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# Characterizing pesticide dissipation in food crops

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**105 The first steps towards simplifying the Northern Zone groundwater requirements** A. Gimsing, The Danish Environmental Protection Agency; F. Stenemo, Geosigma AB; J. Asp, G. Czub, J. Ostgren, Swedish Chemicals Agency; U. Bukss, State Plant Protection Service; R. Holten, P. Mulder, The Norwegian Food Safety Authority; D. Kavaliauskaite, The State Plant Service under the Ministry of Agriculture; R. Silvo, A. Sari, Finnish Safety and Chemicals Agency; J. Raukas, Estonian Agricultural Board. Regulation EC 1107/2009 concerning the placing of plant protection products on the market in the EU entered into force on 14 June2011. Acentral aspect in the new regulation is worksharing and harmonization within and among the three European zones. In the Northern Zone there are different national requirements for assessing the risk of leaching of active substances and metabolites to groundwater. No harmonisation on this point has yet been achieved and the Member States are reluctant to accept assessments on the basis of the other Member States requirements. For the core assessment simulations with the following FOCUS models and scenarios are currently required, as described in the Northern zone guidance document: - PEARL with the Jokioinen scenario (Finnish and Latvian approach) - PELMO Hamburg or MACRO Danish scenarios Karup and Langvad with Danish input parameters - MACRO with Norwegian scenarios Rustad og Heia - MACRO with Swedish scenarios Önnestad, Krusenberg and Näsbygård \nDue to strict deadlines in the regulation EC 1107/2009, it is imperative to minimize the work load for both companies and regulators. A first step towards harmonisation has been to compare the different models and approaches to assess how much the model predictions differ from each other and how they are influenced by external preconditions. A project has been carried out with the purpose of running the different models with hypothetical substances (different combinations of half-lives and sorption properties) and comparing the model predictions with the aim of finding a worst-case ranking order of the models to allow for a stepwise approach to groundwater modelling. The results of this project will be presented and the conclusions and perspectives for the Northern Zone guidance will be discussed. Session: Modelling of chemical fate and exposure in the context of pesticide and biocide regulations Keywords: Groundwater modelling, pesticides, Northern zone, authorisation Presentation preference: Platform and poster

**106 Modelling in Support of an Extended Groundwater Monitoring Study in the EU** P. Sweeney, Syngenta; G. Hoogewegg, S. Zelonis, Waterborne Environmental; P. Hendley, Syngenta Crop Protection, Inc. / Senior Syngenta Fellow; S. Hayes, Syngenta. The groundwater assessment for agrochemicals in the EU has become increasingly hard to pass due to changing parameterisation of models. Registrants have increasingly resorted to monitoring studies to provide higher-tier support for groundwater assessments in addition to modelling. The data available to identify candidate sites for monitoring in the EU are of variable quality and this limits the ability of registrants to identify credible areas to monitor in locations where there is no existing network of monitoring wells. We show how modleling can be used with the data available at a consistent resolution for the EU 27 with reference to an example of a weakly sorbed metabolite of a maize herbicide. Modelling is used from the initial stages of defining a conceptual model of leaching - identifying likely travel times to groundwater and identifying environmental parameters controlling movement of the substance to groundwater - to providing estimates of leaching using a spatial model. Mass flux is the most relevant quantity to estimate and compare likely leaching of particular soil/weather combinations and we propose that a 10km x 10km grid cell is a relevant spatial unit to consider leaching, given the spatial ncertainty inherent in pan-European datasets such as CAPRI. Calculated median mass flux at a European level is combined with estimates of shallow groundwater (defined as < 10m) and cropping density to provide candidate regions that can be sampled at random as part of a statistically robust monitoring program relevant to leaching across the EU. Comparison with field data show the effectiveness of this approach in identifying high density maize-growing regions overlying shallow groundwater. Finally we show how the sites selected for monitoring can be placed in context of vulnerability for the EU.

**107 Characterizing pesticide dissipation in food crops** P. Fantke, Technical University of Denmark; R. Juraske, Swiss Federal Institute of Technology Zurich, ETH ZÃ¼rich; O. Jolliet, University of Michigan / School of Public Health. Ingestion of residues via consumption of food crops is the predominant exposure route of the general population toward pesticides. However, pesticide dissipation in crops constitutes a main source of uncertainty in estimating residues in harvested crop parts and subsequent human exposure. Nevertheless, dissipation is a key mechanism in models assessing pesticide distribution in the crop-environment and the magnitude of residues in harvest. We provide a consistent framework for characterizing pesticide dissipation in food crops for use in modeling approaches applied in health risk and impact assessment. We collected 4,482 unique dissipation half-lives for 341 substances applied to 182 different crop species and fully characterize these data by describing their variance, distribution and uncertainty as well as by identifying the influence of substance, crop and environmental characteristics. We obtain an overall geo-mean half-life over all data points of 3.9 days with 95% of all half-lives falling within the range between 0.6 and 29 days. Uncertainty in predicting a substance-specific geo-mean half-life varies with varying numbers of available data points with the highest uncertainty associated to pesticides with less than seven reported half-lives. Temperature in air was identified to have a significant influence on dissipation kinetics. We, hence, provide estimated half-lives for a default temperature of 20°C, while introducing a correction term for deviating temperature conditions. Diffusive exchange processes also have a significant influence on pesticide dissipation, wherever these processes dominate dissipation rates compared to degradation. In these cases, we recommend not to use measured dissipation half-lives as basis for estimating degradation, which is recommended in cases, where degradation is dominating. We are currently testing the regression to predict degradation half-lives in crops. By providing mean degradation half-lives at 20°C for more than 300 pesticides, we reduce uncertainty and improve assumptions in current practice of health risk and impact assessments.

**108 Characterizing exposure of bystanders and residents to pesticides applied in agricultural fields** M. Ryberg, P. Fantke, Technical University of Denmark; R.K. Rosenbaum, Technical University of Denmark / Division for Quantitative Sustainability Assessment. Humans are exposed to agricultural pesticides via different pathways. Bystanders and residents living near agricultural fields, in particular, are potentially exposed to pesticides primarily via inhalation. However, bystander/resident exposure has not yet been considered in life cycle impact assessment (LCIA), even though bystander/resident exposure is expected to contribute significantly to overall human exposure to pesticides. Therefore, we aim at quantifying human exposure of bystanders/residents to agricultural pesticides applied under realistic field conditions. We start from a pulse application, of which a certain fraction is subsequently lost to air. We thereby build upon an existing model for quantifying pesticide emissions from field applications. The model will calculate the fraction from wind drift and volatilization leaving the field, based on the quantity of pesticide applied to the field. From the emission, the concentration near the receptor – either bystanders or residents living near the field – will be modelled as a function of the distance to the field. Human exposure will furthermore be depending on the duration of the exposure and the inhalation rate. Hence, the exposure differs between bystanders and residents due to different activity patterns. Based on this, intake fractions and – after combination with respective effect information – characterization factors will be derived. Because the impact only affects a fraction of the total population, the results will be normalized, for the characterization to be used together with other exposure pathways where the total population is included. Bystander and resident exposure is expected to be in the same range as exposure via food consumption and is furthermore expected to be higher than exposure of the general public via exposure

# Characterizing pesticide dissipation in food crops

Peter Fantke[1], Ronnie Juraske[2], and Olivier Jolliet[3]

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## 1. Introduction

Ingestion of residues via consumption of food crops is the predominant exposure route of the general population toward pesticides with inhalation as additional route important for applicants and bystanders.

However, quantifying human exposure to agricultural pesticides is associated with uncertainty (Figure 1). Pesticide dissipation in crops constitutes a main source of uncertainty in estimating residues in harvested crop parts, mainly due to lack of experimental data and inconsistent characterization. Nevertheless, dissipation is a key mechanism in models assessing pesticide distribution in the crop-environment and the magnitude of residues in harvested crop parts [1]. To improve current assessments by reducing uncertainty linked to pesticide dissipation in food crops, a consistent approach for characterizing dissipation kinetics based on available experimental data is required.

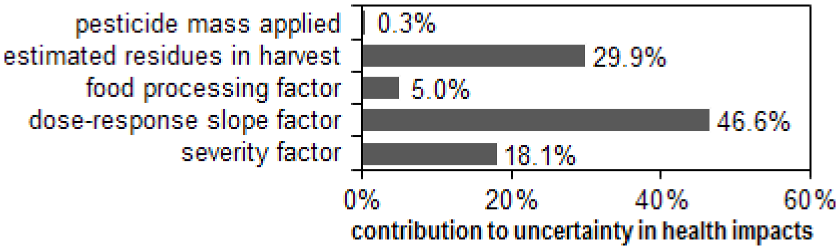


*Figure 1: Contribution of different aspects to uncertainty of health impacts from pesticide use in Europe for exposure via crop consumption.*

## 2. Methods

We provide a consistent framework for characterizing pesticide dissipation in food crops for use in modeling approaches applied in health risk and impact assessment. We first collected 4,482 unique data points for 341 substances applied to 182 different crop species from 801 peer-reviewed references [2]. We fully characterize these data by describing their variance, distribution and uncertainty as well as by identifying the influence of substance, crop and environmental characteristics.

As a next step, we will relate degradation half-lives to be applied in deterministic plant uptake models to experimentally derived dissipation half-lives and provide recommendations for using pesticide degradation half-lives in two distinct cases: (a) where experimental dissipation data are available and (b) where such data are not available.

## 3. Results and discussion

Based on the findings from the literature review in [2], we obtain an overall geo-mean half-life over all data points of 3.9 days with 95% of all half-lives falling within the range between 0.6 and 29 days (Figure 2).

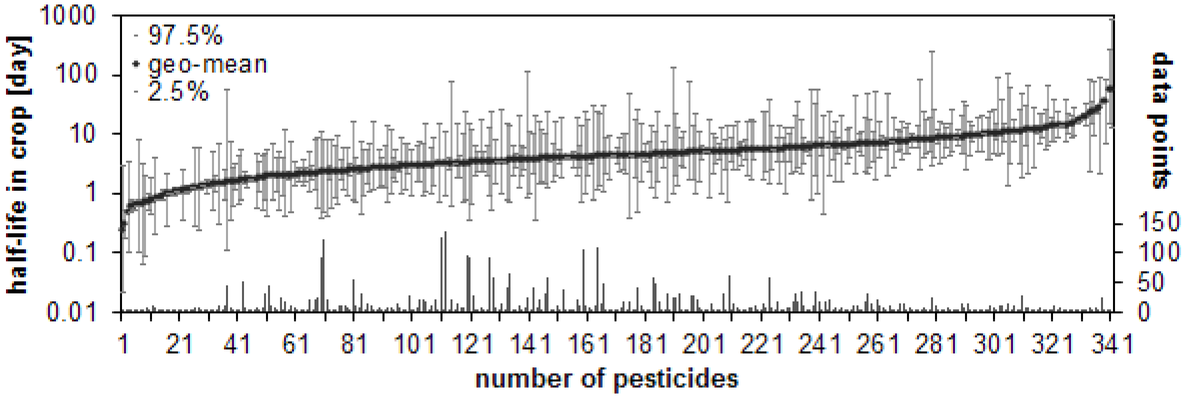


*Figure 2: Variability and number of data points for measured dissipation half-lives of 341 pesticides in crops.*

The number of data points per pesticide thereby ranges from only one or two measurements for 13 and 41 substances, respectively, to 135 samples for the well-studied insecticide endosulfan. Uncertainty in predicting a substance-specific geo-mean half-life varies with varying numbers of available data points with the highest uncertainty associated to pesticides with less than seven reported half-lives (Figure 3).

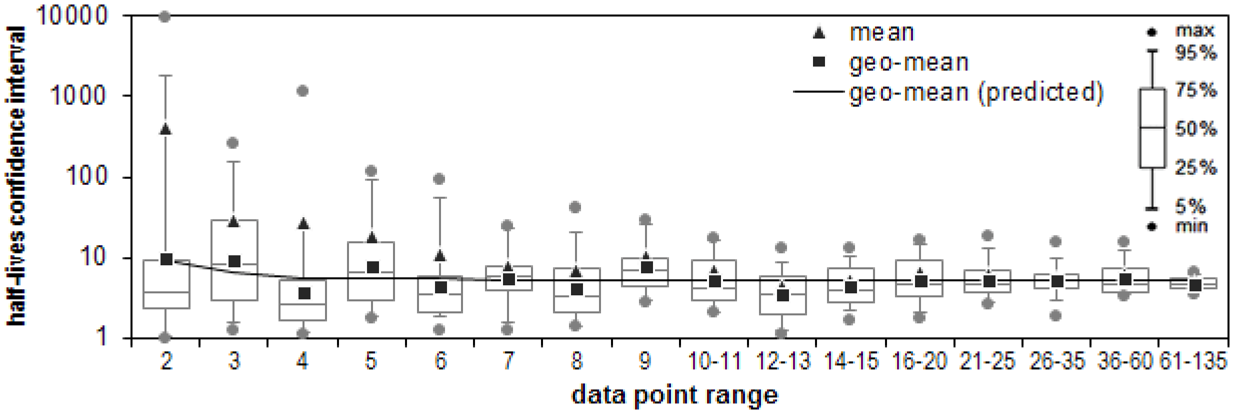


*Figure 3: Uncertainty for different classes of number of measured pesticide dissipation half-lives in crops.*

Unfortunately, only 18% of all reviewed references assessed one or more aspects potentially influencing pesticide dissipation, of which almost no study reported on influences of plant composition. However, among many aspects that could potentially serve as predictor variable in a final model estimating pesticide degradation half-lives from measured dissipation data, such as molecular weight, Kow, Koc, air and soil temperature, air and soil humidity, wind speed, surface-roughness, plant water and lipid content, soil pH and radiation intensity, temperature in air was already identified to have a significant influence on dissipation kinetics. We, hence, provide estimated half-lives for a default temperature of 20°C, while introducing a correction term for deviating temperature conditions.

Diffusive exchange processes also have a significant influence on pesticide dissipation, wherever these processes dominate dissipation rates compared to degradation. In these cases, we recommend not to use measured dissipation half-lives as basis for estimating degradation, which is recommended in cases, where degradation is dominating. We are currently testing the regression to predict degradation half-lives in crops.

## 4. Conclusions

We characterized a wide range of experimentally derived pesticide dissipation half-lives in crops from the peer-reviewed literature and identified a typical variability of less than a factor of 20 and decreasing uncertainty with increasing available data points. A final regression model is currently being prepared to predict degradation half-lives of pesticides in crops for use in existing assessment tools based on the most influential predictor variables represented predominantly by substance properties and environmental conditions. Mean degradation half-lives at 20°C for more than 300 pesticides will be provided. This will reduce uncertainty and improve assumptions in current practice of health risk and impact assessments.

## 5. References

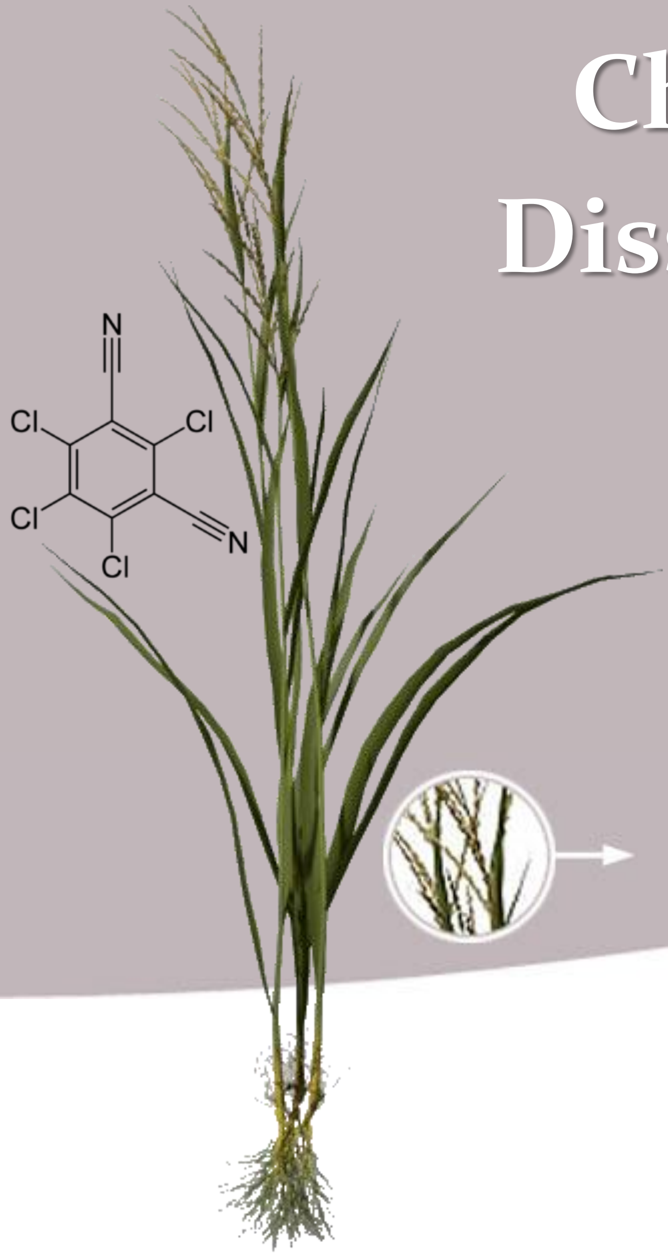
[1] Fantke P, Friedrich R, Jolliet O. 2012. Health impact and damage cost assessment of pesticides in Europe. Environ Int 49: 9-17.

[2] Fantke P, Juraske R. 2013. Variability of pesticide dissipation half-lives in vegetation: A review. Environ Sci Technol (*submitted*).

# Characterizing Pesticide Dissipation in Food Crops

**Peter Fantke | Ronnie Juraske**
**Brenda Gillespie | Olivier Jolliet**

23rd SETAC Europe Annual Meeting | Glasgow | 13-May-2013



DTU Management Engineering
Quantitative Sustainability Assessment
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ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich
University of Michigan

# Problem Setting

- Human exposure to pesticides dominated by **crop intake**
- Crop residues depend on pesticide **dissipation** dynamics
- Models are highly **sensitive** to dissipation **half-lives**

- **Questions:**
  - What data on dissipation **half-lives** in crops are **available**?
  - How to **estimate** missing dissipation half-lives?

# Outline

- **System description**
- **Review of measured dissipation half-lives in crops**
  - Variability in reported half-lives
  - Uncertainty of reported half-lives
- **Estimation of dissipation half-lives**
  - Influence of temperature
  - Imputation of missing temperature data
  - Prediction model design
- **Conclusions and Outlook**

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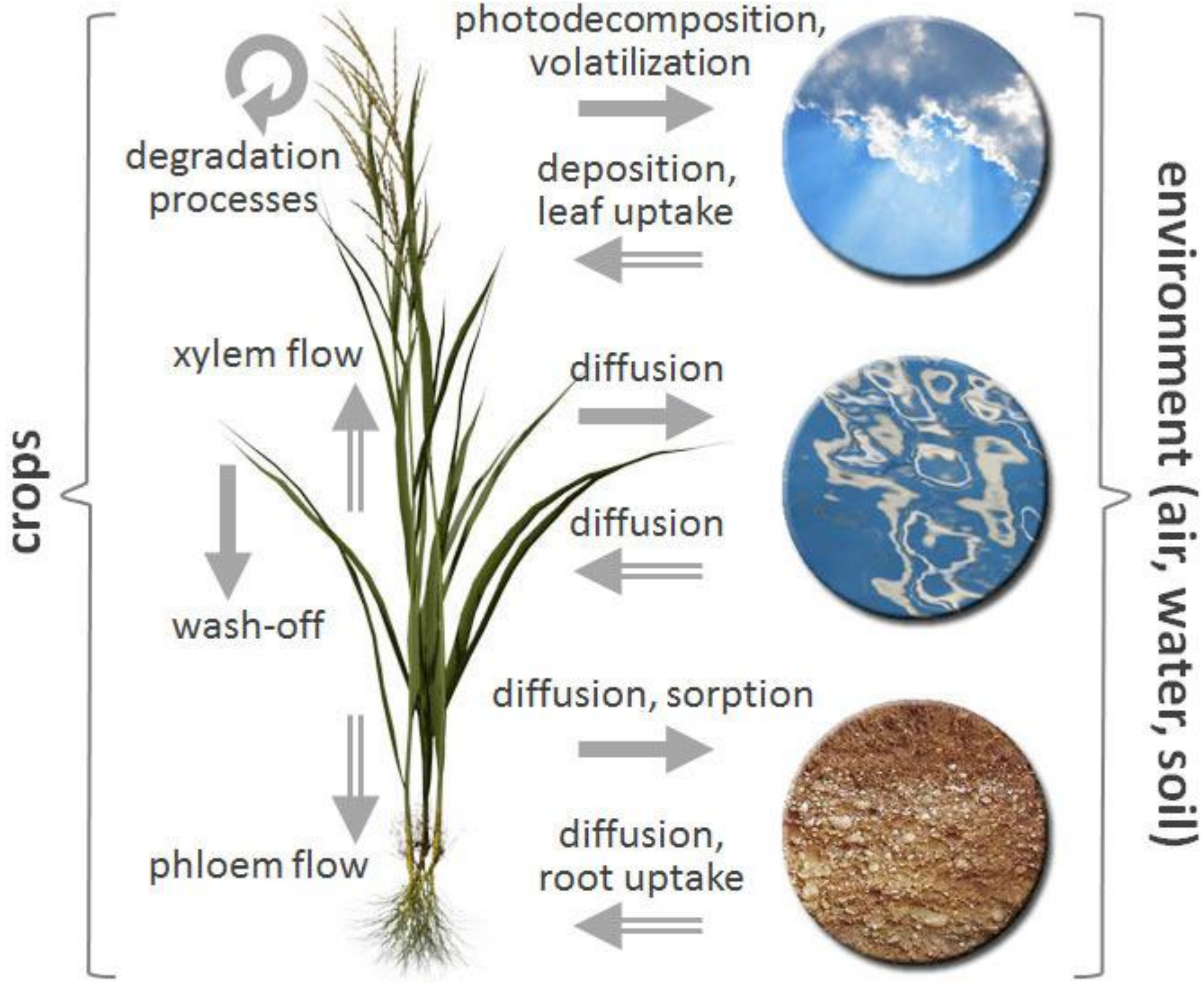
# System Description



crops

degradation processes

xylem flow

wash-off

phloem flow

photodecomposition, volatilization

deposition, leaf uptake

diffusion

diffusion

diffusion, sorption

diffusion, root uptake

environment (air, water, soil)

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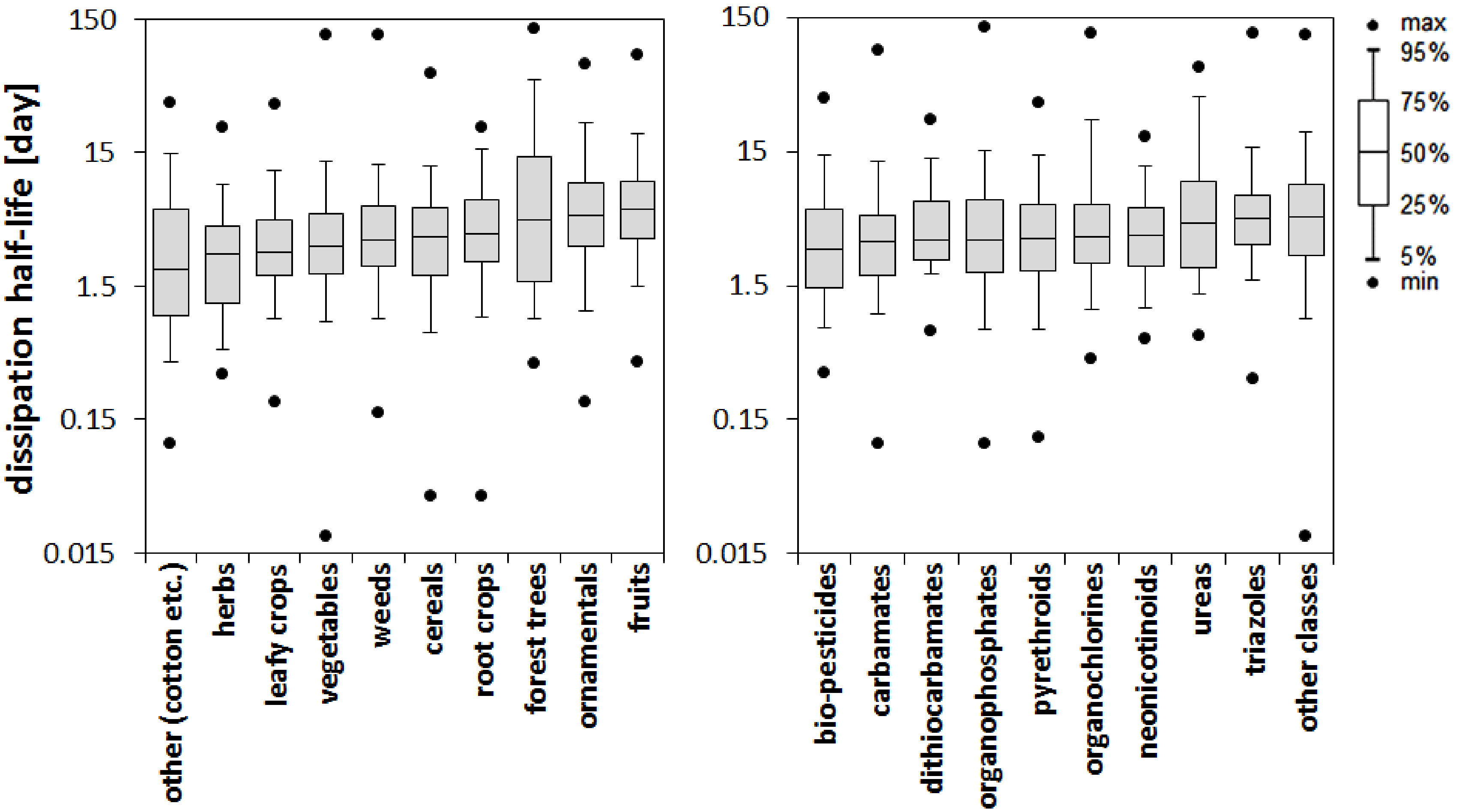
# Variability in Reported Half-Lives

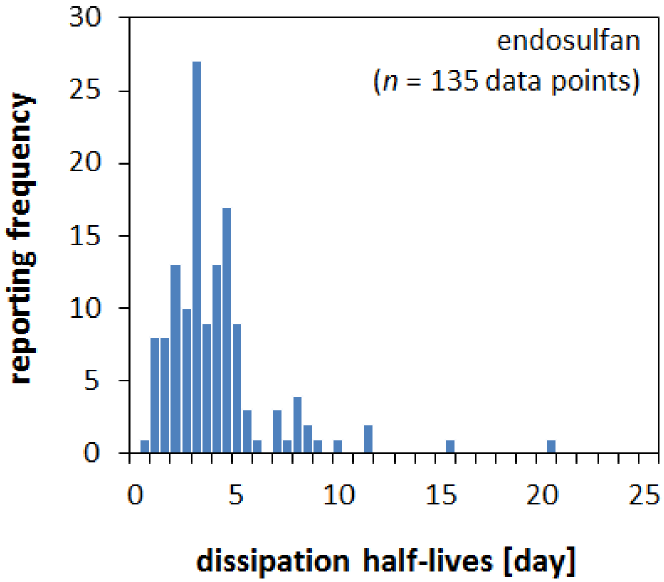
Variability for ***n*=4513** half-lives: 0.6 to 28 days = **factor 46** (95% CI)

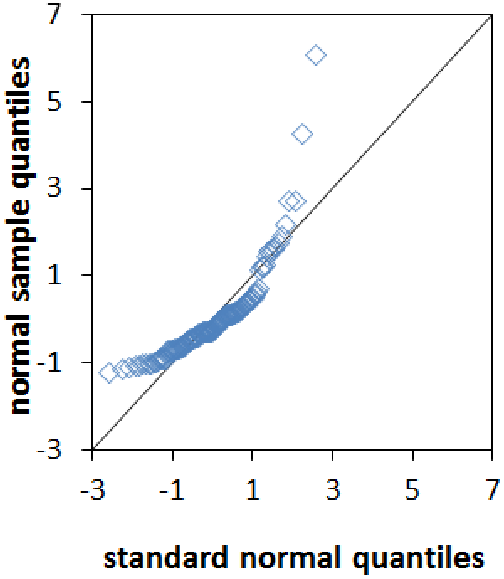


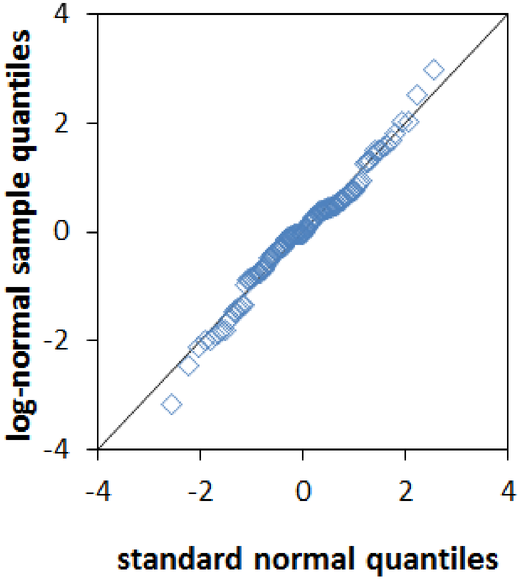
# Variability in Reported Half-Lives

Histogram and quantile-quantile plots **per substance**:

- Variability of the mean of reported dissipation half-lives in crops for substances with high reporting frequency follows ± **log-normal distribution**



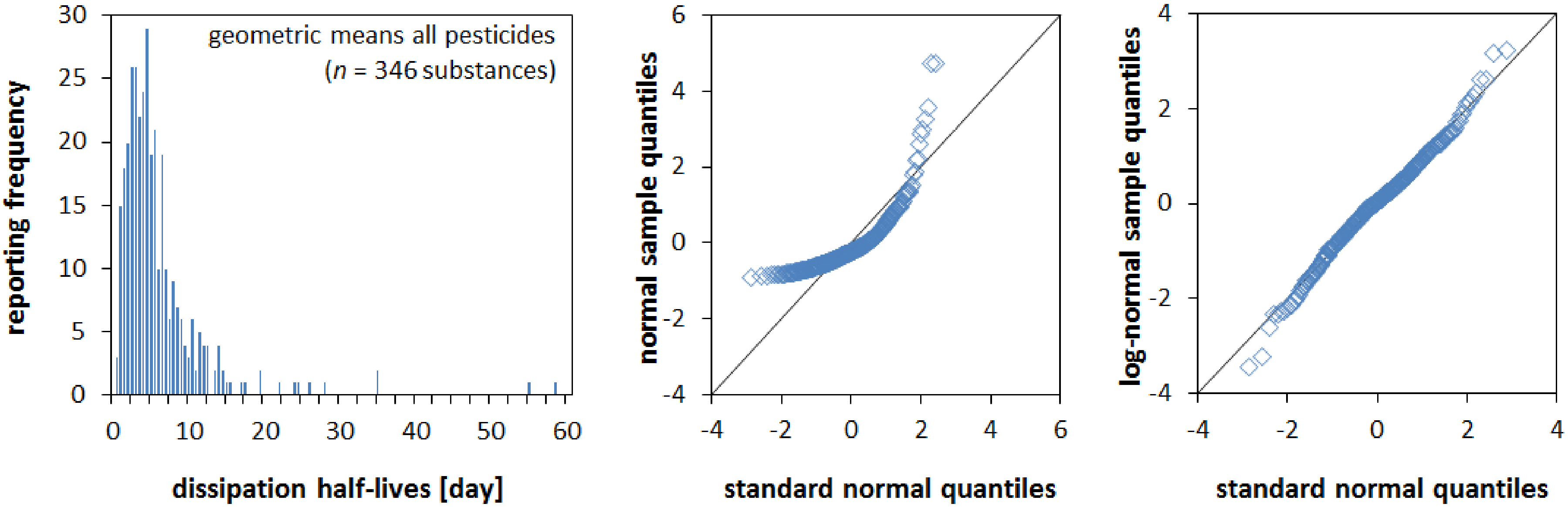




# Variability in Reported Half-Lives

Histogram and quantile-quantile plots **across substances**:

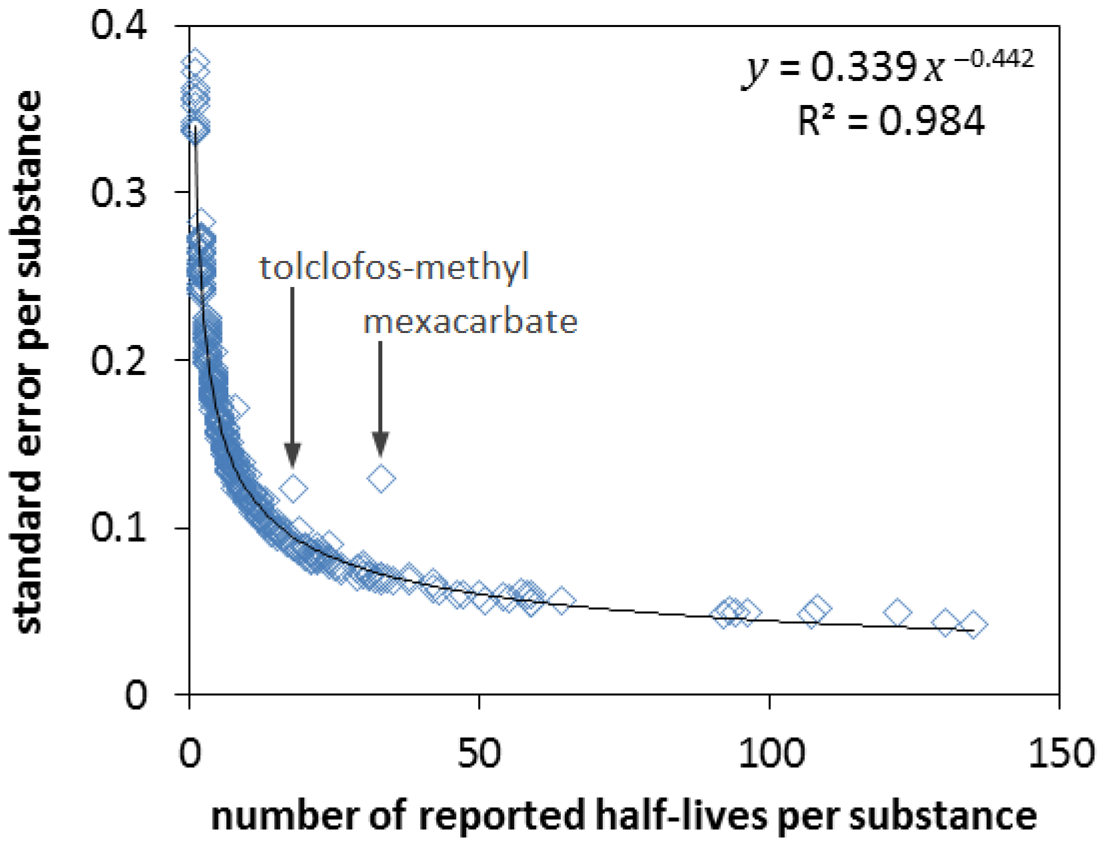
- Variability of the mean of reported dissipation half-lives in crops across all considered substances also follows ± **log-normal distribution**



# Uncertainty of Reported Half-Lives

Standard error of fitting dissipation half-lives from ***n*=336 substances**:

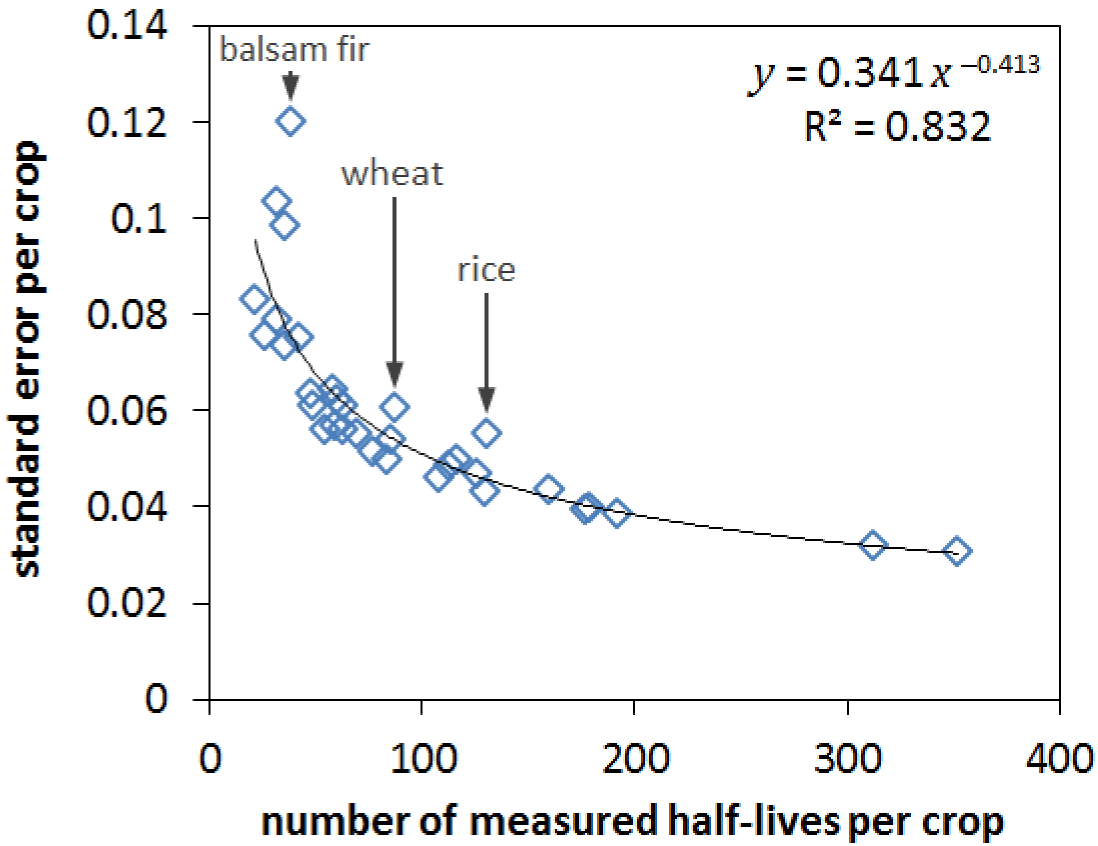
└ For **≥20 data points** per substance, standard error < 0.1 (factor 10)



# Uncertainty of Reported Half-Lives

Standard error of fitting dissipation half-lives from ***n*=33 crops**:

└ For **≥20 data points** per crop, standard error < 0.1 (factor 10)



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# Influence of Temperature

**Non-linear effect** of temperature **negligible** in range 0°C ≤ T ≤ 40°C:

Arrhenius model (adapted for half-lives *HL*):

$$\log HL = \log HL_0 + \left[\frac{E_a}{R} \times \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

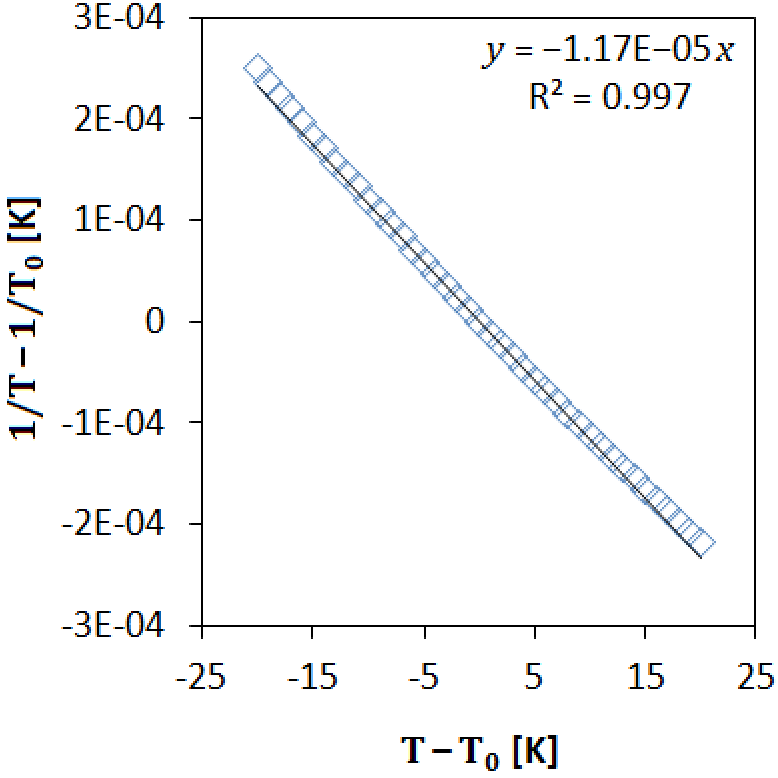
Linear model (***n*=1030** temperatures):

$$\log HL = \log HL_0 + [\beta \times (T - T_0)]$$

$$\beta = \frac{E_a}{R} \times y \;\Rightarrow\; E_a = \frac{\beta \times R}{y}$$

$$E_a = \frac{0.034 \times 8.315}{-1.17\mathrm{E}{-05}} = \mathbf{24.5}\,\frac{\mathbf{kJ}}{\mathbf{mol}}$$

└ **Linear model sufficient!**

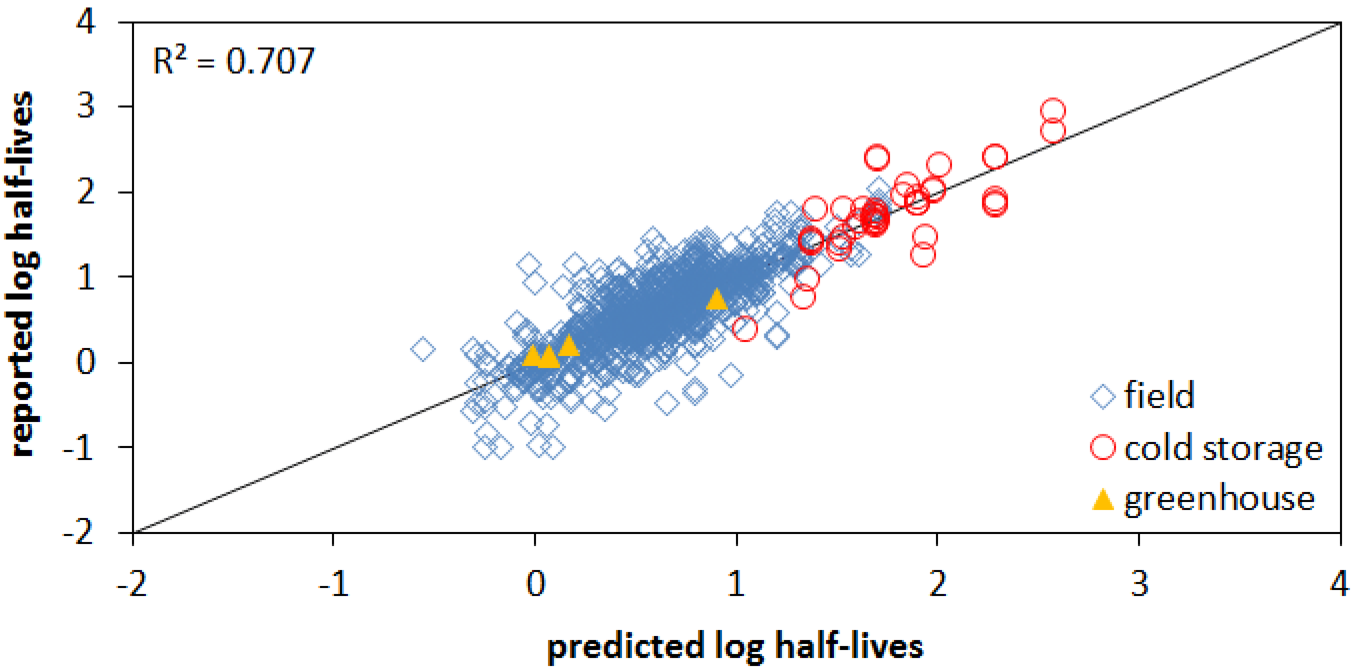


# Influence of Temperature

Prediction of reported dissipation half-lives in crops with linear model

$$\log HL = \log HL_0 + [\beta \times (T - T_0)]$$

└ Comparing ***n*=1030** half-lives with **reported temperature**:



# Imputing Missing Temperatures

**Problem**: **>70%** of reported half-lives come **without temperature** data

**Solution**: **Imputation** of missing temperatures

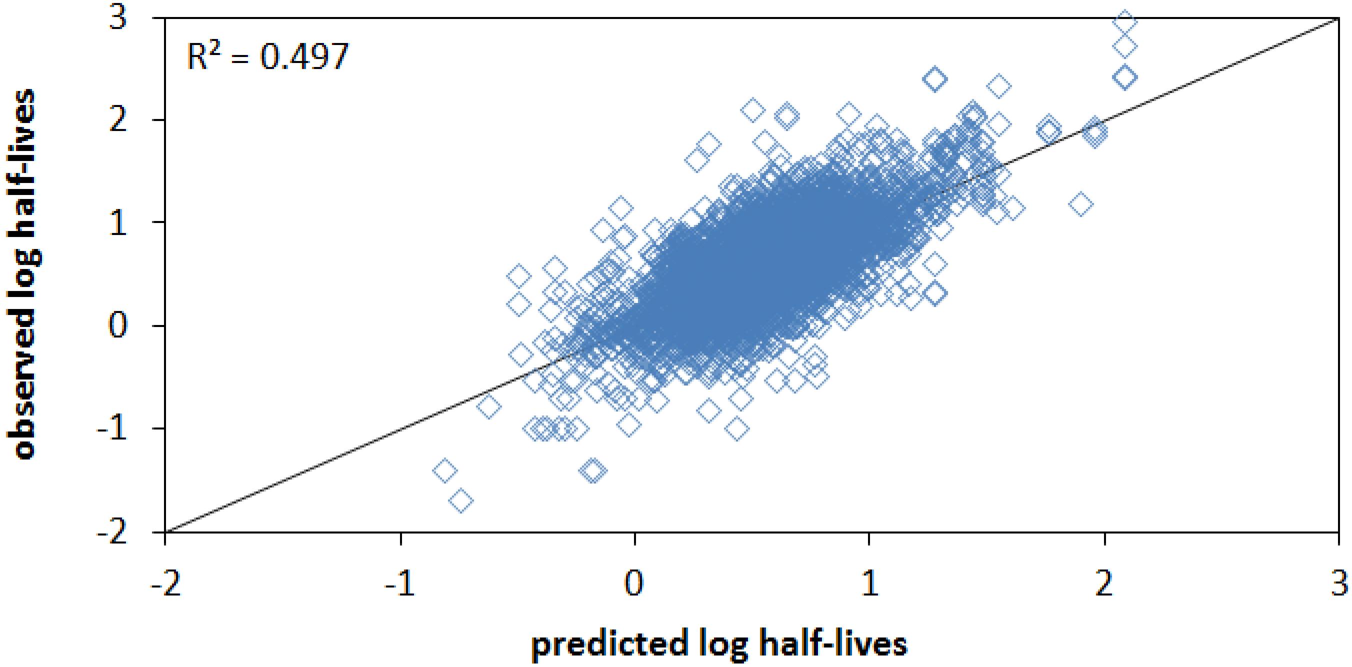
- **Define optimal range** of temperature per crop (FAO, etc.)
  - Compare means of reported temperatures and optimal ranges
  - **Recommended temperature**
    - Fix min/max temperature range for each crop
    - For >5 reported temperatures → mean of reported data
    - Rest → result of fitting reported data to optimal range
- **Multiple imputation** (Markov Chain Monte Carlo method)
  - Use **reported data** where available, else use **imputed data**

# Imputing Missing Temperatures

Prediction of reported dissipation half-lives in crops with linear model

$$\log HL = \log HL_0 + [\beta \times (T - T_0)]$$

└ Comparing ***n*=4513** half-lives with **reported/imputed temperature**:



# Prediction Model Design

Predict **non-reported** dissipation half-lives in crops as a function of:

- **Temperature** (incl. correction factor for cold storage) ← done!
- **Substance class** ← 13 classes **significant**
- **Substance properties** ← MW, log Kaw, log Kow **significant**
- **Crop class** ← 14 classes **significant**
- **Component** that is harvested ← not significant!

**Proposed structure of final model** (in progress):

$$\log HL = \alpha + \beta_T \times (T - T_0) + \beta_{\text{subst}} \times \{0; 1\}_{\text{subst}} + \beta_{\text{MW}} \times \text{MW} + \ldots$$

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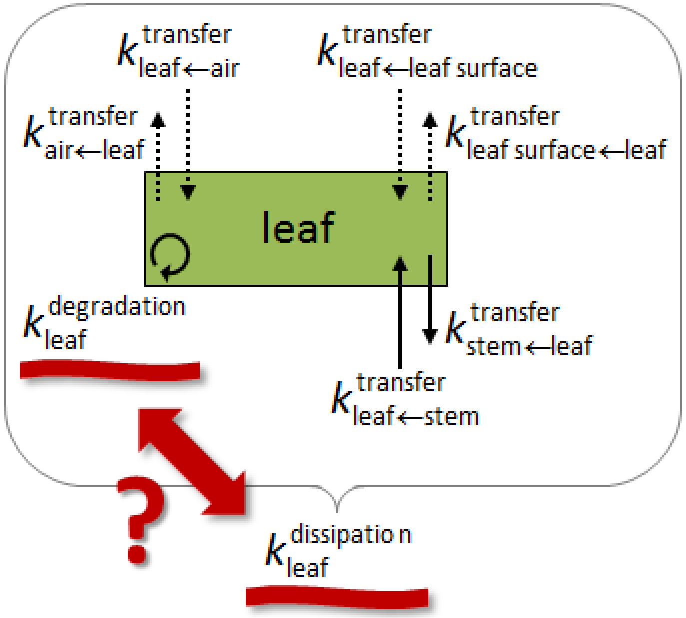
# Conclusions and Outlook

## Conclusions

- **Temperature** is main influence on dissipation half-lives in crops
- Missing temperatures can be **imputed**
- Additional **correction** required to predict half-lives

## Outlook

- Models require ‚**degradation**‘, not ‚dissipation‘ → flagging based on **optimizing** degradation term in mass balance system



# Thank you!

Database of 4513 Reported Pesticide Dissipation Half-Lives in Crops:

Fantke and Juraske 2013,
ES&T 47, 3548-3562
or http://db.dynamicrop.org