Dynamic Multicrop Model to Characterize Impacts of Pesticides in Food

Peter Fantke*
Institute of Energy Economics and the Rational Use of Energy, University of Stuttgart, Hessbruehlstrasse 49a, 70565 Stuttgart, Germany

Ronnie Juraske
Institute of Environmental Engineering, Swiss Federal Institute of Technology Zurich, CH-8093 Zurich, Switzerland

Assumpció Antón
Institute of Agriculture and Food Research and Technology, 08348 Cabrils, Barcelona, Spain

Rainer Friedrich
Institute of Energy Economics and the Rational Use of Energy, University of Stuttgart, Hessbruehlstrasse 49a, 70565 Stuttgart, Germany

Olivier Jolliet
Environmental Health Sciences, School of Public Health, University of Michigan, 109 S. Observatory, Ann Arbor, Michigan 48109-2029, United States
Quantis, EPFL Science Park (PSE-D), CH-1015 Lausanne, Switzerland

ABSTRACT: A new dynamic plant uptake model is presented to characterize health impacts of pesticides applied to food crops, based on a flexible set of interconnected compartments. We assess six crops covering a large fraction of the worldwide consumption. Model estimates correspond well with observed pesticide residues for 12 substance-crop combinations, showing residual errors between a factor 1.5 and 19. Human intake fractions, effect and characterization factors are provided for use in life cycle impact assessment for 726 substance-crop combinations and different application times. Intake fractions typically range from $10^{-2}$ to $10^{-8}$ kg intake kg applied$^{-1}$. Human health impacts vary up to 9 orders of magnitude between crops and 10 orders of magnitude between pesticides, stressing the importance of considering interactions between specific crop-environments and pesticides. Time between application and harvest, degradation half-life in plants and residence time in soil are driving the evolution of pesticide masses. We demonstrate that toxicity potentials can be reduced up to 99% by defining adequate pesticide substitutions. Overall, leafy vegetables only contribute to 2% of the vegetal consumption, but due to later application times and higher intake fractions may nevertheless lead to impacts comparable or even higher than via the larger amount of ingested cereals.

INTRODUCTION

Life cycle impact assessment (LCIA) has been used as a tool to characterize potential toxic impacts on human health and the environment attributable to pesticide use.\textsuperscript{1–3} LCIA thereby builds upon substance-specific characterization factors (CF) combining pesticide exposure and toxicity potentials to represent contributions of pesticides to overall human health and environmental impacts. Human health impacts of pesticides, however, are still poorly represented in existing LCIA approaches, since only effects from diffuse emissions are considered, thereby disregarding ingestion exposure from residues in field crops after direct pesticide application. While in case of diffuse emissions environmental media like air and soil serve as emission target...
Table 1. Selected Crops and Represented Archetypes According to a Set of Systematic Criteria Including Share of Crop on Human Consumption of Archetype (φcrop) and Share of Archetype on Total Human Vegetal Consumption (φarchetype)

<table>
<thead>
<tr>
<th>crop</th>
<th>archetype</th>
<th>consumption share</th>
<th>residues</th>
<th>characteristics</th>
<th>knowledge base</th>
<th>adaptable models</th>
<th>experimental residue data</th>
</tr>
</thead>
<tbody>
<tr>
<td>wheat</td>
<td>cereals</td>
<td>68%</td>
<td>24%</td>
<td>medium</td>
<td>Fantke et al.⁷</td>
<td>Cao¹⁶</td>
<td></td>
</tr>
<tr>
<td>paddy rice</td>
<td>paddy cereals</td>
<td>97%</td>
<td>13%</td>
<td>medium</td>
<td>Fantke et al.⁷</td>
<td>Reinf et al.¹¹</td>
<td></td>
</tr>
<tr>
<td>tomato</td>
<td>herbsaceous fruits and vegetables</td>
<td>15%</td>
<td>26%</td>
<td>high</td>
<td>Inao et al.¹⁷</td>
<td>Jurasek et al.⁶,²⁰</td>
<td></td>
</tr>
<tr>
<td>apple</td>
<td>fruit trees</td>
<td>13%</td>
<td>17%</td>
<td>high</td>
<td>Trapp¹⁰</td>
<td>Kumar et al.²³</td>
<td></td>
</tr>
<tr>
<td>lettuce</td>
<td>leafy vegetables</td>
<td>14%</td>
<td>2%</td>
<td>high</td>
<td>Paraiba²²</td>
<td>Xu et al.²⁴</td>
<td></td>
</tr>
<tr>
<td>potato</td>
<td>roots and tubers</td>
<td>51%</td>
<td>18%</td>
<td>medium</td>
<td>Jurasek et al.⁹</td>
<td>Juraske et al.⁹</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Paraiba and Kataguri²⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Abdel-Gawad et al.²⁹</td>
<td></td>
</tr>
</tbody>
</table>

Compartments, in case of direct application the cultivated food crop receives the applied mass. As a first attempt to account for effects of direct application, recent studies contrasted residues from direct and diffuse sources for human intake fractions (iF) in fruits and vegetables⁴,⁵ and concluded that ingestion of directly treated food crops is the most important human exposure route. As a result, detailed exchange processes between environmental media and vegetation have been introduced in multimedia models designed for LCIA, traditionally considering steady-state conditions. However, for pesticide residues and related impacts, steady-state is usually not reached during the short time period from substance application to ultimate crop harvest, which is why the evolution of residues needs to be assessed dynamically. In addition, pesticide uptake and translocation mechanisms vary considerably between crop species and may indicate significant differences in related health impacts.⁶ Consequently, differing crop-specific characteristics need to be considered as provided for individual crop species by recently developed plant uptake models.⁷–¹¹ Fantke et al.⁷ compare a wide range of crop-specific uptake models assessing environmental fate of pesticides after direct application and conclude that none of the existing tools is able to contrast various crops consumed by humans. This implies a major drawback in characterizing human toxicity for LCIA, the present paper aims at introducing a consistent approach for answering the following questions:

(i) How can human intake of pesticides via ingestion of different food crops and related health impacts be characterized and evaluated in a transparent, consistent and concise way?

(ii) What is the influence of crop characteristics, substance properties and application times on the dynamic behavior of pesticides in crops and on subsequent human intake?

(iii) What are the differences between crop-specific characterization factors from direct pesticide application to different food crops and generic characterization factors from continuous, diffuse emissions to the environment?

(iv) How can substitution of pesticides be evaluated and their health impacts compared on a similar functional basis?

To answer these questions, we developed a new dynamic assessment model for human health impacts due to uptake of pesticides into multiple crop types (dynamICROP) based on a transparent matrix algebra framework. We selected six food crops covering a large fraction of the worldwide consumption of vegetal origin, thereby representing the most important crop archetypes. For each archetype, substance-specific human ingestion intake fractions are calculated and evaluated. In addition, the influence of crop and substance characteristics as well as the time between application and harvest on pesticide characterization is discussed. Finally, crop-specific characterization factors are provided—differentiated according to human cancer and noncancer effect information—along with generic characterization factors to also account for diffuse pesticide emissions.

### MATERIALS AND METHODS

**Selection of Crops.** We introduce six characteristic plant species representing the most relevant crop archetypes with respect to human vegetal food based on a systematic criteria approach. Selection criteria are human consumption quantity, expected pesticide residues in harvest, crop characteristics (cropping practice, plant phenotype, and harvested components), availability of knowledge from other models, and finally availability of experimental data for comparison with modeled residues. Human consumption is analyzed based on global FAO statistics of 159 food crops.¹² Ranges of expected residues in food products are estimated based on maximum residue levels (MRL),¹³ considering MRL data from 70 countries, the European Commission¹⁴ and the Codex Alimentarius Commission.¹⁵ Table 1 summarizes the criteria analysis and lists selected crop species accounting for 45% of the global vegetal consumption in 2007.¹² These crops cover the most important archetypes, that is, cereals (wheat), paddy cereals (rice), herbaceous fruits and vegetables (tomato), fruit trees (apple), leafy vegetables (lettuce), as well as roots and tubers (potato). Based on these archetypes, the model framework can be easily adapted to assess additional species.

**Assessment Framework.** For human impacts, we followed the general LCIA cause-effect chain by linking applied pesticide masses to health impacts via environmental fate, exposure and effects.³⁰ The human-toxicological population impact score,
IS\text{total},_,x [DALY ha\(^{-1}\)], caused by intake of active ingredient \(i\) (hereafter referred to as “pesticide”) applied to crop \(x\) that is harvested at time \(t\) is expressed as the product of the characterization factor for human toxicity, \(\text{CF}_{i,x}(t)\) [DALY kg\(^{-1}\)applied], coupled with the life cycle inventory output, that is, the total mass of pesticide applied, \(m_{\text{app},i,x}\) [kg applied ha\(^{-1}\)]:

\[
\text{IS}_{\text{total},_,x} = \sum_{i=1}^{n} IS_{i,x}(t) = \sum_{i=1}^{n} \text{CF}_{i,x}(t) \times m_{\text{app},i,x}
\] (1)

with IS\text{total},_,x as total impact score per crop, expressed in DALY (disability adjusted life years as measure for overall population health impacts) per hectare. We determine the characterization factor by multiplying the human effect factor for pesticide health impacts) per hectare. We determine the characterization factor accounting for reduction in pesticide residues between harvest and final consumption. Mass in harvest is a result of the mass balance system of differential equations that is solved analytically by means of matrix algebra implemented in Matlab coupled with a spreadsheet as fully described in Fantke et al.\(^7\):

\[
\vec{m}(t) = e^{\mathbf{K}t} \vec{m}(0)
\] (5)

with \(\vec{m}(t)\) a column vector of substance masses at time \(t\) in the different compartments [kg], and \(\mathbf{K}\) the square matrix of first-order rate coefficients \([\text{d}^{-1}]\), in which diagonal elements represent overall removal rate coefficients in compartments and off-diagonal elements correspond to single intercompartmental transfer rate coefficients. In contrast to other plant uptake models focusing on a single-species environment, the present model accounts for system characteristics of various crops based on a flexible set of interconnected compartments. This allows to directly compare modeled crop-specific residues with experimentally derived concentrations in harvested plants and to contrast model results against official MRLs. Parameters determining the fate processes are physicochemical properties of applied pesticides, system initial and boundary conditions as well as crop-specific characteristics.

**Crop Characteristics.** Initial deposition of pesticides on plant surfaces directly after application depends on the crop-specific leaf area index (LAI) representing leaf growth stage, and furthermore the pesticide capture coefficient being a measure of a crop’s capture efficacy.\(^34\) While the latter can be seen as a fixed value, crop growth and related LAI development are time-dependent. Crop growth development is applied for all studied crops, describing an initial exponential growth that finally saturates at some maximum level.\(^7\)\(^,\)\(^11\) However, evolution of leaf area follows a more complex behavior. Crop-specific LAI curves based on experimental data are applied for wheat,\(^33\) paddy rice,\(^36\) tomato,\(^37\) apple,\(^38\) lettuce\(^39\) and potato\(^40\) as shown in Figure S1 (SI). After a pesticide is applied to a crop, a certain fraction of the initial dose has the potential for drifting from the agricultural site. In most cases, drift mainly depends on application method, pesticide formulation, environmental conditions and crop type.\(^41\) Typical crop type- and application method-specific drift values are applied as loss fractions. Finally, in order to evaluate the effect of food processing on the magnitude of pesticide residues in the studied crops, food processing factors for washing, peeling, cooking, juicing, and baking are adopted from Kaushik et al.\(^42\)

**Model Evaluation.** Internal model consistency was continuously examined by checking the underlying mass balance, that is, ensuring that the sum of elimination and biodistribution pathways at any time equals the total pesticide mass applied. Second, modeled residues are evaluated by analyzing whether model simulations adequately represent collected experimental data from the literature as given in Table 1. The measure used to estimate model prediction quality compared with experiments is the residual error, also known as standard deviation of the log of residuals between observed and modeled concentrations.\(^43\) A residual error of, for example, 0.5 implies a deviation between modeled and experimental data of approximately a factor \(10\)\(^{0.5}\), which is satisfactory. Third, we studied model sensitivity to determine the influence of the most important parameters on output variability.

In addition, the newly calculated crop-specific characterization factors for direct residues are compared and eventually combined.

\[
\vec{m}_i(t) = e^{\mathbf{K}t} \vec{m}_i(0)
\]
with generic characterization factors accounting for diffuse emission pathways as calculated with the USEtox model\textsuperscript{5} for the set of selected substances.

## RESULTS

### Pesticide Residues in Crops

Modeled residues are compared with measured concentrations of eleven different pesticides applied to the six selected crops (Figure 1). Experimentally derived maximum concentrations are reported to range from 29 mg kg\textsuperscript{-1} in apples at the day of application to 0.01 mg kg\textsuperscript{-1} in potato tubers measured 15 days after the tested pesticide was applied, demonstrating a variability of 3 orders of magnitude between crops. Measurements and model estimates correspond well with total crop-specific residual errors ranging between 0.08 (factor 1.5 deviation) for fenitrothion applied to lettuce and 0.64 (factor 19) for propisochlor sprayed on rice with an overall residual error of 0.33 (factor 4.5) over all 12 substance-crop combinations. A higher accuracy of prediction is observed in crops where the final commodity stands in direct contact with the applied pesticide (apple, lettuce, tomato, and wheat). In comparison, crops in which the pesticide has to pass an additional medium like paddy water (rice) or soil (potato) in order to reach the harvested good, on average showed higher uncertainties.

### Human Intake Fractions

We calculated intake fractions and characterization factors as measures normalized to one unit mass of applied pesticide for 726 potential substance-crop combinations, that is, 121 substances applied to six crops. Intake fractions of a pesticide can vary between 4 and 14 orders of magnitude for fenoxaprop-p and flufenacet, respectively, when applied to different crops at recommended doses and harvested at typical times after applications. In contrast, iF between all pesticides applied to the same crop can vary between three (potato) and sixteen (wheat) orders of magnitude, thereby indicating that substance properties are almost as influential on iF as crop properties.

The lowest intake fraction is found for metam sodium applied to apple with \( iF = 1.7 \times 10^{-20} \text{kg intake kg applied} \), whereas the highest intake fraction is found for epoxiconazole applied to lettuce with \( iF = 1.9 \times 10^{-1} \text{kg intake kg applied} \). Intake fractions for all potential substance-crop combinations are provided in Table S2 (SI).

Substance degradation in plants and the time between pesticide application and crop harvest are known to predominantly determine model sensitivity.\textsuperscript{7,20} In Figure 2, we present intake fractions as a function of the substance degradation half-life in plants—typically varying between 1 and 10 days—for different times to harvest. For all crops but potato, intake fractions are typically in the range of \( 10^{-2} \) and \( 10^{-8} \text{kg intake kg applied} \) for typical times between application and harvest. Decreasing the half-life in plants results in continuously decreasing iF, with the magnitude of decrease being amplified up to 10 orders of magnitude with higher time lag between application and harvest. In this case, the difference in degradation of pesticides within crops has more time to establish a significant influence. When looking at potato, there is little influence of the degradation half-life in plant. Instead, the residence time in soil is a main factor of influence affecting iF variation in Figure 2. Residence times in soil are more adequate than half-lives to examine iF variation for potato, since they encompass the various removal processes in soil and since the pesticide always has to pass the heterogeneous soil layer, before entering the tuber. In this case, soil characteristics become predominant.\textsuperscript{9,28}

How crop and substance characteristics as well as time to harvest are influencing the variation of intake fractions is contrasted in Figure 3. For the same generic time between application and harvest of 20 days (dark boxes), potato shows the lowest range of intake fractions with a median of \( 2.7 \times 10^{-7} \text{kg intake kg applied} \) and less than 3 orders of magnitude variation between 5th and 95th percentiles. Potato is followed by cereals and fruit crops, for which we basically obtain a similar behavior with median iF

![Figure 1. Measured and modeled pesticide residues in plant components harvested for human consumption for each of the six studied crops with residual error (ER) for each substance-crop combination.](image-url)
ranging from $2 \times 10^{-5}$ to $2.5 \times 10^{-4}$ kg$_{\text{intake}}$ kg$_{\text{applied}}^{-1}$ and typical variation ranges from 2 to 4 orders of magnitude between pesticides. In contrast, lettuce as leafy crop shows highest iF with a median of $4.3 \times 10^{-4}$ kg$_{\text{intake}}$ kg$_{\text{applied}}^{-1}$ and 6 orders of magnitude variation. Another set of influencing factors are the intrinsic crop characteristics, mainly due to losses during application via wind drift, LAI growth over time and food processing after harvest. Drift fractions, however, are not only crop-specific, but also depend on application method, for example, foliar spray or soil injection, whereas loss fractions due to food processing also differ between substances. In practice, times between application and harvest depend on crop species, pest occurrence, weather conditions and a pesticide’s mode of action. However, since for LCIA we are interested in providing best estimates, we also need to distinguish between pesticide target classes for arriving at typical times to harvest. For fungicides and insecticides, officially reported minimum preharvest intervals are selected. Herbicides, in contrast, are usually applied pre-emergent or during early crop growth resulting in relatively long times to harvest between 55 and 150 days as discussed in the SI. Overall, average times to harvest range between 5 days for fungicides/insecticides applied to tomato and 150 days for herbicides applied to wheat and apple (SI Table S1). Varying application times lead to additional iF variation between pesticides with herbicides showing lower intake fractions and higher variation due to their longer time lags between application and harvest. (Figure 3, gray middle box-plots). For fungicides and insecticides, the later application leads to higher intake fraction, especially for tomato and lettuce, for which application can take place only 5–10 days before harvest (Figure 3, left box-plots). Figure 3 also enables us to compare direct pesticide application modeled dynamically with diffuse emissions calculated by USEtox assuming steady-state conditions and continuous input (see two white box-plots at the right end of Figure 3). With the generic time to harvest of 20 days, all crops except potato show higher iF due to direct application residues compared to iF due to continuous, diffuse emissions. For recommended times to harvest, median iF of herbicides applied to all crops and of fungicides/insecticides applied to cereals decrease below USEtox values. In contrast, for fungicide/insecticide applied shortly before harvest (tomato, lettuce), median intake fractions
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Table 2. Median Values with 5th and 95th Percentiles (In Brackets) of Crop-Specific Application Amount mapp, Intake Fraction iF, Characterization Factor CF, Crop-Independent Effect Factor EF, and Impact Score IS for 121 Pesticides

<table>
<thead>
<tr>
<th>Crop</th>
<th>mapp [kg ha⁻¹]</th>
<th>iF [DALY kg intake kg applied]</th>
<th>CF [DALY kg⁻¹]</th>
<th>EF [DALY kg intake]</th>
<th>IS [DALY ha⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>wheat</td>
<td>0.16 (0.001–2.9)</td>
<td>1.0 × 10⁻¹ (3.4 × 10⁻¹–6.6 × 10⁻¹)</td>
<td>1.2 × 10⁻¹ (5.7 × 10⁻¹–1.7 × 10⁻⁰)</td>
<td>1.3 × 10⁻⁰ (1.4 × 10⁻⁰–2.3 × 10⁻⁰)</td>
<td>4.8 × 10⁻⁰ (8.1 × 10⁻¹–4.7 × 10⁻¹)</td>
</tr>
<tr>
<td>rice (paddy)</td>
<td>0.75 (0.002–3.8)</td>
<td>6.9 × 10⁻¹ (2.3 × 10⁻¹–2.3 × 10⁻⁰)</td>
<td>1.1 × 10⁻¹ (1.1 × 10⁻¹–2.3 × 10⁻¹)</td>
<td>1.3 × 10⁻⁰ (1.3 × 10⁻⁰–2.3 × 10⁻⁰)</td>
<td>3.6 × 10⁻⁰ (4.2 × 10⁻⁰–2.6 × 10⁻⁰)</td>
</tr>
<tr>
<td>tomato</td>
<td>0.27 (0.001–5.3)</td>
<td>3.9 × 10⁻¹ (1.4 × 10⁻¹–2.3 × 10⁻⁰)</td>
<td>1.1 × 10⁻¹ (1.1 × 10⁻¹–2.3 × 10⁻¹)</td>
<td>1.3 × 10⁻⁰ (1.3 × 10⁻⁰–2.3 × 10⁻⁰)</td>
<td>3.6 × 10⁻⁰ (4.2 × 10⁻⁰–2.6 × 10⁻⁰)</td>
</tr>
<tr>
<td>apple</td>
<td>0.86 (0.004–12)</td>
<td>4.3 × 10⁻¹ (1.4 × 10⁻¹–2.3 × 10⁻⁰)</td>
<td>1.1 × 10⁻¹ (1.1 × 10⁻¹–2.3 × 10⁻¹)</td>
<td>1.3 × 10⁻⁰ (1.3 × 10⁻⁰–2.3 × 10⁻⁰)</td>
<td>3.6 × 10⁻⁰ (4.2 × 10⁻⁰–2.6 × 10⁻⁰)</td>
</tr>
<tr>
<td>lettuce</td>
<td>0.02 (0.003–1.6)</td>
<td>1.8 × 10⁻⁰ (2.4 × 10⁻¹–4.7 × 10⁻²)</td>
<td>1.1 × 10⁻¹ (1.1 × 10⁻¹–2.3 × 10⁻¹)</td>
<td>1.3 × 10⁻⁰ (1.3 × 10⁻⁰–2.3 × 10⁻⁰)</td>
<td>3.6 × 10⁻⁰ (4.2 × 10⁻⁰–2.6 × 10⁻⁰)</td>
</tr>
<tr>
<td>potato</td>
<td>0.89 (0.002–10)</td>
<td>1.8 × 10⁻⁰ (2.4 × 10⁻¹–4.7 × 10⁻²)</td>
<td>1.1 × 10⁻¹ (1.1 × 10⁻¹–2.3 × 10⁻¹)</td>
<td>1.3 × 10⁻⁰ (1.3 × 10⁻⁰–2.3 × 10⁻⁰)</td>
<td>3.6 × 10⁻⁰ (4.2 × 10⁻⁰–2.6 × 10⁻⁰)</td>
</tr>
</tbody>
</table>

*See text for explanation.

Figure 4. Human toxicity impact scores of different scenarios expressed in DALY per ha of applied fungicides, insecticides, herbicides and total pesticides applied on wheat, and relative impact scores normalized to scenario no. 1.

from diffuse emissions strongly underestimate overall intake by up to 4 orders of magnitude. Finally, in the case of potatoes, residues from direct application of all pesticides remain of minor importance, that is, with lower median iF values, than diffuse emissions.

Characterization Factors and Impact Scores. Characterization factors for the set of 121 pesticides applied to the six selected food crops are calculated according to eq 2 to characterize the direct impact per kg of pesticide applied. However, characterization factors for substance-crop combinations not known to be officially authorized shall only be used as reference for further crops. Therefore, overall impacts per ha are only calculated for a subset of 181 substance-crop combinations authorized for use in at least one of the countries listed in the Codex Alimentarius with given recommended amounts applied. The whole source to impact pathway from pesticide application to human impacts is summarized in Table 2. Variability is before all due to variation in intake fraction (15 orders of magnitude). Additional limited variability is introduced by human effect factors, more specifically by substance-specific dose—response slope factors. Information related to cancer effects is given in Rosenbaum et al. for less than 20% of the 121 pesticides, which is in line with Huijbregts et al. In addition, 77% of substances with available information related to cancer do not show any cancer potential (effect factors set to zero). This indicates that most of today’s pesticides are rather leading to noncancer effects. All in all, effect factors vary by 3.5 orders of magnitude between pesticides. The combination of large variations in intake fractions with lower variations in effect factors leads to an overall variation in characterization factors of almost 17 orders of magnitude (Table 2). Combining this with variability in applied pesticide mass of 4 orders of magnitude tends to reduce the overall variability on the impact score to 13 orders of magnitude, suggesting that some of the pesticides applied at low dose tend to have rather high toxicity potentials. Detailed information is provided in the SI on cancer and noncancer potentials (SI Table S3), crop-specific and generic characterization factors (SI Tables S4 and S5), and finally impact scores (SI Figure S2).

Functional Assessment and Pesticide Substitution. When assessing the change in impacts linked to substitution of pesticides, a functional assessment is required, ensuring that the combination and quantities of pesticides applied are able to control a set of distinct pests in an equivalent way.

Figure 4 presents an example of how to conduct crop-specific substitution of different pesticides. Pesticide target classes focus
on distinct pest categories, for example, fungi, insects, weeds. Substitution, hence, must be discussed separately within each pesticide target class, for example, insecticides can only be substituted by other insecticides targeting the same insect pests. In scenario no. 1, we exemplarily combined applications of β-cyfluthrin and carbaryl on wheat against a set of common wheat-damaging insects (wheat bulb fly, cereal leaf beetle, aphids, and thrips). This insecticide mix is substituted by a combination of the less human health impacting insecticides α-cypermethrin and deltamethrin in scenario no. 3. Individual insecticides and application rates are chosen to ensure a similar ability to control the same unwanted insects in both scenarios. Figure 4 demonstrates that substituting scenario no. 1 by scenario no. 3 reduces the total impact score of applied insecticides by more than 4 orders of magnitude to less than 0.1% of the impact score of scenario no. 1. This approach is similarly applied to fungicides and herbicides, where substituting scenario no. 1 by scenario no. 3 results in impact scores reduced by more than 2 and 6 orders of magnitude, respectively. Scenario no. 2 represents an intermediary situation showing some, but not as much reduction in impact scores for all target classes as scenario no. 3. Background information for this example of pesticide substitution is provided in Table S6 (SI).

**DISCUSSION**

**Potential and Limitations.** The presented approach demonstrates the importance of dynamic pesticide assessment and enables us to distinguish between various food crops. By identifying the combined influence of crop characteristics, application times and substance properties we demonstrate that it is crucial to choose appropriate times to apply pesticides and that diffuse emission pathways may be significant for early application, but strongly underestimate human intake for late application before harvest. For practical implementation, we therefore recommend to use our crop-specific characterization factors to account for direct application residues. We thereby stress that results must always be interpreted as a function of times to harvest, that is, recalculations are required to account for changing the date of pesticide application. To account for impacts from diffuse emissions in addition to direct residues, initial loss fractions to air and soil during application should be multiplied by the USEtox characterization factors for emissions to urban air and agricultural soil, respectively. For typical foliar application, crop-specific loss fractions to air range from 5 to 25% and to soil from 5 to 70%, respectively, where the latter also depends on crop development stage. All presented crop-specific characterization factors are global averages and based on generic values for most underlying parameters, such as human lifetime and body weight. Hence, for a spatial assessment, these parameters need to be adjusted accordingly. The present approach is so far limited to neutral organic substances, since inorganics require a different consideration of their partitioning behavior and ionizable compounds require considering electrochemical interactions for the dissociated species.

**Differences between Crops.** Variation in crop-specific intake is mainly driven by distinct characteristics between crop archetypes, for example, with respect to harvested plant components, from which we can basically classify food crops into roots and tubers, fruits and cereals, as well as leafy vegetables. Overall, leafy vegetables only contribute to 2% of the total human vegetal consumption, but may nevertheless lead to human impacts comparable or even higher than via ingestion of cereals. Cereals, on the other hand, contribute to 37% of the human vegetal consumption (including paddy cereals), but substances are usually applied earlier for these crops, leading to lower intake fractions. Highest impacts are expected via consumption of herbaceous crops and fruit trees with usually high intake fractions and consumption, while roots and tubers only contribute little due to very low intake fractions.

**Pesticide Substitution.** Whenever developing substitution scenarios, we strongly recommend considering aspects related to pesticide authorization, since a substance may be authorized for use on particular crops in some countries, but not in others, because of decreased susceptibility of target pests (resistance) to certain pesticides. Furthermore, for considering multiple applications at different application times, eq 1 can be summed up over various applications in addition to summing up over pesticides. However, usually only the latest application plays a predominant role due to increasing reduction of intake fractions with time. 9

**ASSOCIATED CONTENT**

Supporting Information. The dynamic multicrop model is available at http://dynamicrop.org. Detailed information on LAI development, application rates, intake fractions, human effect information, characterization factors, impact scores and pesticide substitution is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*Phone: (+49) 711 685 878 45; fax: (+49) 711 685 878 73; e-mail: peter.fantke@ier.uni-stuttgart.de.

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