compartment, and \( EF_p \) (impact/kg intake or impact/kg dissolved) is the effect factor finally relating exposure to impacts. For human toxicity, fate and exposure factors can be summarized into human population intake fractions, \( If_{p,c} \) (kg intake/d per kg emitted/d).

For human toxicity, impacts are expressed as population-level disease incidence risk, which is denoted as incidence or disease ‘case’ when cumulatively exceeding 1, and for ecotoxicity, impacts are expressed as potentially affected fraction (PAF) of exposed species, integrated over compartment volume and the pesticide’s residence time in the environment. We recommend the following mapping of PestLCI Consensus to USEtox compartments for consistently combining initial distribution and secondary emission fractions to respective characterization factors (Figure 1).
Air (PestLCI Consensus) is assigned to continental rural air (USEtox), field soil surface and field soil are assigned to continental agricultural soil, and groundwater is assigned to continental freshwater. Off-field surfaces are assigned to continental agricultural soil, natural soil (including urban areas) and freshwater according to the area share of each compartment in a given region (i.e. respectively 29%, 70% and 1% in Martinique). Other initial distribution and emission compartments (crop components and degradation) are not linked to USEtox.

2. Coupling emissions with dynamiCROP for crop residues

Equation 4 is valid when characterization factors relate to emitted pesticide mass. Impacts related to pesticide mass ending up in the harvested components of the treated field crops consumed by humans are a major contributor to human disease burden, but are currently usually missing in LCA studies, and related emissions to field crop surface (output of PestLCI Consensus) are hence not characterized. To consider such impacts, we recommend to use the dynamiCROP model (Fantke et al. 2011a, Fantke et al. 2011b), which was recently integrated for some parameterized scenarios into USEtox (Fantke & Jolliet 2016). We propose to use dynamiCROP to obtain residue-related characterization factors for crop $x$ (i.e. impacts from intake of pesticide residues in consumed crop components) as:

$$ CF_{p,c} = hF_{p,c}(t) \times PF_f \times EF_p = iF_{p,c} \times EF_p $$

(5)
where $h_{p,c}(t)$ ($kg_{in~crop~harvest}/kg_{emitted}$) is the harvest fraction relating pesticide residues at harvest time $t$ (d) in crop components that are harvested for human consumption to pesticide mass emitted into a given environmental compartment, $PF_f$ ($kg_{in~processed~food}/kg_{in~crop~harvest}$) is a residue reduction factor due to food processing step $f$ (e.g. washing, cooking), and $EF_p$ (impact/kg intake of processed food) is the human toxicity effect factor as defined in eq. 4. Harvest fraction and food processing factor can be combined into residue-related intake fractions, $IF_{p,c}$ ($kg_{intake}/kg_{emitted}$), consistent with intake fractions from USEtox (see eq. 4). Assuming for example that a harvested crop is mainly consumed freshly, a washing-related food processing factor of $PF_f = 0.56$ can be applied across pesticides (Kaushik et al. 2009). The harvest fraction as originally defined in dynamiCROP refers to total pesticide residues in crops (via all emission compartments) and relates to mass applied (Fantke et al. 2013). Related characterization factors for pesticide residues in crops, however, would not be consistent with using initial distribution or secondary emissions into different environmental compartments as defined in eq. 1. The harvest fraction $h_{p,c}(t)$ is hence adapted to relate to initial distributions and emissions, thereby consistently coupling dynamiCROP with PestLCI Consensus results:

$$h_{p,c}(t) = \frac{\sum h m_{res,p,h}(t)}{m_{app,p} \times mf_{p,c}} = \frac{\sum h m_{res,p,h}(t)}{m_{emi,p,c}}$$  \hspace{1cm} (6)$$

where $m_{res,p,h}(t)$ ($kg_{in~crop~harvest}/FU$) is the pesticide residual mass in crop components $h$ harvested at time $t$ (d) for human consumption. Since dynamiCROP uses matrix algebra to simultaneously solve a system of differential equations for $m_{res,p,h}(t)$, we realized the adaptation by transforming the input mass vector (i.e. $m_{emi,p,c}$ at time $t = 0$) into a diagonal matrix. Combining these initial conditions diagonal matrix with the fundamental matrix (i.e. mass fractions transferred between compartments at time $t$) yields emission compartment-specific $m_{res,p,h}(t)$. For details about the underlying matrix solution see Fantke et al. (2013).

Mass applied, $m_{app,p}$ ($kg_{applied}/FU$), distribution fractions, $mf_{p,c}$ ($kg_{emitted}/kg_{applied}$), emitted to a given environmental compartment matched between PestLCI Consensus (emission output) and dynamiCROP (input for residue calculations), and emitted mass, $m_{emi,p,x}$ ($kg_{emitted}/FU$) are defined in eq. 2. A full calculation example with 3 illustrative compartments (air, crop, soil) and showing the steps for adapting dynamiCROP in a way that it does not refer to the total mass applied (original approach) but instead to the mass emitted into specific environmental compartments (new approach) is shown in Figure 2.
Figure 2. Illustrative example of how the dynamiCROP model is adapted to provide output that refers to mass emitted into environmental and crop compartments, which is consistent with outputs from LCI emission models, such as PestLCI Consensus, for use in LCA.

The entire matrix framework as implemented in dynamiCROP and as adapted for LCA (i.e. starting at LCI pesticide emission results and arriving at characterization factors at midpoint and damage level for human toxicity impacts for pesticide residues) is shown for the example case of fungicide azoxystrobin (CAS: 131860-33-8) applied to wheat as archetypal cereal crop is presented in Figure 3a-d.
Figure 3a. Starting point in dynamiCROP to derive characterization factors based on emission outputs, showing initial mass conditions at application time (top) and at harvest time $t$ (bottom).

Figure 3b. Distribution of residual pesticide mass (top) and pesticide fractions in harvest (bottom).
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Figure 3c. Human intake fractions derived from pesticide fractions in crop harvest and food processing factors reducing pesticides in harvested crop components (top) and related human toxicity effect factors per kg pesticide intake into the human population (bottom).

Figure 3d. Final step to arrive at human toxicity characterization factors for pesticide residues at midpoint level (top), and related severity factors DF (middle) to yield damage-level characterization factors linking human lifetime loss (expressed in disability-adjusted life years, DALY) to emitted pesticide mass via pesticide residues in crop harvest as exposure pathway (bottom).
The air compartment (PestLCI Consensus) is assigned to air (dynamiCROP), field soil surface is assigned to soil, and field crop surface is assigned to leaf surface and fruit surface (see Figure 1) according to their total crop surface area contributions:

\[
m_{f,p,\text{leaf}} = \frac{\text{LAI}}{\text{LAI} + FAI} \quad \text{for leaf surfaces}
\]
\[
m_{f,p,\text{fruit}} = \frac{\text{FAI}}{\text{LAI} + FAI} \quad \text{for fruit surfaces}
\]

where \(m_{f,p,\text{leaf}}\) (kg emitted to leaf surface/kg emitted to field crop surface) and \(m_{f,p,\text{fruit}}\) are the initial mass fractions emitted to compartment \(c = \{\text{field crop surface}\}\) reaching respectively crop leaf and fruit surface areas, and \(\text{LAI} \quad (m^2_{\text{leaf surface}}/m^2_{\text{soil}})\) and \(\text{FAI} \quad (m^2_{\text{fruit surface}}/m^2_{\text{soil}})\) are respectively the crop-specific leaf and fruit area indices. The dynamiCROP model is currently applicable for assessing organic substances.

The dynamiCROP model version that is adapted for LCA, calculating all results factors per kg emitted into different environmental compartments, is further described and can be requested from http://dynamicrop.org/model.php.

3. Conclusions

Combining residue-related characterization factors (dynamiCROP) with characterization factors for environmentally mediated exposures of the general population (USEtox) ensures that all relevant initial distribution and emission fractions (PestLCI Consensus) are accounted for, building on a consistent combination of the three underlying models (see Figure 1). Connecting compartments between PestLCI Consensus and dynamiCROP for secondary emission fractions requires further research as there are currently potential overlaps in modeled plant uptake processes (light gray arrows in Figure 1).

References


Nemecek T, Schnetzer J (2011) Methods of assessment of direct field emissions for LCIs of agricultural production systems, Swiss Centre for Life Cycle Inventories, Duebendorf, Switzerland
