Dynamic multi-crop model to characterize impacts of pesticides in food

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Which food crop has highest pesticide load?
Goals

After the course, all participants will be able to:

• Explain the principles and processes involved in the distribution of pesticides applied to different food crops,

• Quantify potential health impacts from pesticide intake via food crop consumption, and

• Discuss different potentials for pesticide substitution.
Contents

• Background and scope
• Mass balance system
• From harvest fraction to intake fraction
• Characterization: factors and model
• Pesticide substitution
• Highlights and Summary
• **Background and scope**
  
  • Mass balance system
  
  • From harvest fraction to intake fraction
  
  • Characterization: factors and model
  
  • Pesticide substitution
  
  • Highlights and Summary
Problem Statement

- Pesticide application
- Deposition onto crops & soil incl. crop uptake
- Loss via wind drift, run-off & leaching
- Residues in harvested crop components
- Concentration in air & water, food residues
- Ingestion (treated crops)
- Ingestion (other)
- Inhalation

Total human exposure

Input: Present models (usually steady-state)

Output
Problem Statement

Problem: crop residues so far not considered!
Followed Approach – Aim

We aim at ...

- Quantifying potential health impacts caused by pesticide use (no arbitrary measures like ‘MRL’),
- Comparing pesticides in terms of their health impact,
- Giving recommendations for optimizing pesticide use.

Methodological tool of choice ...

- Life Cycle Impact Assessment (LCIA)
- Based on average values, not worst case assumptions (basis for comparative assessment)
Followed Approach – Impact Pathway

characterization factor
intake fraction
harvest fraction

application
mass in environment
harvest
intake
damage

environmental fate and crop uptake
harvested crop components
food processing

dose-response and severity
Followed Approach – Scope

Considered crops:

• Wheat       (68% of cereals)
• Paddy rice   (97% of paddy cereals)
• Tomato       (15% of herbaceous vegetables)
• Apple        (13% of fruit trees)
• Lettuce      (14% of leafy vegetables)
• Potato       (51% of roots and tubers)

45% of global vegetal consumption
• Background and scope
• **Mass balance system**
• From harvest fraction to intake fraction
• Characterization: factors and model
• Pesticide substitution
• Highlights and Summary
Physical System

evapotranspiration and gaseous deposition

particle deposition

volatilization and sorption

root uptake

xylem flux

phloem flux

biotransformation

root uptake
Modeled System

- System input
- System loss
- Diffusive transfer
- Advective transfer
- Degradation

- Xylem flux
- Phloem flux
- Evapotranspiration and gaseous deposition
- Particle deposition
- Volatilization and sorption
- Root uptake
- Root uptake
- Cell wall cuticle wax layer deposit
- Biotransformation
- RCF
- TCF
- LCF
- FCF
- Partitioning
Modeled System – Mass Balance

\[ \frac{d\vec{m}(t)}{dt} = \mathbf{K} \vec{m}(t) \]

| \vec{m} : vector of masses [kg] |
| \mathbf{K} : matrix of rate constants \( k \) [d\(^{-1}\)] |
| \( t \) : time [d] |

Solution for pulse application ...

\[ \vec{m}(t) = \exp(\mathbf{K} t) \vec{m}(0) \]

→ System will be diagonalized (decomposed) to arrive at solution with matrix exponential

→ Further reading: Fantke et al., 2013, *EMS*, 40: 316-324
Mass Balance – Rate Constants

\[
\frac{d\vec{m}(t)}{dt} = \mathbf{K} \vec{m}(t)
\]

\[
\vec{m} : \text{vector of masses [kg]}
\]
\[
\mathbf{K} : \text{matrix of rate constants } k \text{ [d}^{-1}\text{]}
\]
\[
t : \text{time [d]}
\]

Matrix of rate constants for ...

- Diffusive/advective transfers between compartments
  → 'off-diagonal elements'
- Degradation processes within compartments
  → incorporated into 'main diagonal elements'
## Mass Balance – Rate Constants

\[
\frac{d\mathbf{m}(t)}{dt} = \mathbf{K}\mathbf{m}(t)
\]

**Symbols:**
- \(\mathbf{m}\) : vector of masses [kg]
- \(\mathbf{K}\) : matrix of rate constants \(k\) [d\(^{-1}\)]
- \(t\) : time [d]

**Matrix \(\mathbf{K}\):**

\[
\begin{array}{cccc}
\text{air} & \text{soil} & \cdots & \text{leaf} \\
\hline
\text{air} & -k_{\text{air, total}} & k_{\text{air} \leftarrow \text{soil}} & \cdots & k_{\text{air} \leftarrow \text{leaf}} \\
\text{soil} & k_{\text{soil} \leftarrow \text{air}} & -k_{\text{soil, total}} & \cdots & 0 \\
\text{leaf} & k_{\text{leaf} \leftarrow \text{air}} & 0 & \cdots & -k_{\text{leaf, total}} \\
\end{array}
\]
Mass Balance – Rate Constants

\[
\frac{d\vec{m}(t)}{dt} = \mathbf{K} \vec{m}(t)
\]

\[\mathbf{K} = \begin{pmatrix}
k_{11} & \cdots & k_{1n} \\
\vdots & \ddots & \vdots \\
k_{n1} & \cdots & k_{nn}
\end{pmatrix}
\]

with \(k_{ij} = \begin{cases} 
\frac{k_{ij}}{k_{loss,i} + \sum_{l=1, l\neq i}^{n} k_{li}} & \text{for } i \neq j \\
- \left( k_{loss,i} + \sum_{l=1, l\neq i}^{n} k_{li} \right) & \text{for } i = j
\end{cases}\)

- \(\vec{m}\): vector of masses [kg]
- \(\mathbf{K}\): matrix of rate constants \([d^{-1}]\)
- \(t\): time [d]
Mass Balance – Initial Conditions

\[ \frac{d\vec{m}(t)}{dt} = K \vec{m}(t) \]

- \( \vec{m} \): vector of masses [kg]
- \( K \): matrix of rate constants \( k \) [d\(^{-1}\)]
- \( t \): time [d]

**Initial mass (applied pesticide mass) ...**
- Is defined as part of vector \( \vec{m}(t) \) at time \( t = 0 \)
- \( \rightarrow \) application time

**Final mass (pesticide residues) ...**
- Vector \( \vec{m}(t) \) at time \( t > 0 \) \( \rightarrow \) harvest time
Mass Balance – Example

Insecticide cyromazine applied to wheat

harvest time = day 67

grains: 0.28 g/kg

example:
100 g applied/ha,
6 t grain yield/ha

≅ 4.7 µg/kg_{grains}
(MRL: 50 µg/kg_{grains})
Mass Balance – Evaluation

- Tebuconazole vs. Chlorothalonil (Wheat)
- Propisochlor vs. Carbaryl (Rice (Paddy))
- α-Cypermethrin vs. Captan (Tomato)
- Propargite vs. Captan (Apple)
- Azoxystrobine vs. Fenitrothion (Lettuce)
- Chlorpyrifos vs. Prothiofos (Potato)
• Background and scope
• Mass balance system
• **From harvest fraction to intake fraction**
• Characterization: factors and model
• Pesticide substitution
• Highlights and Summary
Harvest Fraction

Mass in all harvested crop parts relative to total applied mass

\[ hF = \frac{\sum_{i=1}^{n} m_i(t)}{m_{\text{app}}} \]

- Pesticide mass in harvest
- Applied pesticide mass

<table>
<thead>
<tr>
<th>( hF )</th>
<th>harvest fraction [kg_{in, harvest}/kg_{applied}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_i )</td>
<td>residual mass in compartment ( i ) [kg_{in, harvest}]</td>
</tr>
<tr>
<td>( m_{\text{app}} )</td>
<td>total applied mass [kg_{applied}]</td>
</tr>
<tr>
<td>( t )</td>
<td>harvest time [d]</td>
</tr>
</tbody>
</table>
Intake Fraction

Mass taken in via consumption relative to total applied mass

\[ iF = hF \times PF \]

- \( iF \): human intake fraction \([\text{kg}_{\text{intake}}/\text{kg}_{\text{applied}}]\)
- \( hF \): harvest fraction \([\text{kg}_{\text{in harvest}}/\text{kg}_{\text{applied}}]\)
- \( PF \): food processing factor \([\text{kg}_{\text{intake}}/\text{kg}_{\text{in harvest}}]\)

Food processing ...
Intake Fraction – Example
Comparison of 121 pesticides

time to harvest

kg intake per kg applied

crop consumption
Intake Fraction – Influencing Aspects

Δt : time to harvest

Δt : time to harvest

intake fraction

Δt = 10
Δt = 30
Δt = 100

wheat

degradation half life in crop [days]

potato

residence time in soil [days]
• Background and scope
• Mass balance system
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• **Characterization: factors and model**
• Pesticide substitution
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Characterization Factor

Human toxicity potential relative to total applied mass

\[ CF = iF \times \beta \times DF \]

- \( CF \): human toxicity characterization factor [DALY/kg\text{applied}]
- \( iF \): human intake fraction [kg\text{intake}/kg\text{applied}]
- \( \beta \): dose-response slope factor [incidence risk/kg\text{intake}]
- \( DF \): severity factor [DALY/incidence]

Human toxicity effect factor [DALY/kg\text{intake}]

\( \rightarrow \) DALY: disability-adjusted life year
Human Toxicity Effect Factor

Dose-response based on human trials ➔ not available
  • Not ethically defendable
  • Most human studies focus on acute exposure

Dose-response based on animal trials ➔ uncertain!
  • Cancer effects: derived from chronic lifetime dose affecting 50% of exposed population (ED_{50})
  • Non-cancer effects: ED_{50} rarely available ➔ ED_{50} estimated from no-observed effect level (NOEL) assuming linear slope
Characterization Factor – Application
Pesticides applied to fruit trees in EU24 in 2003

Parathion-Methyl
Characterization Model – dynamiCROP

dynamiCROP ...

• Is a dynamic plant uptake model,
• Covers human exposure to pesticides from crop intake,
• Includes various crop types,
• Is based on matrix algebra (flexible compartment set),
• Uses Matlab to solve the matrix exponential,
• Is available for download at http://dynamicrop.org
Characterization Model – Framework

<table>
<thead>
<tr>
<th>INPUT DATA FRAMEWORK</th>
<th>Substance Property Data</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Crop Property Data</td>
</tr>
<tr>
<td></td>
<td>System Data / Boundary Conditions</td>
</tr>
<tr>
<td></td>
<td>Exposure / Effect Data</td>
</tr>
<tr>
<td>FATE PROCESSES FRAMEWORK</td>
<td>Primary Processes</td>
</tr>
<tr>
<td></td>
<td>Secondary Processes</td>
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<tr>
<td></td>
<td>System Loss Processes</td>
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<tr>
<td>MASS COMPUTATION FRAMEWORK</td>
<td>Matrix Framework</td>
</tr>
<tr>
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<td>System Eigendecomposition</td>
</tr>
<tr>
<td></td>
<td>Mass Conditions (steady state / time $t$)</td>
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<tr>
<td></td>
<td>Contributions to System Evolution</td>
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<tr>
<td>EXPOSURE / IMPACT FRAMEWORK</td>
<td>Harvest Fractions</td>
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<td>Food Processing Factors</td>
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<tr>
<td></td>
<td>Direct Intake Fractions</td>
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<tr>
<td></td>
<td>Effect Framework (DRFs / ED$_{50}$)</td>
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<tr>
<td>OUTPUT DATA FRAMEWORK</td>
<td>Data Extraction</td>
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<tr>
<td></td>
<td>Uncertainty / Sensitivity Framework</td>
</tr>
<tr>
<td></td>
<td>Evaluation of Results</td>
</tr>
</tbody>
</table>
Characterization Model – Example Results
Health impacts from pesticides applied in EU24 in 2003

<table>
<thead>
<tr>
<th>crop class</th>
<th>DALY/year</th>
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<tbody>
<tr>
<td>cereals</td>
<td>6.78</td>
</tr>
<tr>
<td>maize</td>
<td>3.77</td>
</tr>
<tr>
<td>oil seeds</td>
<td>8.82</td>
</tr>
<tr>
<td>potato</td>
<td>1.35</td>
</tr>
<tr>
<td>sugar beet</td>
<td>0.34</td>
</tr>
<tr>
<td>grapes/vines</td>
<td>724</td>
</tr>
<tr>
<td>fruit trees</td>
<td>113</td>
</tr>
<tr>
<td>vegetables</td>
<td>1100</td>
</tr>
<tr>
<td>total</td>
<td>1959 (4.75 to 808,535)</td>
</tr>
</tbody>
</table>

total ≡ 2.6 hours lost per person over lifetime
[upper limit: 45 days per person over lifetime]

Other stressors (EBoDE Report, 2011)
→ Exposure to particulate matter PM$_{2.5}$: 195 days/person
→ Non-smoker exposure to second-hand smoke: 24 days/person
Characterization Model – Uncertainty

Squared geometric standard deviation (GSD²) = 428

→ Output uncertainty range: from geomean/428 to geomean×428
(output variability >16 orders of magnitude across pesticides)
Characterization Model – Limitations

dynamiCROP is so far limited to ...

• Assess neutral organic pesticides,

• Assessing parent compounds (metabolites not included in assessment → can be assessed separately),

• Combination of Excel and Matlab (or only Matlab) → parameterized version works without Matlab
Characterization Model – Parameterization

\[ y = y^{\text{crop}} + y^{\text{soil}} + \ldots \]

with

\[ \log y^{\text{crop}} = \alpha^{\text{crop}} + \beta^{\text{crop}} \times z \]

\[ z = f(\Delta t, \text{half-life}, \ldots) \]

... (factor 4 – 66 mean deviation over harvest fraction range of 10 orders of magnitude)
• Background and scope
• Mass balance system
• From harvest fraction to intake fraction
• Characterization: factors and model
• **Pesticide substitution**
• Highlights and Summary
Pesticide Substitution – Example

Focus (in comparing pesticides): human health impacts

Example crop: wheat

Assumption: all pesticides equally effective
Pesticide Substitution – Target Pests

Target pests for wheat as example crop (comparing what?)

• Fungi: e.g. leaf rust, mildew

• Insects: e.g. aphids, thrips

• Weeds: e.g. couch grass, foxtail
# Pesticide Substitution – Scenario

<table>
<thead>
<tr>
<th>scenario</th>
<th>pesticide</th>
<th>target pests</th>
<th>kg_app/ha</th>
<th>DALY/ha</th>
<th>DALY/ha</th>
<th>%</th>
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<tr>
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<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td></td>
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<td>1</td>
<td>(\beta)-cyfluthrin</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td>13.75</td>
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<tr>
<td></td>
<td>carbaryl</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>1.48</td>
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<tr>
<td>2</td>
<td>cyhalothrin</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<td>x</td>
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<td>0.015</td>
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<td>deltamethrin</td>
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<td>x</td>
<td>x</td>
<td>x</td>
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<td></td>
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<td>E</td>
<td>F</td>
<td>G</td>
<td>H</td>
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<tr>
<td>1</td>
<td>cyproconazole</td>
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<td>x</td>
<td>x</td>
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<td></td>
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<td>x</td>
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<td>x</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<td>x</td>
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<tr>
<td>3</td>
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<td>x</td>
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<td></td>
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<td></td>
<td>x</td>
<td>x</td>
<td></td>
<td>1.5</td>
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<tr>
<td></td>
<td>mancozeb</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J</td>
<td>K</td>
<td>L</td>
<td>M</td>
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<tr>
<td>1</td>
<td>pendimethalin</td>
<td>x</td>
<td>x</td>
<td></td>
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<td></td>
<td>x</td>
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<td></td>
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<td>x</td>
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<td>2</td>
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<td></td>
<td>propoxycarbazone-sodium</td>
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<td>x</td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>glyphosate</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>1.37</td>
</tr>
</tbody>
</table>
Pesticide Substitution – Results

fungicides
A: azoxystrobin, cyproconazole
D: epoxyconazole, fenpropimorph, pyraclostrobin
G: chlorothalonil, mancozeb, tebuconazole

insecticides
B: β-cyfluthrin, carbaryl
E: cyhalothrin, esfenvalerate
H: α-cypermethrin, deltamethrin

herbicides
C: fenoxyprop-P, pendimethalin, prosulfocarb
F: glyphosate
I: iodosulfuron, propoxycarbzone-sodium
Pesticide Substitution – Limitations

In reality, substitution must also consider ...

• Pesticide authorization (country-specific),
• Crop rotation and climate/soil conditions,
• Pest resistance toward certain pesticides,
• Varying pesticide costs (application count, etc.),
• Other impacts (ecotoxicity, groundwater contamination, etc.)
• Background and scope
• Mass balance system
• From harvest fraction to intake fraction
• Characterization: factors and model
• Pesticide substitution
• **Highlights and Summary**
Highlights

• We are able to characterize health impacts from food crop consumption

• Characterization factors available for 6 crop archetypes and >300 commonly used pesticides

• dynamiCROP model available → dynamic version (matrix-based) and parameterized version (linear, for inclusion in steady state frameworks)

• Highest uncertainties → dose-response and half-lives
Summary

• Exposure of general public to pesticides dominated by residues in food crops

• Lowest residues: root crops, highest residues: leafy crops (wash your salad!), but also fruits and vegetables

• Dynamic assessment required (time to harvest important)

• LCIA helps to compare impacts between pesticides and between stressors (pesticide health impacts low in comparison with e.g. PM → consider uncertainty!)

• Pesticide substitution helps reducing health impacts (other impacts may dominate → include in scenarios!)
Further Information?


Contact: pefan@dtu.dk