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## REVIEWS AND ANALYSES

### Simulation of Pesticide Persistence in the Field on the Basis of Laboratory Data—A Review

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#### ABSTRACT

Simulations of pesticide fate in soils are often based on persistence models developed nearly 30 years ago. These models predict dissipation in the field on a daily basis by correcting laboratory degradation half-lives for actual soil temperature and moisture content. They have been extensively applied, but to date no attempt has been made to evaluate existing studies in a consistent, quantitative way. This paper reviews 178 studies comparing pesticide soil residues measured in the field with those simulated by persistence models. The simulated percentage of initial pesticide concentration at the time of 50% measured loss was taken as a common criterion for model performance. The models showed an overall tendency to overestimate persistence. Simulated values ranged from 12 to 96% of initial pesticide concentrations with a median of 60%. Simulated soil residues overestimated the target value (50% of initial) by more than a factor of 1.25 in 44% of the cases. An underestimation by more than a factor of 1.25 was found in only 17% of the experiments. Discrepancies between simulated and observed data are attributed to difficulties in characterizing pesticide behavior under outdoor conditions using laboratory studies. These arise because of differences in soil conditions between the laboratory and the field and the spatial and temporal variability of degradation. Other possible causes include losses in the field by processes other than degradation, deviations of degradation from first-order kinetics, discrepancies between simulated and actual soil temperature and moisture content, and the lack of soil-specific degradation parameters. Implications for modeling of pesticide behavior within regulatory risk assessments are discussed.

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THE prediction of environmental concentrations of a pesticide in soil, surface water, and ground water is a significant part of the data package submitted for pesticide registration. These predictions often involve the use of mathematical simulation models such as GLEAMS (Leonard et al., 1987), LEACHP (Hutson and Wagenet, 1992), PRZM (Carsel et al., 1998), PESTLA (van den Berg and Boesten, 1998), PESTRAS (Tiktak et al., 1994), PELMO (Jene, 1998), and MACRO (Jarvis, 1994). One of the most important processes influencing the environmental behavior of a pesticide is its degradation in soil. For relatively mobile compounds, the likelihood of leaching to ground water increases with increasing persistence and simulation models are generally very sensitive to parameters characterizing this process (Boesten, 1991; Leonard et al., 1987; Soutter and Musy, 1999; Tiktak et al., 1994). An adequate description of degradation and the selection of appropriate parameters are, therefore, prerequisites for reliable modeling. The mechanisms of degradation, its influencing factors, and approaches to describe degradation mathematically are outlined in detail in several publications (Beulke, 1998; Hamaker, 1972; Walker, 1987). The aspects most relevant to this study are briefly described below.

Although degradation of pesticides may be the result of chemical reactions (Wolfe et al., 1990), biological degradation by soil microorganisms is the most important process for most compounds (Torstensson, 1980; Torstensson, 1987). Degradation may follow nonlinear kinetics and a number of approaches exist to describe this phenomenon mathematically (Alexander and Scow,

1989; Duffy et al., 1993; Gustafson and Holden, 1990; Simkins and Alexander, 1984). However, pesticide residues are assumed to decline exponentially (i.e., according to linear, first-order kinetics) in many simulation models, as this is considered to describe pesticide persistence with sufficient accuracy and allows robust estimation of model parameters (Carsel et al., 1998; Hutson and Wagenet, 1992; Jarvis, 1994; Jene, 1998; Leonard et al., 1987; van den Berg and Boesten, 1998):

$$C_{(t)} = C_0 \exp(-kt) \quad [1]$$

where  $C_{(t)}$  is the concentration at time  $t$  ( $\text{mg kg}^{-1}$  soil),  $C_0$  is the concentration at time 0 ( $\text{mg kg}^{-1}$  soil),  $k$  is the degradation rate ( $\text{day}^{-1}$ ), and  $t$  is the time (days). First-order kinetics reflect the assumption that the availability of degrading microbial cells and/or enzymes is unlimited in relation to the usually very small concentration of the compound in soil. Half-lives (i.e., times for 50% degradation of the initial amount of a pesticide) can be derived from degradation rates:

$$H = \frac{\ln 2}{k} \quad [2]$$

where  $H$  is the half-life (days).

Studies conducted for registration purposes involve the determination of first-order half-lives under controlled temperature and moisture conditions in the laboratory. These can be used as input data for simulation models. To allow extrapolation of laboratory half-lives to the varying temperature and moisture conditions in the field, quantitative relationships between half-lives and these factors are required. The temperature dependence of degradation is often described using the Arrhenius equation or similar approaches (Hutson and Wagenet, 1992; Jarvis, 1994; Jene, 1998; Truman et al., 1998; van den Berg and Boesten, 1998):

$$H_{(T)} = A_1 \exp(E_a/RT) \quad [3a]$$

such that:

$$H_{(T_2)} = H_{(T_1)} \exp[E_a(T_1 - T_2)/(RT_1T_2)] \quad [3b]$$

where  $H_{(T)}$  is the half-life at temperature  $T$  (days),  $T$  is the temperature (K),  $A_1$  is a coefficient (days),  $E_a$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $H_{(T_2)}$  is the half-life at temperature  $T_2$  (days), and  $H_{(T_1)}$  is the half-life at temperature  $T_1$  (days).

The influence of soil moisture is generally quantified by an equation proposed by Walker (1973) in the following or slightly modified forms (Hutson and Wagenet, 1992; Jarvis, 1994; Jene, 1998; van den Berg and Boesten, 1998):

$$H_{(M)} = A M^{-B} \quad [4]$$

where  $H_{(M)}$  is the half-life at moisture  $M$  (days),  $A$  is the half-life at a moisture content of  $1 \text{ kg H}_2\text{O } 100 \text{ kg}^{-1}$  soil dry matter (days),  $M$  is the moisture content ( $\text{kg H}_2\text{O } 100 \text{ kg}^{-1}$  soil), and  $B$  is a coefficient (unitless).

The parameters  $E_a$ ,  $A$ , and  $B$  can be derived by fitting Eq. [3b] and [4] to half-lives or pesticide residue data determined at a range of temperature and moisture conditions in the laboratory. Pesticide persistence in

the field can then be predicted on the basis of these parameters and actual or predicted on-site temperature and moisture data. However, it is still not clearly understood whether this extrapolation of laboratory data to field conditions is valid. In several model validation studies, discrepancies between observed and simulated soil residues of a pesticide or its concentrations in leachate have been attributed to an inaccurate simulation of degradation. In a Swedish lysimeter study, the rapid degradation of dichlorprop determined under laboratory conditions in two soils was not typical of degradation in the lysimeters (Bergström and Jarvis, 1994). Leaching of the pesticide could not be modeled unless the degradation rate was markedly decreased from the laboratory value. The pesticide leaching model PESTRAS underestimated dissipation of ethoprophos in a Dutch field study (Tiktak et al., 1998). One possible explanation was an accelerated degradation in the field compared with the laboratory. The following review was carried out to provide more information on the applicability of laboratory half-lives to outdoor conditions.

### Approach to Model Evaluation

Walker (1973, 1974) implemented the first-order degradation equation together with the relationships between half-lives, soil temperature, and moisture into a simulation model to predict pesticide persistence in the field in the upper 5 cm of the soil. In the first version of the model, soil temperature and moisture measured at various depths were used as input data. Alternatively, soil moisture was calculated from rainfall and potential evapotranspiration. Soil temperature at 2-cm depth was derived from that measured at 10-cm depth. The model has subsequently been revised to calculate soil moisture and temperature from daily rainfall and minimum and maximum air temperature (Walker and Barnes, 1981). It divides the simulation period into time steps of 0.05 d and calculates the variation of soil temperature within each day using a sine function. All versions of the model calculate the degradation rate in the field using the parameters  $E_a$ ,  $A$ , and  $B$  (Eq. [3b], Eq. [4]) and actual measured or estimated soil temperature and moisture conditions. Output is given in a daily time-step.

The model has been extensively applied, but to date no attempt has been made to review existing comparisons between simulated and observed pesticide residues in a consistent, quantitative way. In the present investigation, model performance was evaluated using a common criterion for all considered studies. A total of 178 comparisons between measured and simulated dissipation of pesticides in the field was available for model evaluation. These included a number of studies by Walker and coworkers in addition to work by other authors using the original or slightly modified versions of the model (Auspurg, 1986; Berger, 1989; Beulke, 1998; Bunte, 1991; Duefer, 1991; Gottesbüren, 1991; Gottesbüren and Pestemer, 1994; Heiermann, 1998; Leistra and Smelt, 1981; Main et al., 1995; Nicholls et al., 1982; Pestemer and Auspurg, 1987; Pestemer et al., 1988; Poku and Zimdahl, 1980; Rocha and Walker, 1995;

Table 1. Pesticides mentioned in this review.

Common name	Chemical name†	Number of studies reviewed	Source
2,4,5-T	(2,4,5-trichlorophenoxy)acetic acid	4	Walker and Smith, 1979
Alachlor	2-chloro-2',6'-diethyl-N-methoxymethylacetanilide	4	Walker et al., 1992
Atrazine	6-chloro-N <sup>2</sup> -ethyl-N <sup>4</sup> -isopropyl-1,3,5-triazine-2,4-diamine	29	Nicholls et al., 1982; Rocha and Walker, 1995; Walker, 1978; Walker and Zimdahl, 1981
Chloridazon	5-amino-4-chloro-2-phenylpyridazin-3(2H)-one	—	
Chlorotoluron	3-(3-chloro- <i>p</i> -tolyl)-1,1-dimethylurea	10	Duefer, 1991; Gottesbüren, 1991; Heiermann, 1998; Pestemer et al., 1988
Chlorsulfuron	1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea	1	Walker and Brown, 1983a
Chlorthal-dimethyl	—	1	Walker, 1978
Dichlorprop	( <i>RS</i> )-2-(2,4-dichlorophenoxy)propionic acid	—	
Diffenican	2',4'-difluoro-2-( $\alpha,\alpha,\alpha$ -trifluoro- <i>m</i> -tolylloxy)nicotinamide	1	Main et al., 1995
Dinitramine	N <sup>1</sup> ,N <sup>3</sup> -diethyl-2,6-dinitro-4-trifluoromethyl- <i>m</i> -phenylenediamine	2	Poku and Zimdahl, 1980
Ethofumesate	( $\pm$ )-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl	8	Beulke, 1998; Gottesbüren, 1991; Gottesbüren and Pestemer, 1994; Heiermann, 1998
Ethoprophos	<i>O</i> -ethyl <i>S,S</i> -dipropyl phosphorodithioate	2	Leistra and Smelt, 1981
Isoproturon	3-(4-isopropylphenyl)-1,1-dimethylurea	9	Berger, 1989; Heiermann, 1998
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	12	Walker, 1976b, 1978; Walker and Zimdahl, 1981
Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one	7	Bunte, 1991; Walker, 1978; Walker and Bond, 1978
Metazachlor	2-chloro- <i>N</i> -(pyrazol-1-ylmethyl)acet-2',6'-xylidide	3	Beulke, 1998
Methabenzthiazuron	1-(1,3-benzothiazol-2-yl)-1,3-dimethylurea	4	Bunte, 1991; Gottesbüren, 1991; Pestemer and Auspurg, 1987
Metolachlor	2-chloro-6'-ethyl- <i>N</i> -(2-methoxy-1-methylethyl)aceto- <i>o</i> -toluidide	4	Walker and Zimdahl, 1981
Metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one	3	Nicholls et al., 1982; Pestemer and Auspurg, 1987; Walker, 1978
Napropamide	( <i>RS</i> )- <i>N,N</i> -diethyl-2-(1-naphthylloxy)propionamide	1	Walker, 1974
Pendimethalin	<i>N</i> -(1-ethylpropyl)-2,6-dinitro-3,4-xylidide	2	Gottesbüren, 1991
Prometryne	N <sup>2</sup> -N <sup>4</sup> -di-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine	3	Walker, 1976a
Propyzamide	3,5-dichloro- <i>N</i> -(1,1-dimethylpropynyl)benzamide	17	Pestemer et al., 1988; Walker, 1973, 1976c
Simazine	6-chloro-N <sup>2</sup> ,N <sup>4</sup> -diethyl-1,3,5-triazine-2,4-diamine	44	Bunte, 1991; Walker, 1976a,b, 1978; Walker et al., 1983
Terbutryn	N <sup>2</sup> -tert-butyl-N <sup>4</sup> -ethyl-6-methylthio-1,3,5-triazine-2,4-diamine	6	Auspurg, 1986
Triallat	S-2,3,3-trichloroallyl di-isopropyl(thiocarbamate)	1	Gottesbüren and Pestemer, 1994
Trifluralin	$\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro- <i>N,N</i> -dipropyl- <i>p</i> -toluidine	—	

† IUPAC name according to Tomlin (1997).

Walker, 1973, 1974, 1976a,b,c, 1978; Walker and Bond, 1978; Walker and Brown, 1983a; Walker et al., 1983, 1992, Walker and Smith, 1979; Walker and Zimdahl, 1981). In the majority (56%) of the studies, sandy loam soils were used. The remaining experiments were carried out on various soil types ranging from sands to clays, with each soil type investigated in not more than 5% of the studies. In 61% of the cases, the soils were cropped. With the exception of two studies with ethoprophos (soil applied insecticide and nematicide), all experiments investigated the dissipation of herbicides including simazine (25%), atrazine (16%), propyzamide (10%), linuron (7%), and chlorotoluron (6%). All pesticides used in the evaluated studies or mentioned in this review are listed in Table 1 with their common names and chemical names. The papers reviewed in this investigation present pesticide residues measured at intervals after application in graphical or tabular form. Sampling depth was 10 cm in 53% of the studies. Minimum and maximum depths to which soil was sampled were 5 cm (10%) and 40 cm (1%), respectively.

The measured data were interpolated and the time for 50% loss of the initially recovered concentration

(preferred method) or the initially applied concentration was determined. The concentration simulated by the model at this time was then taken from the graphs or obtained by interpolation of tabulated values. The graphical method is demonstrated in Fig. 1. It should be noted that measurements of pesticide residues in the

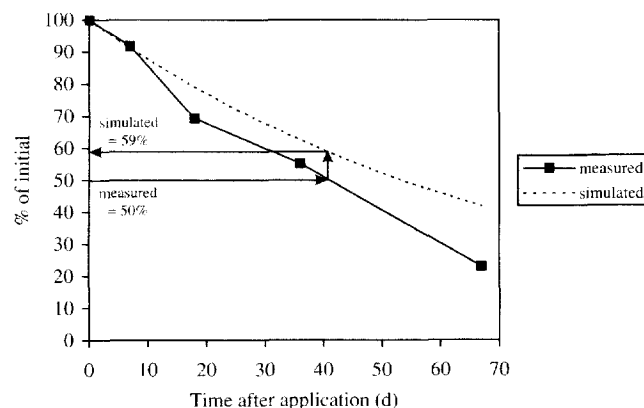


Fig. 1. Graphical method to determine the simulated percentage of the initial concentration corresponding to a measured value of 50% of the initial concentration.

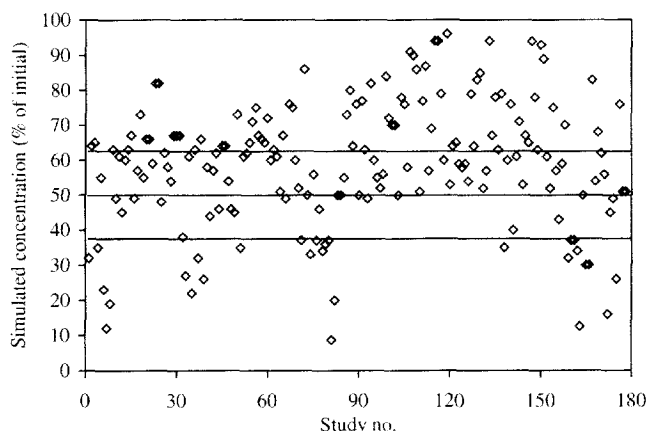


Fig. 2. Simulated pesticide concentration at the time of measurement of 50% loss in 178 published studies.

field can be subject to considerable fluctuation and that this literature study considered only a single datapoint within the experimental period.

Persistence models per se are only rarely used within the regulatory process, but their concepts form part of more complex models that describe the transport of water and pesticide through the soil profile, for example LEACHP (Hutson and Wagenet, 1992), PESTLA (van den Berg and Boesten, 1998), and MACRO (Jarvis, 1994). To reduce the complexity of the reviewing process and to facilitate the interpretation of results, only studies with the original persistence model or modified versions have been included in the quantitative evaluation. The results are nonetheless relevant to degradation subroutines of more complex models.

## RESULTS AND DISCUSSION

### Quantitative Assessment

Results of the literature review are summarized in Fig. 2 and 3. Figure 2 shows the simulated values for all 178 studies at the time when 50% loss of the pesticide was observed. Exact agreement between observed and simulated values is achieved for datapoints falling on the 50% line. Simulated values ranged from 12% to 96% of initial pesticide concentrations. The agreement between simulated percentages of the initial concentration and the target value (50%) was reasonable for a considerable number of studies. There was, however, a clear tendency to overestimate measured data. The median simulated value was 60%, which is considerably larger than the target value (50%). The tendency of the model to overestimate measured data is further illustrated in Fig. 3, which presents a frequency distribution of the factors by which simulated data differed from observed data. Of the 178 studies, 28.1% overestimated the observed value by up to a factor of 1.25. An underestimation by up to a factor of 1.25 was found in only 11.2% of the studies (Fig. 3). Simulated values overestimated those observed by more than a factor of 1.25 in 43.8% of the studies, while an underestimation by more than a factor of 1.25 occurred in only 16.9% of the studies.

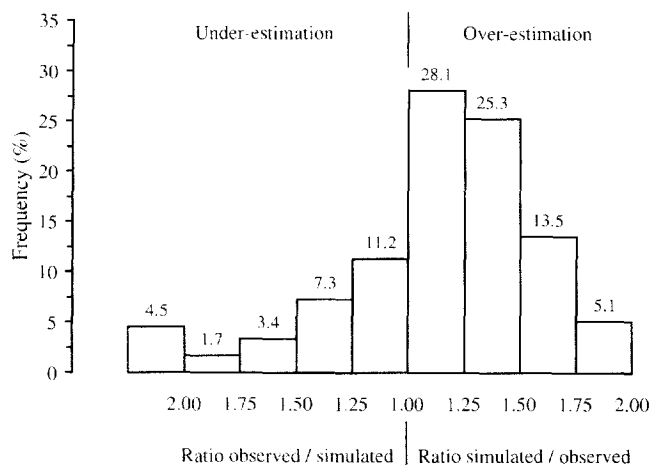


Fig. 3. Frequency distribution of factors by which simulated percentages of initial pesticide concentrations under- or overestimated those observed (=50% of initial).

The results from this review confirm the frequently stated tendency for the model to overestimate pesticide persistence in the field (Pestemer and Auspurg, 1987; Walker, 1976c, 1978; Walker et al., 1983; Walker and Zimdahl, 1981). Statistical analyses were carried out to assess whether the simulated percentage of initial pesticide concentrations was related to either soil type or organic carbon content. An analysis of variance was performed to investigate the effect of soil type on simulated values and a significant effect was found at the 5% probability level. However, the number of studies per soil class differed markedly and a large scatter of data occurred within each class (Table 2). A linear regression analysis showed that no significant relationship exists between the simulated percentage of initial pesticide concentrations and the soil organic carbon content at a probability level of 5%.

### Possible Reasons for Discrepancies Between Simulated and Observed Data

Several possible reasons for the mismatch between simulated and observed persistence of pesticides in the field can be identified:

**Losses in the Field in Addition to Degradation.** In a number of studies, a rapid decline of measured concentrations was observed early after application, whereas the persistence model predicted that little change in residues would occur. For example, this was found in six comparisons between simulated and measured residues of linuron and metolachlor (Walker and Zimdahl, 1981), in eight studies with simazine (Walker et al., 1983), in five studies with chlorotoluron (Duefer, 1991), and in 17 studies with atrazine (Rocha and Walker, 1995). The authors suggested that losses by photodegradation, volatilization, or wind erosion shortly after application when the pesticide is likely to remain at or near the soil surface could be responsible for the rapid initial decline of soil residues. Processes other than degradation that lead to the dissipation of pesticide residues in soil are not considered by the persistence models and

**Table 2. Simulated percentages of initial pesticide concentration classified by soil texture.**

Texture class†	Number of observations‡	Mean simulated % of initial concentrations§	Standard deviation
Clay loam & sandy silt loam	24	64.8 (a)	15.3
Sandy loam	101	62.1 (ab)	15.5
Sand & loamy sand	19	54.7 (ab)	19.6
Sandy clay loam & silty clay	5	53.0 (ab)	7.6
Clay	6	46.8 (b)	34.1
Silt loam & silty clay loam	17	42.0 (b)	20.0

† Soil texture is given according to the UK textural classification system (Hodgson, 1997); selected classes were aggregated because of the small number of individual observations within each class.

‡ No information on soil texture was given in six studies. These were excluded from the analysis.

§ Means with identical letters are not significantly different at the 5% probability level (Newman-Keuls test).

this may have contributed to discrepancies between simulated and measured data. However, the significance of photodegradation, volatilization, and wind erosion differs between pesticides and is difficult to quantify.

Pesticide leaching below the sampling depth also is not simulated by the persistence models. Annual losses of pesticides below the root zone may vary between 0.1 and 1% of the applied amount when there is no heavy rainfall shortly after application and can reach 5% following worst-case rainfall events (Flury, 1996). However, the sampling depth in the 178 studies evaluated was usually very shallow (0–10 cm or less in 83% of the studies) and losses below the sampling depth may have occurred for mobile pesticides. Experimental evidence is missing for most of the studies and the significance of this process for discrepancies between simulated and measured pesticide residues is difficult to assess. Walker (1976a) compared observed soil residues of simazine and prometryne with those simulated by the persistence model and did not find leaching of these herbicides out of the sampling depth (8 cm). In a further study, Walker (1978) carried out 17 comparisons between simulated and observed residues of eight herbicides and found a better fit of the persistence model for less mobile compounds (trifluralin, chlorthal-dimethyl, linuron, and metamitron) than with the more mobile compounds (simazine, atrazine, and propyzamide). The least satisfactory fit was obtained with the most mobile compound (metribuzin) and the author suggested that a significant proportion of the amount applied may have leached out of the sampling depth (8 cm). Kookana et al. (1995) investigated the distribution of soil residues of nine pesticides within the profile of a sandy soil for 5 mo. Mean leaching depths increased in the order chlorthal-dimethyl (<5 cm) < linuron and simazine (6 cm) < propyzamide (8 cm) < prometryne (9 cm) < metribuzin (12 cm). Harris et al. (1994) measured soil residues of isoproturon in a clay soil. The mass of isoproturon found below 10-cm depth accounted for approximately 7% of the total mass (28 d after application).

**Discrepancies Between Laboratory and Field Conditions.** One of the main model assumptions is that the ability of a soil to degrade a pesticide under natural conditions in the field can be characterized by laboratory half-lives. A further possible reason for discrepancies between measured and simulated values is that this assumption is not valid.

Soils are often subjected to a number of preparation procedures before being used for laboratory degrada-

tion experiments (e.g., sieving, mixing, drying, and re-moistening). These may have strong effects on soil biological, physical, and even chemical conditions, which then markedly differ from those in undisturbed soils in the field. Walker and Brown (1981) investigated the degradation of metamitron, atrazine, and propyzamide after storage of soils for 7 mo either at 5°C, frozen, or sieved and air-dried in comparison with fresh soil. They found considerable differences in degradation rates between the pretreatments and between stored and fresh soil for metamitron and atrazine. Degradation rates of propyzamide were significantly reduced in soil stored air-dry only. Further examples of such effects have been reviewed by Guth (1980).

Laboratory degradation studies generally investigate pesticide persistence under static conditions. Degradation in such systems may differ from that under dynamic flowing conditions in the field (Guo and Wagenet, 1999).

Pesticide application in the field often occurs while soils are cropped, although this has not always been the case in the experiments used for evaluating model performance. The plant rhizosphere may enhance the degradation of xenobiotics (Crowley et al., 1997). For example, root exudates can provide a food supply for soil microorganisms involved in pesticide degradation. In contrast, no readily available substrate is added to soils used for laboratory experiments. Microbial biomass, therefore, often declines during soil incubation over an extended period in the laboratory. This may result in a decrease in pesticide degradation rates over time and in an overestimation of first-order half-lives (Anderson, 1987; Beulke, 1998).

In the laboratory, soils are exposed to a set of constant temperature and moisture conditions. The derived parameters describing temperature and moisture dependence of degradation are used to predict degradation rates in the field. During the course of outdoor experiments, however, temperature and moisture are fluctuating during relatively short intervals and this can alter the effect of these variables on pesticide degradation. Faster degradation of atrazine was found under fluctuating moisture conditions than was expected from degradation rates at constant soil water contents (Hurle, 1982). A comparison of the degradation of metamitron at a constant temperature (22°C) with its degradation under temperatures fluctuating daily between 10 and 20°C revealed a 2.5-fold increase of degradation under varying conditions (Kubiak, 1986). In a further study (Jurado-Exposito and Walker, 1998), degradation under

fluctuating temperature and/or moisture conditions agreed relatively well with data derived from under constant conditions for isoproturon and alachlor, but was different for propyzamide.

The relationship between degradation rates and soil moisture is based on water contents rather than water tensions. However, an identical amount of water is held at different tensions in a sieved, thoroughly mixed soil sample in the laboratory or under undisturbed conditions in the field. Since water tension seems to be more relevant for the degrading activity of soil microflora than water content, the relationships derived in the laboratory may not be directly transferable to the field.

**Deviations from First-Order Kinetics.** Deviations from first-order kinetics in laboratory studies may introduce considerable uncertainty in the estimated half-lives and degradation parameters, which may in turn result in discrepancies between predicted and observed dissipation of pesticides in the field. The 178 comparisons between measured and simulated soil residues evaluated in this review included those by Walker (1976a) for simazine (six comparisons) and prometryne (three comparisons). Degradation of both herbicides in the laboratory was influenced by the initial pesticide concentration, which suggests that a linear degradation model is not applicable. Deviations of degradation from first-order kinetics were also found in some, but not all, of the 21 laboratory studies with simazine carried out by Walker et al. (1983). The authors pointed out that the deviation of degradation from first-order kinetics is a possible reason for mismatches between simulated and measured pesticide residues (Walker, 1976a; Walker et al., 1983). In most of the remaining studies included in this review, degradation in the laboratory was described relatively well by first-order kinetics, although the dependence of degradation on initial pesticide concentrations was usually not investigated (Auspurg, 1986; Rocha and Walker, 1995; Walker, 1976b,c, 1978).

**Discrepancies Between Temperature Regimes in Laboratory Studies and in the Field.** A marked underestimation of pesticide residues was found following application of pendimethalin (Gottesbüren, 1991; two studies), methabenzthiazuron (Gottesbüren, 1991; one study), isoproturon (Berger, 1989; two studies), and ethofumesate (Heiermann, 1998; one study) in autumn or winter. Parameters describing the temperature dependence of degradation are usually derived from degradation studies within a temperature range from 5 or 10°C up to 30°C. The inclusion of data determined at high soil temperatures is justified if persistence is to be simulated over spring and summer. However, those same parameters may not be appropriate to characterize the effect on degradation of the low temperatures during autumn and winter (Gottesbüren, 1991; Heiermann, 1998).

**Discrepancies Between Simulated and Actual Soil Temperature and Moisture.** A further possible reason for discrepancies between simulated and observed data is a mismatch between predicted and actual soil temperature and moisture conditions. Walker (1973) validated his method for deriving soil temperatures from measure-

ments at 10-cm depth and for calculating moisture from rainfall and potential evapotranspiration. He found practically no difference between pesticide residues simulated on the basis of estimated temperatures and moistures and those derived from detailed measurements. Calculated and observed soil moisture contents were also shown to match well in a subsequent publication (Walker, 1974). Walker and Barnes (1981) again found good agreement between measured soil temperatures or moisture contents and those simulated by their revised version of the model using air temperatures and rainfall as input variables. However, soil temperatures were overestimated in winter and underestimated in spring and early summer in work by Gottesbüren (1991). He stated that this may have contributed to the observed underestimation of persistence after autumn application of pendimethalin in two studies and of methabenzthiazuron in one study.

**Lack of Soil-Specific Degradation Parameters.** Results from modeling of pesticide residues in soil are not only influenced by the degradation half-life selected. They also depend on the parameters describing the temperature and moisture dependence of these half-lives ( $E_a$ ,  $B$ ). This was demonstrated through sensitivity analyses for modified versions of the model developed by Walker and coworkers (Beulke, 1998; Bunte, 1991; Gottesbüren, 1991; Heiermann, 1998). In most of the studies evaluated, these parameters were derived from laboratory experiments using the soil on which the field study was carried out (93%). However, these parameters remain uncertain. Replicate experiments can result in different  $E_a$  and  $B$  values (Gottesbüren, 1991). In addition, the range of temperature and moisture conditions considered has a marked influence on the estimated parameters, causing differences in the simulated losses of pesticide in the field (Beulke, 1998; Heiermann, 1998). Regulatory studies often fail to provide sufficient experimental information to determine soil-specific parameters and default values supplied with persistence or pesticide leaching models are used instead. This introduces further uncertainties into the results of pesticide fate modeling.

**Variability of Half-Lives.** An additional issue in the use of laboratory data to simulate pesticide behavior in the field is the large variability in laboratory half-lives from experiments with soil taken from different points within the same field or taken at different times during the year. Walker and Brown (1983b) investigated the degradation of two herbicides in the laboratory using soil sampled from 10 subplots of an area of 80 × 80 m. Half-lives of metribuzin and simazine ranged from 25 to 48 d and from 25 to 30 d, respectively. The coefficient of variation in laboratory half-lives in 20 soil samples from an area of 6 × 1.5 m was 25% for metribuzin and 23% for simazine. Samples taken from a single field plot at monthly intervals between May and September showed a considerable variability of laboratory half-lives for metribuzin (coefficient of variation = 23%), but not for simazine (coefficient of variation = 2%). The small-scale spatial variability of pesticide persistence was also demonstrated in several field studies.

Coefficients of variation of DT50 values (time for dissipation of 50% of the initial concentration) for chloridazon and metamitron within three fields were found to range from 11.1 to 110% (Vischetti et al., 1997). In a further study, DT50 values of isoproturon in 25 subplots of one field ranged from 31 to 483 d (Beck et al., 1996).

Within each of the 178 studies reviewed in this investigation, pesticide persistence was simulated in a deterministic way. Each simulation consisted of a single model run using only one DT50 value as an input parameter. The spatial or temporal variability of degradation in the field was thus not taken into account.

### Implications for Modeling

Discrepancies between measured pesticide residues in the upper soil layer and those simulated by persistence models are not attributable to errors in half-lives alone. However, this parameter is of major importance. Simulated leaching of mobile compounds to depth is generally very sensitive to chemical half-life (Boesten, 1991; Leonard et al., 1987; Soutter and Musy, 1999; Tiktak et al., 1994) and the estimation of values that are likely to reflect the field situation as closely as possible is fundamental. To improve the relevance of laboratory data, modifications in experimental procedures are desirable. These include the investigation of pesticide degradation under flowing conditions and the incubation of soil samples at fluctuating soil temperature and moisture conditions. Also, soil temperatures in any laboratory study should not significantly exceed the range of temperatures expected in the field. The biological activity of the soil samples should be verified throughout the experiment wherever possible.

Several processes such as volatilization, photolysis, uptake by plants, or leaching below sampling depth jointly contribute to pesticide loss in the field. The persistence models evaluated in this study did not differentiate between these processes. In contrast, more complex pesticide simulation models often calculate some or all of these processes separately. This has effects on the parameters used as input for the degradation subroutine. All processes that are explicitly simulated must be excluded and the remaining aspects should be aggregated into a *lumped* dissipation parameter. However, these lumped parameters cannot be derived from laboratory studies where degradation is the major process causing a decrease in pesticide concentrations. The use of information from field persistence studies may be an alternative. Often, the time-course of pesticide residues in the field can be approximated by first-order kinetics. The resulting DT50 value reflects the time to 50% loss of the pesticide due to a number of dissipation processes. A clear advantage of field DT50 values over laboratory half-lives is that they are determined under conditions specific for the field (undisturbed soils, cropped soils, fluctuating temperature and moisture conditions) and thus closely match the situation that is to be modeled. They integrate all individual dissipation processes in a single parameter. Consequently, subroutines other than degradation that allow the separate

simulation of individual dissipation processes (e.g., volatilization) must be switched off if field DT50 values are used for modeling. Field DT50 values reflect the variation in degradation over the course of the field study due to fluctuations in soil temperature and moisture. If these values are used for modeling, the subroutines describing temperature and moisture dependence of degradation must be switched off. This means that the influence of actual temperature and moisture conditions on degradation cannot be considered, making the transfer of field half-lives determined within one climatic region to another difficult. An additional approach is the determination of degradation parameters via inverse modeling. This technique can be used to derive those parameter values that give the best fit between outputs of a pesticide persistence or leaching model and experimental data obtained under outdoor conditions (e.g., soil residues, concentrations in leachate from a lysimeter). Tools are available to repeatedly run the model, compare the output with experimental data, and modify input parameters until the fit between simulated and observed data meets preselected criteria (Doherty et al., 1994). Best-fit DT50 values derived by inverse modeling reflect not only degradation, but also pesticide losses through all processes that are not explicitly considered in the model used (e.g., volatilization). The parameter provided is corrected for effects of fluctuations in temperature and moisture conditions and corresponds to reference conditions set within the model. The DT50 values determined by inverse modeling can thus be used for simulations under different climatic conditions.

Inverse modeling is frequently used within hydrological modeling to estimate input parameters that are uncertain and/or difficult to derive from direct measurements (Poeter and Hill, 1997; Samper-Calvete and Garcia-Vera, 1998). In contrast, this technology has only occasionally been applied to pesticide fate modeling (Gottesbüren, 1991, 1998). These studies concluded that inverse modeling is a promising approach to derive degradation parameters more relevant to the field situation, but further investigation into its advantages and pitfalls as well as the development of standard protocols and guidance to the user are desirable. Inverse modeling should not be considered as an alternative to experimental laboratory and field studies, but as a complimentary approach. The analysis of the combined results is likely to provide valuable information that could not be obtained if inverse modeling or experimental studies were used on their own.

### CONCLUSIONS

A correct characterization of pesticide degradation in simulation models is fundamental for regulatory risk assessments of leaching to ground and surface water. Several current models are based on the concepts developed by Walker and coworkers. An evaluation of these concepts revealed that there is an overall tendency to overestimate pesticide residues in the field. This may lead to an overestimation of predicted concentrations



in ground or surface waters. Discrepancies between simulated and observed pesticide residues can be partly attributed to the use of degradation parameters derived in the laboratory for prediction of pesticide persistence in the field. Laboratory parameters may mismatch degradation under outdoor conditions as a result of the preparation of soil samples prior to their use in the laboratory (e.g., drying and sieving) and incubation of uncropped soil under static conditions at constant temperature and moisture. Although additional possible reasons for the discrepancy between simulated and observed persistence in the field have been identified, the determination of degradation rates more relevant to the field situation appears desirable.

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