Scaling procedure to reduce the effect of spatial heterogenously distributed pesticide residues on the kinetic analysis of the field dissipation

Klaus Platz, Bernhard Jene, Beate Erzgräber, Bernhard Gottesbüren
BASF Aktiengesellschaft, Agricultural Center, 67117 Limburgerhof, Germany

Background

Scattering of residues in soil samples obtained from field dissipation studies pose a serious problem for the estimation of dissipation and formation rates of pesticides and their metabolites. The scattering of residues may be attributed to natural variability (i.e. in degradation rates) but an uneven distribution during application is also possible e.g. in furrow or band application. In the case of uneven application some samples will be taken from spots with high residue level that show increased concentrations of all analytes (parent and metabolites) compared to samplings at different time points that are taken from spots with lower initial concentration. (Figures 1 and 2)

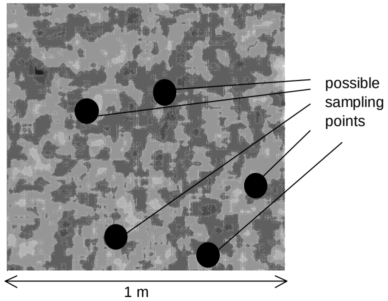

Figure 1: Schematic structure of the spatially heterogeneous distribution of a substance in a natural field soil

Scaling Procedure:

A scaling procedure was developed to reduce the effect of the spatial heterogeneity caused by inhomogeneous application on the kinetic analysis of the residue decline.

1. The total sum of analytes are fitted to an appropriate best-fit dissipation model e.g. First Order Multiple Compartment (FOMC) according to Gustafson & Holden (1990).

2. For each time point of measurement, a scaling factor between the observed (measured) and the to be fitted concentration is derived. The scaling factor is assumed to represent the effect of the heterogeneous application (Figure 3).

3.For each time point the concentrations of the parent and the metabolites are multiplied with the respective scaling factor to eliminate the influence of the variability of the residues caused by the heterogeneity of the application.

4. A kinetic analysis of the scaled residues is made to obtain the intrinsic degradation and formation rates of the substances.

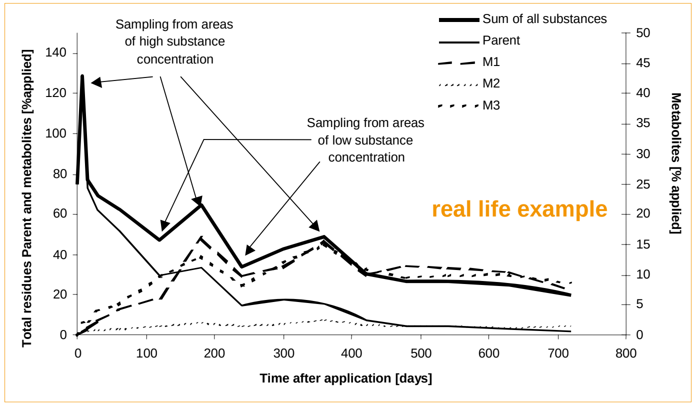

Figure 2: Course of the relative concentrations of parent and metabolites and the total sum of all substances

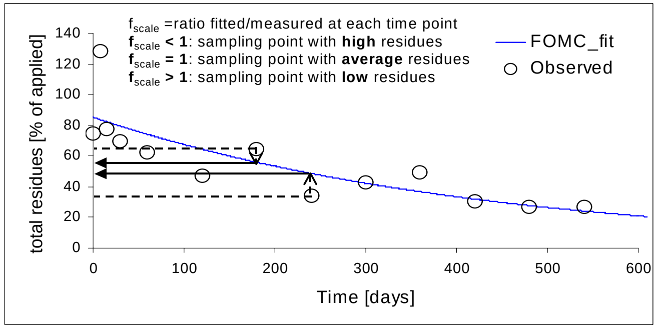

Figure 3: Derivation of scaling factors based on best fit to scattered residues

Examples

(i) A synthetic dataset with known DT_{50}-values of a parent and a metabolite is used for a forward simulation. The simulated residues are artificially scattered and the scaling procedure is successfully used to minimise the scatter. The re-calculation of the intrinsic DT50 was significantly improved using the scaled compared to the scattered data (Table 1 and Figure 4)

Para-meter	Original		Scattered data			Scaled (reduced scatter)		
	Rate	DT50	Rate	type-I error	DT50	Rate	type-I error	DT50
	$[d^{-1}]$	[d]	$[d^{-1}]$		[d]	$[d^{-1}]$		[d]
k_{12}	0.05	8.7	0.043	0.033	6.2	0.050	< 0.001	7.8
k_{13}	0.03		0.069	0.039		0.039	< 0.001	
k_{23}	0.05	13.9	0.025	**0.339**	27.7	0.046	**< 0.001**	15.1

Table 1: Kinetic parameters for the synthetic dataset as originally used for the forward simulation and re-estimated with and without reducing the data scatter

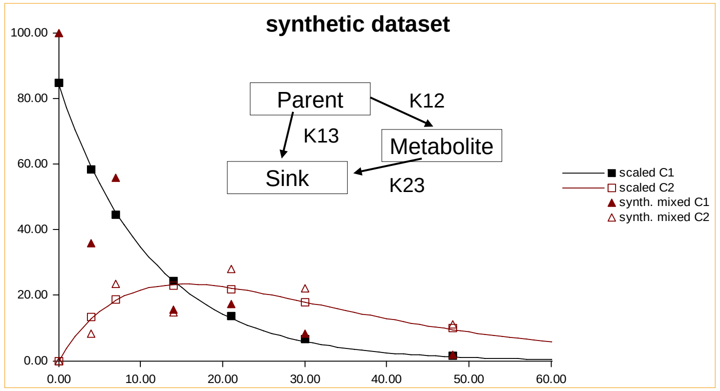

Figure 4: Synthetic data set: “scattered” and scaled residues; Curves are fitted to the scaled data

(ii) Using a real example (see Figure 2) the scaling procedure was successfully applied to reduce the scatter of the residues and to fit the kinetic behaviour of e.g. the metabolite M3 (Figure 5).

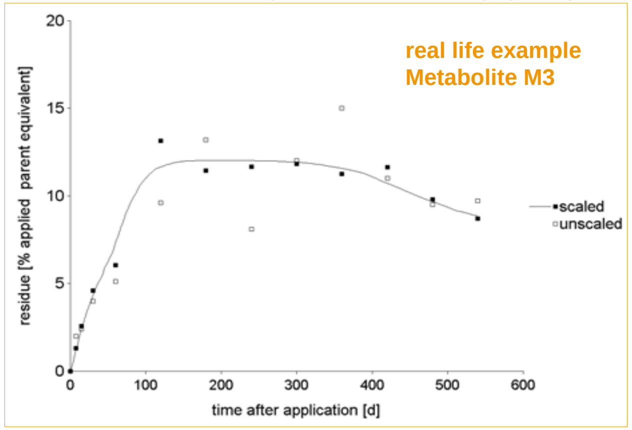

Figure 5: Kinetic fit of metabolite M3 after the scaling compared to the unscaled data (real example)

Conclusions

The scaling procedure allows to reduce the scattering of the measured residues resulting from heterogeneous application and sampling. The significance levels of the estimated kinetic parameters can be improved considerably especially for analytes with low concentration levels for which kinetic parameters can hardly be estimated with scattered residues. The “intrinsic true” kinetics are not altered.

References:

Gustafson, D.I., Holden, R. (1990). Nonlinear pesticide dissipation in Soil: A new model based on spatial variability. Environ. Sci. Technol., Vol. 24, No. 7, 1032-1038