

Modeller subjectivity in estimating pesticide parameters for leaching models using the same laboratory data set

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Abstract

User-dependent subjectivity in the process of testing pesticide leaching models is relevant because it may result in wrong interpretation of model tests. About 20 modellers used the same data set to test pesticide leaching models (one or two models per modeller). The data set included laboratory studies on transformation and sorption of ethoprophos and bentazone in soil from the top 25 cm, at two or three temperatures. All modellers received the raw data from these studies without guidance for deriving the model input parameters. The modellers were asked to provide the values of the half-lives and sorption coefficients which the model considered would use for this soil layer at 10°C (and at field capacity for the half-lives). The half-life of ethoprophos ranged from 92 to 346 days with an average of 191 days and a coefficient of variation of 29%. The half-life of bentazone ranged from 33 to 204 days with an average of 83 days and a coefficient of variation of 46%. The linear and Freundlich sorption coefficients of ethoprophos ranged from 1.7 to 4.3 dm³ kg⁻¹ with an average of 3.4 dm³ kg⁻¹ and a coefficient of variation of 21%. The linear and Freundlich sorption coefficients of bentazone ranged from 0.08 to 0.14 dm³ kg⁻¹ with an average of 0.11 dm³ kg⁻¹ and a coefficient of variation of 13%. This variability caused by the interpretation of the modeller is so large that it overrules conceptual differences between models in many cases. The most important cause of the variability in the half-lives was the expert judgement involved in establishing the relationship between transformation rate and soil temperature. Differences in fitting procedures played only a minor role for the half-lives but they were an important cause of the variability in the linear sorption coefficient. Some recommendations are proposed to reduce the effect of user-subjectivity on modelling results in future model tests. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In pesticide registration procedures within the EU, a first assessment of pesticide leaching may be made on the basis of model calculations for a specific scenario (e.g. Brouwer et al., 1994). The most important pesticide input parameters are based on results of laboratory studies with top-soil material, which are transformed into a few parameter values (e.g. K_{OM} and half-life at 20°C). The Vredepeel data set (described by Boesten and Van der Pas, 1999, 2000) was sent to about 20 modellers who each tested one or more pesticide leaching models; this resulted in tests of in total 11 models (see overviews by Vanclooster and Boesten, 2000 and by Tiktak, 2000). In the first instance, the modellers derived the values of the transformation rate and sorption parameters mostly from the laboratory studies with soil from the experimental site and with the two pesticides considered (Tiktak, 2000). Thereafter most modellers also used the field data from the Vredepeel data set to calibrate these parameters. Tiktak (2000) concluded that differences in transformation and sorption parameters derived by the different modellers were so large that they tended to overrule the differences between models.

The model tests for the Vredepeel data set suggest that user-dependent subjectivity in estimating model input parameters from the results of the laboratory studies may lead to substantial differences in model input and therefore also in model outcome. This phenomenon is undesirable in view of the important role of these input parameters in pesticide registration procedures, which should be robust. Moreover, the user-dependent subjectivity may hamper harmonisation of the pesticide registration procedure at the EU level, so ways need to be found to minimise it. The large number of modellers involved with the Vredepeel data set offers a good opportunity for the analysis of user-dependent subjectivity. The aim of this study is to find its main causes via an inventory of the procedures used by each modeller. The study only considers parameter values derived from the laboratory studies (so excluding any field calibration or other information from the literature), because this is most relevant in pesticide registration procedures. It is limited to the top soil material because most information was available for this material (for deeper soil layers only limited information on transformation rates was available; Boesten and Van der Pas, 2000).

The problem of user-dependent subjectivity in modelling of pesticide leaching has received only limited attention so far. Brown et al. (1996) studied the modeller subjectivity using three pesticide leaching models and five modellers. They prescribed the transformation rate and sorption parameters to all modellers and considered the effect of the variability in input parameters that could not be derived from the experimental information provided (e.g. dispersion length). Our study is complementary to that of Brown et al. (1996) because we focus only on variability in the transformation rate and sorption parameters.

2. Procedure of the ring test

As described by Boesten and Van der Pas (1999, 2000), the transformation and sorption of ethoprophos and bentazone were measured using soil from the 0–25 cm layer collected

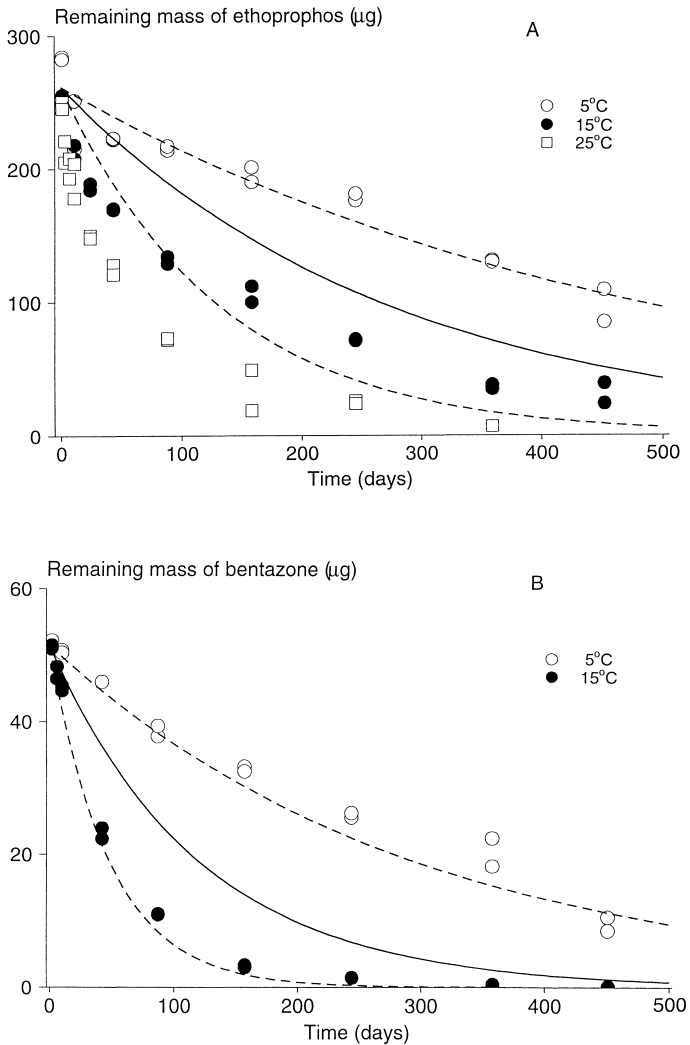


Fig. 1. Results of the incubation studies with ethoprophos (part A) and bentazone (part B) and soil material from the top 25 cm at Vredepeel. The solid line is calculated with the average of the half-lives derived by the modellers and the dashed lines are calculated with the shortest and the longest half-life (modellers were asked to provide the half-life which the model would use at 10°C).

at the experimental field in Vredepeel (The Netherlands). The transformation rate of ethoprophos in soil was measured at 5, 15 and 25°C and the rate of bentazone transformation was measured at 5 and 15°C (see Fig. 1). The bentazone transformation rate was not measured at 25°C because it was anticipated that bentazone would not be exposed to soil temperatures above 15°C in the 0–25 cm layer (see Boesten and Van der Pas, 2000).

The moisture content in all transformation studies was 0.17 kg kg^{-1} and the studies lasted for about 450 days. During the transformation rate studies, two duplicates were sampled and analysed at all incubation times. Concentrations were measured in the total incubation system and in the liquid phase (separated via centrifugation). The incubation for 450 days is too long for a transformation rate study (Anderson, 1987), but the study aimed also at measuring long-term sorption kinetics via the measurement of the concentration in the liquid phase.

Sorption isotherms of ethoprophos were measured at 5 and 25°C in a soil–water suspension with a solid–liquid ratio of 1 kg dm^{-3} by shaking for 24 h at three initial concentrations (see Fig. 2a). Sorption isotherms of bentazone were measured at 5 and 15°C in a soil–water suspension with a solid–liquid ratio of 2 kg dm^{-3} by shaking for 24 h at four initial concentrations (see Fig. 2b). At all concentrations triplicates were sampled and analysed for both pesticides. Bentazone sorption was measured at 15°C and not at 25°C because of the argument described in the preceding paragraph.

All modellers received the raw data of these transformation and sorption experiments without guidance for deriving the model input parameters.

As described by Vanclooster et al. (2000), the test of the different models by the various modellers was organised via three workshops: workshop 1 dealt with the data sets and the models, workshop 2 with the results of the model tests for water flow and tracer movement, and workshop 3 with the results of the model tests for ethoprophos and bentazone. So between workshops 2 and 3, the modellers had to estimate the pesticide input parameters. Before workshop 3, a questionnaire was sent to all modellers who used the Vredepeel data set. It contained the following questions:

1. Specify the half-life for both pesticides that your model will use at 10°C and at field capacity.
2. Specify the Freundlich or linear sorption isotherm parameters; if the parameters are a function of soil temperature in your model, then give the values at 10°C .

The questionnaire included a definition of the Freundlich isotherm and the units to be used. Note that modellers may have modified the values of these parameters after having attended workshop 3. Here, only their estimates before attending this workshop are presented. So the results reported here are based on individual assessments and there was almost no interaction between the modellers. If values given by a modeller seemed to be based on evident errors (a few cases), I contacted the modeller and asked for clarification. If calculation errors had been made, estimated parameter values were changed. So the results presented here are intended to be free of evident errors in processing the data.

The justification for the fixed temperature (10°C) is that it is close to the average temperature at 2.5 cm depth in soil (8.7°C) over the whole experimental period in Vredepeel. Most models contain a temperature-relationship for the transformation rate, so comparing the half-life at a representative temperature in the field is the most straightforward procedure (the alternative would be to ask for the temperature relationship which is more complicated).

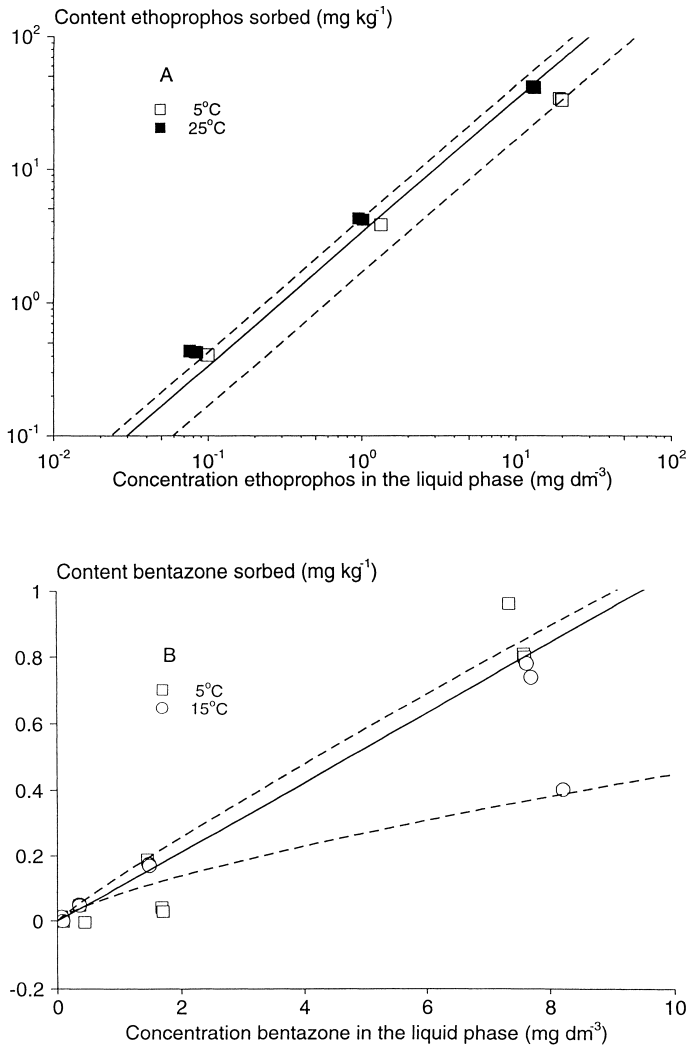


Fig. 2. Results of sorption measurements with ethoprophos (part A) and bentazone (part B) and soil material from the top 25 cm at Vredepeel. The solid line is calculated with the average of the Freundlich coefficients derived by all modellers assuming $N = 1$. The dashed lines are calculated with the sorption parameters corresponding with the highest and lowest sorption.

3. Parameter estimation procedures followed by individual modellers

3.1. Mathematical equations

The most important equations needed to describe the procedures followed by individual modellers and to define the input parameters are given here. If transformation

follows first-order kinetics, the remaining mass of pesticide in the incubation system, m , can be described with

$$m = m_0 \exp(-kt), \quad (1)$$

in which m_0 is the mass at the start, k the first-order transformation rate coefficient and t is the time. Eq. (1) can be linearised via logarithmic transformation resulting in

$$\ln m = \ln m_0 - kt. \quad (2)$$

For the relationship between soil temperature and the rate coefficient k , two equations are considered. The first one is the Arrhenius equation used by most of the models

$$k = k_{\text{REF}} \exp[-(E_A/R)(1/T - 1/T_{\text{REF}})], \quad (3)$$

in which k_{REF} is the k at reference temperature T_{REF} , E_A the activation energy (J mol^{-1}), R the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K). The second is the more simple exponential equation used by, e.g. the models PELMO (Klein et al., 2000), PESTLA (Boesten and Gottesbüren, 2000) and MACRO (Jarvis et al., 2000)

$$k = k_{\text{REF}} \exp(\gamma(T - T_{\text{REF}})), \quad (4a)$$

$$k = k_{\text{REF}}(Q_{10})^{\Delta T}, \quad (4b)$$

in which γ is a parameter (K^{-1}), Q_{10} is a parameter (dimensionless) and ΔT is defined as $(T - T_{\text{REF}})/10$. As described by Boesten and Van der Pas (2000), Eqs. (4a) and (4b) are identical and Q_{10} equals $\exp(10\gamma)$.

The PELMO model uses a correction factor to adjust the measured transformation rate coefficient to that at field capacity

$$k_{\text{FC}} = k_{\text{M}}(\theta_{\text{FC}}/\theta_{\text{M}})^B, \quad (5)$$

in which θ is the volume fraction of water (dimensionless), B is a parameter (dimensionless), the subscript FC refers to field capacity and the subscript M refers to the measured values.

Both the Freundlich and the linear sorption isotherm are used to describe pesticide sorption. The following Freundlich equation is used:

$$X = K_{\text{F}}C_{\text{REF}}(C/C_{\text{REF}})^N, \quad (6)$$

in which X is the content sorbed (mg kg^{-1}), K_{F} the Freundlich coefficient ($\text{dm}^3 \text{ kg}^{-1}$), C the concentration in liquid phase (mg dm^{-3}), C_{REF} the reference value of C set at 1 mg dm^{-3} and N is the Freundlich exponent. The equation for the linear sorption isotherm is

$$X = K_{\text{L}}C, \quad (7)$$

in which K_{L} is the linear sorption coefficient ($\text{dm}^3 \text{ kg}^{-1}$). Note that K_{F} equals K_{L} if N is 1.

3.2. Procedure followed by each modeller

The procedures used by the modellers to derive the transformation rates of ethoprophos and bentazone at 10°C are summarised in Table 1. Those for deriving the sorption

Table 1

Summary of the procedures used by modellers to derive their model input parameters for the transformation rate of bentazone and ethoprophos for the top 25 cm of the Vredepeel soil profile^a

Modeller	Model(s)	All temperatures used?	Ignored later incubation times?	Fit of k : visual/regression	Procedure for temperature parameters (E_A , Q_{10} , γ)
Boesten	PESTLA	Y	Y	R	γ fitted from data
Brown	MACRO	Y	N	R	Default value of γ
Erzgräber	PRZM-2	Y	N	R	Q_{10} fitted from data
Erzgräber	PELMO	Y	N	R	Q_{10} fitted from data
Gottesbüren	PESTLA	Y	Y	R	Default value of γ
Gouy	GLEAMS	N	N	V	Set to zero
Granitza	MACRO	N	Y	R	Default value of γ
Jarvis	MACRO	N	N	V	γ fitted from data
Klein	PELMO	Y	N	R	Q_{10} fitted from data
Mouvet and Baran	LEACHP	N	N	R	Set to zero
Nicholls	PLM	N	N	V	E_A estimated visually from data
Schaefer	PELMO + LEACHP	N	N	R	Default value of Q_{10}
Sweeney	PRZM-3	Y	N	R	Default value of γ
Tiktak	PESTRAS	Y	N	R	γ fitted from data
Trevisan and Errera	LEACHP	N	N	R	Q_{10} fitted from data
Trevisan and Errera	PRZM-2	N	N	R	Set to zero
Trevisan and Errera	VARLEACH	N	N	R	Default value of E_A
Vischetti	VARLEACH	N	N	R	E_A fitted from data
Walker	VARLEACH + LEACHP	N	Y	R	Default value of E_A

^a Legend for last column: “data” indicates values of the transformation rate coefficient, k , that each modeller derived from the laboratory studies by Boesten and Van der Pas (2000); default value of γ is 0.08 K^{-1} , default value of Q_{10} is 2.0 and default value of E_A is 56 kJ mol^{-1} .

parameters are summarised in Table 2. In this section some further details of the procedures are given.

The half-lives estimated by Aden are not included in the comparison because her definition of the transformation rate is different from that in Eq. (1). Aden fitted Eq. (6) to the ethoprophos and bentazone sorption data using linear regression after logarithmic transformation (two fits per pesticide: one for each of the two temperatures). For each pesticide she averaged the K_F and N values obtained at the two temperatures.

Boesten fitted Eq. (2) to all transformation data shown in Fig. 1 using linear regression and ignoring data points with incubation times longer than 100 days (see Boesten and Van der Pas, 2000). The resulting rate coefficients were fitted to Eq. (4a) via linear regression after logarithmic transformation. Boesten estimated the sorption parameters as described by Boesten and Van der Pas (2000).

Brown fitted Eq. (2) to all transformation data shown in Fig. 1 using linear regression and including all data. The resulting five rate coefficients were converted to the equivalents at 10°C with Eq. (4a) assuming $\gamma = 0.08 \text{ K}^{-1}$. These equivalents were averaged per substance. Brown fitted Eq. (7) to the sorption data at different temperatures using linear regression after having discarded six outliers out of the 23 data points for bentazone. The resulting two values of K_L for each pesticide were averaged.

Erzgräber fitted Eq. (2) to all transformation data shown in Fig. 1 using the Topfit software package described by Heinzl et al. (1993). She applied non-linear regression without logarithmic transformation and used all data. The resulting rate coefficients were fitted to Eq. (4b) for each pesticide via linear regression after logarithmic transformation. For PELMO, the rate coefficients were converted to 10°C with Eq. (4b). The resulting values were corrected for soil moisture with Eq. (5) using a volume fraction of liquid at field capacity estimated by PELMO. For PRZM-2, rate coefficients were converted to the average air temperature over the whole experimental period (12.3°C estimated from the daily maximum of air temperature) with Eq. (4b). Erzgräber fitted Eq. (6) to the sorption data using linear regression after logarithmic transformation (two fits for the two temperatures for each pesticide). She averaged both K_F and N obtained for the same pesticide at different temperatures. PRZM-2 needs a linear sorption coefficient as input and Erzgräber set this coefficient equal to the Freundlich coefficient.

Gottesbüren considered only bentazone. He fitted Eq. (2) to the transformation data shown in Fig. 1 using linear regression and ignoring data points with incubation times longer than 100 days. The resulting transformation rates were fitted to Eq. (4a) to obtain the half-life at 20°C. This was used as input to the PESTLA model in combination with the default value $\gamma = 0.08 \text{ K}^{-1}$. Gottesbüren did not consider the sorption data shown in Fig. 2 but used the decline with time of soil pore water concentrations measured during the incubation study at 5°C (see Boesten and Van der Pas, 1999). These were fitted with a non-linear regression procedure to a two-site model for sorption kinetics which is based on Eq. (6) for the equilibrium part and on an additional rate equation for the non-equilibrium part (see Boesten and Gottesbüren, 2000).

Gouy fitted a line corresponding to Eq. (1) in between of the transformation data of 5 and 15°C shown in Fig. 1 (fit on basis of visual correspondence). The values obtained were rounded off and should be considered as rough approximations. This is justifiable because GLEAMS describes the transformation rate in a simplified way: the rate does not

Table 2

Summary of the procedures used by modellers to derive their model input parameters for the sorption isotherms of bentazone and ethoprophos for the top 25 cm of the Vredepeel soil profile^a

Modeller	Model(s)	Both temperatures used?	All data per temperature used?	Linear or Freundlich isotherm?	Fitting procedure for isotherm parameters
Aden	SIMULAT	Y	N	F	LR after LT
Boesten	PESTLA	N	N	F	LR after LT
Erzgräber	PELMO	Y	N	F	LR after LT
Gottesbüren	PESTLA	N	N	F	Non-linear regression
Klein	PELMO	Y + N	N	F	LR after LT
Mouvet and Baran	LEACHP	Y	Y	F	LR after LT
Schaefer	PELMO	Y	N	F	LR after LT
Tiktak	PESTRAS	N	Y	F	Non-linear regression
Brown	MACRO	Y	N	L	LR
Erzgraeber	PRZM-2	Y	N	L	LR after LT
Gouy	GLEAMS	Y	Y	L	Visual fit
Granitza	MACRO	Y	Y	L	Averaged X/C quotients
Jarvis	MACRO	Y	Y	L	LR
Mery, Remy and Delmas	PRZM-2	N	Y	L	LR
Nicholls	PLM	Y	Y	L	Visual fit
Sweeney	PRZM-3	Y	Y	L	LR
Trevisan and Errera	P R Z M - 2 + LEACHP + VARLEACH	Y	Y	L	Averaged X/C quotients
Vischetti	VARLEACH	Y	N	L	Averaged X/C quotients
Walker	VARLEACH + LEACHP	N	N	L	LR after LT

^a Legend for last column: LR is abbreviation for linear regression, LT is abbreviation for logarithmic transformation and X/C quotient is the content sorbed divided by the concentration in liquid phase (see Eq. (7)).

vary with soil moisture content, temperature or depth. Gouy fitted Eq. (7) to the sorption data (separate values for each temperatures). The resulting values for the different temperatures were averaged and rounded; these averages should be considered as rough approximations.

Granitza fitted Eq. (1) to the transformation data of 15°C for bentazone and to the data of 25°C for ethoprophos (Fig. 1) including only data from the first 157 incubation days and using the Topfit software package as described by Heinzl et al. (1993). This package applies non-linear regression without logarithmic transformation. He used the resulting half-lives in combination with a default value of γ (i.e. 0.08 K^{-1}). Granitza used Eq. (7) to describe the sorption data. He averaged all X/C quotients per pesticide combining the results from the different temperatures.

Jarvis fitted Eq. (1) to the transformation data of 5 and 15°C (see Fig. 1) using a graphical program (fit on basis of visual correspondence). He used Eq. (4a) to calculate the rate coefficient at 10°C. Jarvis fitted Eq. (7) to the sorption data via linear regression. For bentazone, the data of 5 and 15°C were combined. For ethoprophos, the data of 5 and 25°C were analysed separately and an intermediate sorption coefficient was taken.

Klein fitted Eq. (2) to the transformation data shown in Fig. 1 using linear regression and including all data. The resulting rate coefficients were fitted to Eq. (4b) via linear regression after logarithmic transformation to derive the rate coefficients at 10°C. Klein applied the PELMO model which uses Eq. (5) to transform the measured rate coefficient to the value used at field capacity. The parameter B was 0.718, θ_{FC} was 0.224 and θ_M was 0.19. Klein fitted Eq. (6) to the sorption data of ethoprophos using linear regression after logarithmic transformation (two fits per pesticide for the two temperatures). He averaged both K_F and N . For bentazone, he applied the same analysis but used only the sorption data collected at 5°C.

Mery, Remy and Delmas applied PRZM-2 and used the option to specify different transformation rates for the liquid and solid phases. Their half-lives (based on the studies at 5°C only) are not included in the comparison because their definition of the transformation rate is different from that in Eq. (1). Mery, Remy and Delmas fitted Eq. (7) to the sorption data via linear regression considering only the studies at 5°C.

Mouvet and Baran applied the LEACHP model. Their runs resulted in an underestimation of soil temperatures with 6–9°C. Therefore they chose to run LEACHP with an option in which the transformation rate is assumed not to vary with temperature. They used only the results of the transformation rate studies at 15°C to estimate the half-life. They fitted Eq. (2) to the transformation data of ethoprophos and bentazone obtained at 15°C (Fig. 1) using linear regression and including all data. Mouvet and Baran fitted Eq. (6) to the ethoprophos sorption data using linear regression after logarithmic transformation (two fits per pesticide for the two temperatures). For bentazone, the resulting K_F values were averaged. For ethoprophos, K_F was assumed to vary linearly with temperature between 5 and 25°C. N values were based on the result for one of the two temperatures.

Nicholls fitted Eq. (1) to the transformation data of ethoprophos and bentazone graphically. In the description of the temperature relationship with Eq. (3), he gave more weight to the incubations at 15 and 25°C than to those at 5°C. He fitted Eq. (7)

graphically to the sorption data, estimating one value of K_L based on the results for the two temperatures per pesticide.

Schaefer fitted Eq. (2) to the transformation data of ethoprophos and bentazone measured at 15°C using linear regression and including all data points. He calculated the rate coefficients at 10°C with Eq. (4b) using a Q_{10} value of 2. Schaefer fitted Eq. (6) to the sorption data using linear regression after logarithmic transformation: he combined the data of the different temperatures for each pesticide, so one regression per pesticide was obtained.

Sweeney fitted Eq. (2) to the transformation data of ethoprophos and bentazone using linear regression and including all data. He used Eq. (4a) with $\gamma = 0.08 \text{ K}^{-1}$ to translate each rate coefficient from the incubation temperature to 10°C. The resulting half-lives (three for ethoprophos and two for bentazone) were averaged. Sweeney averaged the three replicates at each concentration in the sorption study and fitted Eq. (7) using linear regression for each of the temperatures. The resulting values of K_L were converted into K_{OC} values and the values for the two temperatures were averaged.

Tiktak fitted Eq. (1) to the transformation data of ethoprophos and bentazone using non-linear regression and including all data. Eq. (4a) was fitted to the resulting rate coefficients to obtain the values at 10°C. Tiktak fitted Eq. (6) to the ethoprophos and bentazone sorption data via non-linear regression considering only the measurements at 5°C.

Trevisan and Errera applied both PRZM-2, VARLEACH and LEACHP. For the PRZM-2 application, they fitted Eq. (2) to the transformation data of ethoprophos and bentazone using linear regression and the measurements at 5°C. For the VARLEACH application they used the half-lives as derived for the PRZM-2 application, however, they combined these with the VARLEACH option in which the user needs to specify the measured half-lives and the moisture content and temperature of the measurement. This option implies use of default values of E_A (56 kJ mol^{-1}) and of B (0.87) for both pesticides. The option further implies that an equation similar to Eq. (5) is used to correct for the effect of the soil moisture content. VARLEACH estimated the moisture content at field capacity to be 0.165 kg kg^{-1} . For the LEACHP application, they fitted Eq. (2) to the transformation data of ethoprophos and bentazone using linear regression and the measurements at 5°C. They fitted Eq. (2) also to the transformation data of ethoprophos at 15°C. They fitted the Q_{10} value of both pesticides using Eq. (4b) and the rate coefficients of ethoprophos at 5 and 15°C. For the PRZM-2, VARLEACH and LEACHP applications, Trevisan and Errera used Eq. (7) to describe the sorption data: all X/C quotients of each pesticide were averaged, so the results from the different temperatures were combined. For ethoprophos, they estimated also parameters for non-equilibrium sorption from the concentrations in the liquid phase during the incubation studies (see Section 2) but these are not considered here.

Vischetti fitted Eq. (2) to the transformation data of ethoprophos and bentazone measured at 5 and 15°C using linear regression and including all data points. The resulting rate coefficients were used to derive the Arrhenius activation energy with Eq. (3). Vischetti used Eq. (7) to describe the sorption data: he averaged all X/C quotients per pesticide, excluding the bentazone sorption points with negative adsorption and combined the results from the different temperatures.

Walker fitted Eq. (2) to the transformation data obtained at 15°C for bentazone and ethoprophos (Fig. 1) including only data from the first 157 incubation days and using linear regression. He used the resulting half-lives in combination with the default value in VARLEACH for E_A (56 kJ mol⁻¹). Walker fitted Eq. (6) to the sorption data obtained at 15°C for bentazone and at 5°C for ethoprophos using linear regression after logarithmic transformation and ignoring two outlying sorption points for bentazone. VARLEACH needs a linear sorption coefficient as input and Walker set this coefficient equal to the Freundlich coefficient. Walker applied also LEACHP using the same input data.

4. Results and discussion

4.1. Transformation parameters

The half-lives derived for the different modeller–model combinations at 10°C are listed in Table 3. The longest half-life for each pesticide is 4–6 times longer than the shortest half-life. The corresponding histograms in Fig. 3 show a wide range of values, especially for bentazone. The coefficient of variation was 29% for ethoprophos and 46% for bentazone. The calculated lines in Fig. 1 illustrate the wide range of the half-lives: the line corresponding to the average half-life is indeed between the results of the incubations

Table 3

Half-lives derived from the laboratory studies with ethoprophos and bentazone in soil material from the top 25 cm at Vredepeel for the modeller–model combinations^a

Modeller	Model(s)	Half-life (days) ethoprophos	Bentazone
Boesten	PESTLA	196	88
Brown	MACRO	231	100
Granitza	MACRO	129	52
Erzgräber	PRZM-2	157	57
Erzgräber	PELMO	166	71
Gottesbüren	PESTLA		33
Gouy	GLEAMS	200	100
Jarvis	MACRO	204	86
Klein	PELMO	202	92
Mouvet and Baran	LEACHP	107	50
Nicholls	PLM	92	44
Schaefer	PELMO	153	50
Sweeney	PRZM-3	231	108
Tiktak	PESTRAS	212	88
Vischetti	VARLEACH	219	78
Trevisan and Errera	LEACHP	180	106
Trevisan and Errera	PRZM-2	346	204
Trevisan and Errera	VARLEACH	204	120
Walker	VARLEACH + LEACHP	200	57
Average		191	83

^a Modellers were asked to provide the half-life that the model would use at 10°C and field capacity.

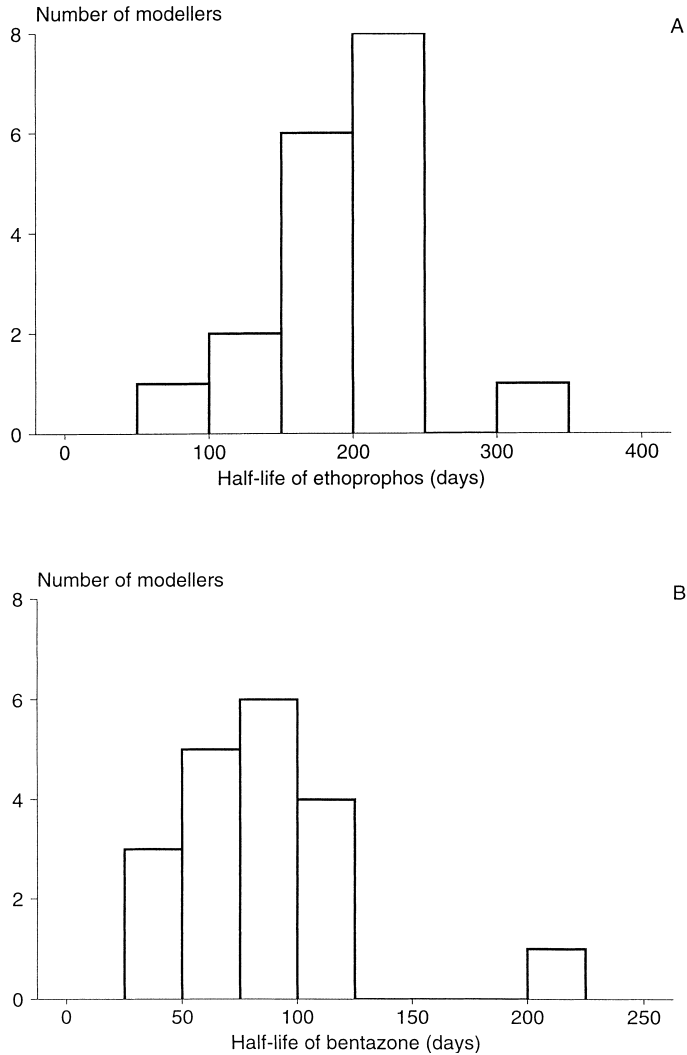


Fig. 3. Histograms of the half-lives derived by the modellers for ethoprophos (part A) and bentazone (part B) for the Vredepeel soil material from the top 25 cm layer. Modellers were asked to provide the half-life that the model would use at 10°C and at field capacity.

at 5 and 15°C for both ethoprophos and bentazone, however, the line corresponding with the shortest half-life for bentazone, is close to the data derived at a temperature of 15°C. So the variability in the estimated half-lives is large. Pesticide leaching models are very sensitive to the transformation rate of the pesticide (e.g. Boesten and Van der Linden, 1991). Therefore the differences shown in Fig. 3 will have a large effect on the results of the model tests as noticed by Tiktak (2000). He concluded that this effect is so large that it will tend to overrule the effect of conceptual differences between models.

The summary of the procedures used by the different modellers to estimate the transformation rate parameters for their model application (Table 1) shows that about 50% of the modellers used the results from only part of the incubation studies. Further, three out of eight modellers who used all data, used a default value for the parameter in the temperature relationship (Q_{10} , E_A or γ). So about 70% of the modellers ignored part of the results of the incubation studies in estimating the transformation input parameters. This is remarkable because all incubation studies were conducted at temperatures within the range measured in the field (Boesten and Van der Pas, 2000). A complication in the data was that the temperature effect found for bentazone was very large. Boesten and Van der Pas (2000) estimated the half-life for bentazone to be 206 days at 5°C and 38 days at 15°C. This is a factor 5 difference in rate for 10°C difference in temperature (so $Q_{10} = 5$) which is very high as compared to measurements for other soil/pesticide combinations reported in the literature (FOCUS Soil Modelling Workgroup, 1997). The discussions during workshop 3 indicated that part of the modellers attributed this high difference to the relationship between transformation rate and temperature below 10°C being not representative for the relationship above 10°C. Therefore some modellers rejected the study at 5°C based on their expert judgement. For ethoprophos the temperature effect was in the expected range: Boesten and Van der Pas (2000) found $Q_{10} = 2.5$, $E_A = 64 \text{ kJ mol}^{-1}$ and $\gamma = 0.09 \text{ K}^{-1}$. These values are comparable to results for other pesticide/soil combinations reported in the literature (FOCUS Soil Modelling Workgroup, 1997). It is likely that the higher coefficient of variation for bentazone (46%) as compared to that for ethoprophos (29%) is caused by the extreme temperature effect for bentazone which resulted in more weight being given to expert judgement.

Table 1 shows that only four out of 16 different modellers rejected later incubation times in the calculation of the transformation rate coefficients. Figs. 1 and 2 show that the incubations lasted about 450 days. However, it is generally recommended to stop such studies after about 100 days because at longer incubation times the microbial activity in soil may decrease distinctly (Boesten and Van der Pas, 2000, continued the study for 450 days for another purpose: estimating parameters for long-term sorption kinetics). The transformation rate may slow down in isolated incubation systems with topsoil material (Anderson, 1987; ISO, 1991; OECD, 1998). The plots of the logarithm of the remaining mass versus time shown by Boesten and Van der Pas (2000) indeed showed that the transformation rate of bentazone and ethoprophos at the incubation temperatures of 15 and 25°C slowed down for incubation times longer than 100–200 days. This was ignored by the large majority of the modellers. The effect of ignoring later incubation times is considerable: the half-life of bentazone at 15°C estimated via linear regression with Eq. (2) and using all incubation times was 41% higher than the half-life based only on incubation times shorter than 100 days. For the half-lives of ethoprophos at 15 and 25°C this percentage was 51 and 38%, respectively.

Table 1 shows that 13 out of 16 modellers applied regression procedures to estimate parameter values, whereas only three used graphical correspondence between a line and the data points. The half-lives found via graphical correspondence were nearly all in the range of those found via regression procedures (see Table 3). From Section 3.2, it can be derived that all modellers but three applied linear regression. Tiktak et al. (1998) studied the effect of applying either linear or non-linear regression to these incubation studies

(including all incubation times). Their results for non-linear regression are given Table 3. Linear regression would have resulted in a half-lives at 10°C that were 13 and 27% higher for bentazone and ethoprophos, respectively. So in the case of Tiktak, the effect of the type of regression was limited.

The choice of the model may also contribute to the variability in the input parameters. A few models (PRZM, GLEAMS) do not consider the effect of soil temperature on the transformation rate. The LEACHP model has an option (used by Mouvet and Baran) which ignores the temperature effect. Then the modeller has to choose the most relevant temperature (e.g. Erzgräber chose 13°C for PRZM-2, Gouy 10°C for GLEAMS, Mouvet and Baran 15°C for LEACHP and Trevisan and Errera 5°C for PRZM-2). Another factor is the moisture content in the incubation study: some models (PELMO, VARLEACH) require this moisture content as an input parameter (using Eq. (5)), whereas most models assume that the input values are for field capacity. The half-life in PELMO and VARLEACH at field capacity is therefore also influenced by the estimation of the moisture content at field capacity. To assess the influence of the moisture content correction, we checked this effect for the values estimated by Klein: it was found to be 13%, so of limited importance, which is the result of the moisture content in the incubation studies being close to that at field capacity (see Boesten and Van der Pas, 2000). In general, these differences between models in handling temperature and moisture effects imply that a part of the variability in Table 3 and Fig. 3 is attributable to differences between models (as opposed to the differences between modellers). A first attempt was made to distinguish those two sources of variation by calculating the coefficient of variation of the half-lives used for a particular model. Only models were considered for which three half-lives were available (MACRO, PELMO and VARLEACH: see Table 3). The average of the coefficient of variation was 16% for ethoprophos and 33% for bentazone. These values should be compared to the coefficient of variation of the whole population of half-lives (29% for ethoprophos and 46% for bentazone). So this indicates that the greater part of the variability is the result of differences between modellers.

4.2. Sorption parameters

The histograms for the linear and Freundlich sorption coefficients in Fig. 4 show that the distribution for ethoprophos was wider than that for bentazone (see Tables 4 and 5 for the individual data). Note that the definitions of the Freundlich and linear sorption coefficients are not identical (Eqs. (6) and (7)). Nevertheless it is justifiable to combine them in the histograms because the Freundlich coefficient is evaluated at a reference concentration of 1 mg dm⁻³ and because the range of concentrations of the sorption data includes this reference value (see Fig. 2). The coefficient of variation of all sorption coefficients shown in Fig. 4 was 21% for ethoprophos and 13% for bentazone. Fig. 4A shows that for ethoprophos the variability in the Freundlich coefficients was smaller than that in the linear sorption coefficients (the coefficients of variation were 13 and 25%, respectively). The calculated lines in Fig. 2 show that the extreme values of the derived sorption parameters correspond with sorption isotherms that are within the range of the measurements.

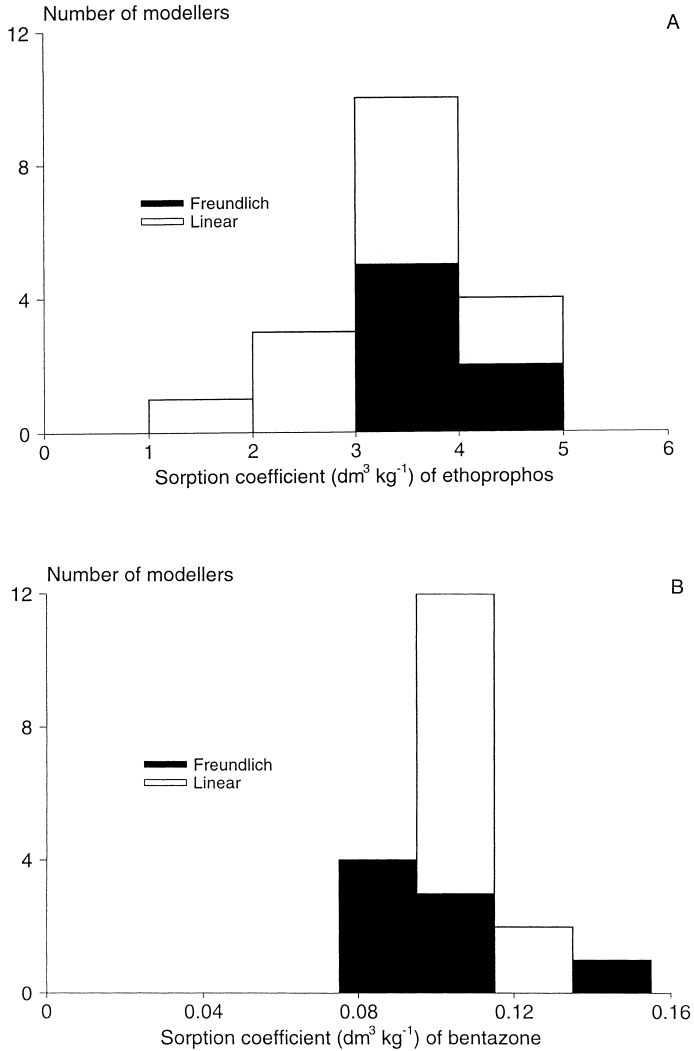


Fig. 4. Histograms of the Freundlich and linear sorption coefficients derived by the modellers for ethoprophos (part A) and bentazone (part B) for the Vredepeel soil material from the top 25 cm layer. Modellers were asked to provide the sorption coefficient that the model would use at 10°C. The number of modellers is stacked (so, e.g. two modellers had a Freundlich coefficient for ethoprophos between 4 and 5 dm³ kg⁻¹ and two modellers had a linear sorption coefficient for ethoprophos in this range).

Table 2 shows that about half of the modellers used only one of the two temperatures for estimating the Freundlich isotherm parameters. The limited variability in the Freundlich coefficients for ethoprophos (Fig. 4) was mainly caused by differences in the procedure of the interpolation between the two measurement temperatures (the Freundlich sorption coefficient for ethoprophos at 25°C was about 45% higher than that at 5°C; Boesten and Van der Pas, 2000).

Table 4

Parameters of the Freundlich sorption isotherms derived from the laboratory studies with ethoprophos and bentazone and soil material from the top 25 cm at Vredepeel for the modeller–model combinations^a

Modeller	Model(s)	Ethoprophos		Bentazone	
		K_F (dm ³ kg ⁻¹)	N	K_F (dm ³ kg ⁻¹)	N
Aden	SIMULAT	3.74	0.84	0.090	1.09
Boesten	PESTLA	4.23	0.87	0.105	0.82
Erzgräber	PELMO	4.29	0.87	0.110	0.92
Gottesbüren	PESTLA			0.083	0.73
Klein	PELMO	3.57	0.87	0.090	0.83
Mouvet and Baran	LEACHP	3.09	0.85	0.110	0.90
Schaefer	PELMO + LEACHP	3.50	0.86	0.085	1.00
Tiktak	PESTRAS	3.09	0.81	0.137	0.90
Average		3.64	0.85	0.101	0.90

^a Modellers were asked to provide the sorption parameters that the model would use at 10°C.

Table 4 shows that the Freundlich exponent of ethoprophos ranged between 0.84 and 0.87 for all modellers, except for Tiktak who found 0.81. Table 2 shows that Tiktak is the only modeller who applied non-linear regression for ethoprophos. However, Tiktak et al. (1998) applied both linear and non-linear regression to these data and showed that this resulted in only small differences in values of the Freundlich exponent. Tiktak was the only modeller who used only the 5°C data for ethoprophos so this is probably the cause of his value being outside the range of the others (see Tiktak et al., 1998).

Table 4 shows that Tiktak derived the highest Freundlich coefficient for bentazone. Probably this is attributable to the non-linear regression procedure he used; almost all

Table 5

Linear sorption coefficient, K_L (as defined by Eq. (7)) derived from the laboratory studies with ethoprophos and bentazone and soil material from the top 25 cm at Vredepeel for the modeller–model combinations^a

Modeller	Model(s)	K_L (dm ³ kg ⁻¹)	
		Ethoprophos	Bentazone
Brown	MACRO	2.43	0.105
Granitza	MACRO	4.29	0.110
Erzgräber	PRZM-2	4.29	0.110
Gouy	GLEAMS	2.50	0.100
Jarvis	MACRO	3.00	0.110
Mery, Remy and Delmas	PRZM-2	1.69	0.120
Nicholls	PLM	3.60	0.100
Sweeney	PRZM-3	3.66	0.100
Vischetti	VARLEACH	3.62	0.105
Trevisan and Errera	VARLEACH + LEACHP + PRZM-2	3.62	0.110
Walker	VARLEACH + LEACHP	2.90	0.127
Average		3.24	0.109

^a Modellers were asked to provide the value that the model would use at 10°C.

modellers used linear regression after logarithmic transformation. The table shows further that Gottesbueren found the lowest Freundlich coefficient and Freundlich exponent for bentazone. This is probably the result of his procedure being completely different from that of the others: he used only the concentration measurements in the pore water at 5°C, so not the data shown in Fig. 2B (see Section 2).

Tables 4 and 5, Fig. 4A show that the linear sorption coefficients tend to be lower than the Freundlich sorption coefficients for ethoprophos. This is partly attributable to the differences between the linear regression procedures for both isotherm equations: linear regression to the linear sorption isotherm equation implies that the weight of each measuring point is proportional to the square of its absolute value. Linear regression to the log-transformed data (as mostly applied for the Freundlich isotherm) implies that the weight of each concentration does not depend on its absolute value. So if concentrations vary two orders of magnitude (as shown for ethoprophos in Fig. 2A), the highest concentration dominates in the regression of the linear equation. This results in a lower value because the sorption coefficient decreases with increasing concentration if the Freundlich exponent is below 1. As the highest concentration may be a quite arbitrary choice of the experimenter, calculation of the linear sorption coefficient by regression should be done for the concentration range most relevant for the field. As shown by Table 2, some modellers did not apply linear regression to the linear sorption isotherm but averaged the X/C quotients (see Eq. (7) for definition of X/C). In this way again equal weight is given to all measurements and the problem of excessive weight to the highest concentration is overcome.

Fig. 2 shows that there was considerable scatter in the triplicate bentazone sorption points, whereas the triplicates for ethoprophos were close to each other. This is attributable to a larger effect of the random error in the measurement of the comparatively weak sorption for bentazone, resulting from the small decrease in the concentration in the liquid phase (Boesten, 1990). It is remarkable that the variation in sorption coefficients derived for bentazone is less than that for ethoprophos (Fig. 4). This indicates that modeller subjectivity may be a more important factor than the quality of the data.

4.3. General discussion

It has been accepted generally that site-specific measurements of pesticide/soil transformation and sorption parameters are needed for meaningful tests of the concepts in pesticide leaching models. For instance, Allen and Walker (1987) measured half-lives of metamitron and metazachlor at standard conditions for 18 UK soils: from their results coefficients of variation of 37–50% can be derived. However, the variation in half-life due to modeller subjectivity (Table 3) is of similar order of magnitude. This indicates that the uncertainty resulting from modeller subjectivity is almost as large as the uncertainty resulting from the use of generic pesticide/soil parameters derived from literature data (as opposed to site-specific data).

Brown et al. (1996) considered the effect of modeller subjectivity resulting from the variability in input parameters that could not be derived from the experimental information provided within the data set. They concluded that the magnitude of the effect was of a similar order of magnitude as the variation associated with field measurements.

Our study dealt with modeller subjectivity resulting from parameters that could be derived from the experimental data. The overview of the comparison of field measurements and model output by Tiktak (2000) indicates that in our case the variation in model output exceeded by far the variation associated with the field measurements (see also e.g. Boesten and Gottesbüren, 2000). So our study strengthens the recommendation by Brown et al. (1996) that more attention must be given to the user-dependence of modelling.

5. Conclusions and recommendations

The modeller subjectivity in deriving the model input parameters for the transformation rate considered in this study, had a large effect resulting in considerable variability in the parameters for both pesticides (especially for bentazone). By far the most important cause of the variability was the expert judgement introduced in establishing the relationship between transformation rate and soil temperature. Other causes were (sequence of decreasing importance): (1) including/excluding incubation times longer than 100–200 days in relation to decreasing microbial activity in isolated laboratory incubation systems; (2) differences in fitting procedures (regression versus graphical and linear versus non-linear regression). A limited part of the variability was not the result from modeller subjectivity but from conceptual differences between models in handling the effects of temperature and moisture on the transformation rate.

The modeller subjectivity in estimating the sorption parameters, as considered in this study, had only a moderate effect on the Freundlich isotherm parameters for ethoprophos and on all isotherm parameters for bentazone. However, the effect was considerable for the linear sorption coefficient for ethoprophos. The causes of the variability introduced by modeller subjectivity were (sequence of decreasing importance): (1) differences in fitting procedures for the linear sorption coefficient (linear regression versus averaging of sorption coefficients); (2) differences in the procedure to interpolate the sorption parameters between the measurement temperatures. Linear regression of the linear sorption isotherm equation implies that the sorption points with the highest concentrations overrule sorption points with concentrations that are an order of magnitude lower. This is only justifiable if the highest concentration is the most relevant one for the field situation to be simulated.

The anticipated effect of this modeller subjectivity is so large that it needs to be reduced, both for testing of models and for model application in pesticide registration procedures. Therefore we recommend to improve the models with respect to the guidance for estimating input parameter (as suggested earlier by Brown et al., 1996). Model tests that aim at testing the predictive value of a model (especially relevant for pesticide registration), should be performed by more than one user. Data sets should be documented in such a way that input parameters can be estimated independently by different modellers; this implies that raw data should be made available (see e.g. Boesten and Van der Pas, 1999). The procedures used to estimate crucial model parameters should be documented carefully by each modeller. For model tests that aim at testing whether model concepts are correct (especially relevant for scientific progress), it is recommended

to have an intensive debate among the modellers (more than one) and the data set provider on interpretation of laboratory and field experiments before performing any model calculation. This should result in consensus a priori about the best estimates of the input parameters to be used for the most meaningful test of the concepts.

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