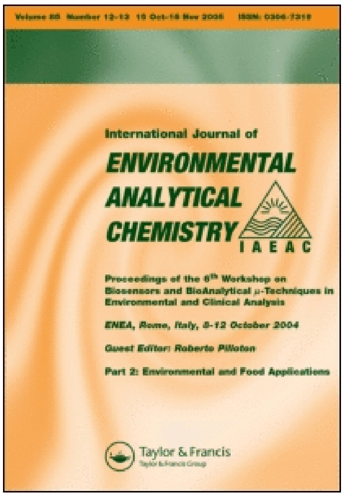

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SIMULATION AND PREDICTION OF DISSIPATION KINETICS OF TWO HERBICIDES IN DIFFERENT PEDO-CLIMATIC SITUATIONS

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Simulations of dissipation kinetics of atrazine and sulcotrione in the 0–10 cm soil layer are obtained with three different numerical models: VARLEACH, PRZM and LEACHP. These simulations are compared to observed residual extractable amounts of herbicide at several times. Observations were done during two years in three different pedo-climatic situations: in the Paris Bassin at Grignon, in the polder of the Mont-Saint-Michel Bay (Brittany) and in the south of France at Roujan (Herault). Comparisons were done taking into account the uncertainties associated with both simulations and observations. They show that the quality of simulations is greatly dependent on the soil, the climate, the year of observation and on the model used. Limits for prediction of herbicide dissipation kinetics in the surface soil layer are discussed.

Keywords: Herbicides; dissipation kinetics; modelling

INTRODUCTION

It is now well recognize that there is an increasing concern for the impact of pesticides on the environment, particularly on water quality. For both management and regulatory purposes, and thus to deal with a sustainable agriculture, it may be useful to predict the fate of pesticides. To this end, there is a growing use of numerical models. Although modelling the fate of pesticides in soil and water has been studied during the last twenty years and has lead to a great number of papers,[1–3] several important questions about model parameters and model performances remain without clear answers. Some of these questions are considered in this paper and some elements of answer are proposed and dis-

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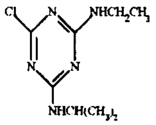
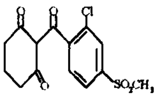
TABLE I Main molecular properties of herbicides.

	Formula	Molecular Mass g mol^{-1}	Water Solubility mg L^{-1}	Vapor Pressure Pa	Data from
ATRAZINE		215.7	33 (20°C)	$4\ 10^{-5}$ (20°C)	Wauchope ct al [9]
SULCOTRIONE		328.8	165 (25°C)	$5.3\ 10^{-6}$ (25°C)	ZENECA [5]

cussed. Accordingly, the aims of this paper are i) to compare observed and simulated dissipation kinetics of two herbicides, using three different global models; ii) to show the possible influence of soil and climate characteristics on the simulation of dissipation kinetics; iii) to suggest a procedure for using simulated kinetics in a prediction process and iv) to discuss some limits encountered when using models for predicting the fate of soil applied herbicides.

MATERIALS AND METHODS

Herbicides and Experimental Data

All experimental data and procedures are fully described elsewhere by Baer.[4] So, only the main information will be given below.

Two herbicides generally used on maize crop were studied: atrazine (6 chloro-2 ethylamino-4 isopropylamino 1,3,5 triazine) and sulcotrione (2-(2 chloro-4 mesylbenzoyl)cyclohexane-1,3-dione). If the first herbicide is used for a long time and well known, the second is a rather new compound from ZENECA,[5] sold in France since 1993. Their main physico-chemical characteristics are given in Table I. Experimental dissipation kinetics in the 0–10 cm soil layer were determined from field plots. For atrazine, dissipation and transport was simultaneously studied with transport of bromide ion using micro-lysimeters which were installed before herbicide application. At given times, two micro-lysimeters were removed, the soil column cut into slices of 5 cm thick and stocked at −20°C before extraction (methanol) and residue analysis (GPC). For sulcotrione, 6 soil samples were taken in the 0–10 cm layer, were extracted by methanol

TABLE II Soil characteristics

Site Soil Type	*Profile depth cm*	*Horizon n° (thickness) cm*	*Granulometric Composition g/100g*			*Organic Carbon g/100g*
			clay	*silt*	*sand*	
Grignon *Orthic Luvisol*	90	1 (30)	22	73	5	1.13
		2 (30)	23	70.5	6.5	0.59
		3 (30)	27	77.2	0.8	0.35
Mont St. Michel *Gleyo-Calcaric-Fluvisol*	150	1 (35)	15.8	69.1	15.1	1.32
		2 (115)	5.1	43.6	51.3	0.55
Roujan *Calcaric Cambisol*	90	1 (90)	19.8	53.4	26.8	0.63

and then analyzed for residues (HPLC).[4] Only, dissipation data in the 0–10 cm layer will be presented and discussed in this paper. Physical soil parameters, sorption coefficients and degradation rates were determined in the laboratory by classical methods.[4]

Experimental Sites

The study has been conducted at three experimental sites characterized by different soils and climates. The first site is localized at Thiverval-Grignon in the Bassin Parisien and the experimental plot was situated in a field cropped with maize since three years. The second site is in the polders of the Mont-Saint Michel Bay in Brittany and the experimental plot was situated in a field cropped with maize for only one year. There is a water table at about 1.5m depth. The third site is in the south of France near the town of Beziers and the experimental plot was in a vineyard the slope of which varies between 6 and 15%. Main soil characteristics are given in Table II. Table III shows some climatic data given as sums over 100 days from the application date of the herbicide which is different for atrazine and sulcotrione. This period was chosen for characterizing the climates at the different sites because it corresponds generally to the dissipation of more than 95% of the applied herbicide.

Numerical Models

Numerous models have been described and several reviews have been published on the subject.[1,2,3] However, some models are more interesting than others because either they are widely used or they give more or less complete descrip-

TABLE III Meteorological condition at the different sites. The sums are calculated for 100 days periods after herbicide application.

Herbicide	*Site* *year*	*Date**	$\Sigma Tmax$	$\Sigma Tmin$	ΣP *mm*	ΣPET *mm*	$\Sigma (P-PET)$ *mm*
Atrazine	Grignon		—	—	—	—	
	1993	22-04	2051	1108	196	365	−168.4
	1994	03-05	2352	1226	190.5	444.5	−254
	Mont-St. Michel						
	1993	05-05	2005	1061	213	291	−78
	1994	19-05	2242	1186	219.5	338.6	−119.1
	Roujan						
	1993	29-04	2587	1390	82	471.3	−390.3
	1994	09-05	2856	1525	69	506.5	−437.5
Sulcotrione	Grignon						
	1994	31-05	2440	1310	168	404.1	−236.1
	Mont-St. Michel						
	1994	09-06	2270	1209	258	318.9	−60.9

Tmax and Tmin: maximum and minimum air temperature
P: precipitation (rain only for sites under study)
PET: potential soil evaporation and transpiration
*: application date

tion of the fate of pesticides in the soil. Accordingly, we have chosen to report results obtained with three global models: VARLEACH,[6] PRZM2[7] and LEACHM3.1[8](LEACHP is the version for pesticides). These models simulate the global variation of pesticide concentration in the soil as function of depth and time. They include all phenomena leading to the dissipation of pesticides and allow to obtain both dissipation kinetics in given soil layers and distribution of pesticides in the soil profile. Detailed descriptions are given in author's papers but it is worth emphasizing four points:

- according to the number of input parameters, the order of model increasing complexity is VARLEACH < PRZM < LEACHP. This order is also that of increasing difficulty to feed the models with numerical values.
- water transfer is described with the Richards equation in LEACHP, while it is simply described on a capacity model basis in VARLEACH and PRZM.
- in VARLEACH and in LEACHP, the degradation rate is allowed to vary with the soil water content and the soil temperature; it is constant in PRZM. In the three models, degradation is described as a global first order kinetic.
- adsorption is described as a linear, instantaneous and reversible phenomenon in the three models.

Soil physical parameters used for simulation are given in Table IV. For LEACHP, diffusion and hydrodynamic dispersion coefficients were not measured and recommanded values by authors were used. Adsorption coefficients

TABLE IV Measured physical parameter values used for simulations

Site *Soil Type*	*Profile depth cm*	*Horizon n°*	*Bulk density kg/L*	*Volumetric water content at*			*Ksat* mm d^{-1}*
				−5 kPa	*−200 kPa*	*−1500 kPa*	
Grignon *Orthic Luvisol*	90	1	1.3	0.387	0.208	0.163	1200
		2	1.5	0.387		0.163	
		3	1.5	0.387		0.163	
Mont St. Michel *Gleyo-Calcaric-Fluvisol*	150	1	1.3	0.384	0.28	0.096	960
		2	1.5	0.384		0.096	
Roujan *Calcaric Cambisol*	90	1	1.25	0.45	0.23	0.149	2200

*Ksat: hydraulic conductivity of water saturated soil

(Kd) were determined for each soil-herbicide couple using a batch equilibrium method[4] and experimental values used for simulation are given in Table V. Degradation rates were determined also for each soil-herbicide couple at two temperatures (15 and 28°C) and two soil water contents (50 and 90% field water capacity).[4] Half-life values ($t_{1/2}$) were deduced from first order rate constants and their relations to soil water content and temperature were determined.

- For VARLEACH, these relations are described by Walker and Arrhenius formulae respectively:

$$t_{1/2} = A\omega^{-B} \text{ and } t_{1/2} = t_0 e^{\frac{Ea}{RT}}$$

where A, B and t_0 are three constants which are determined experimentally, ω is the gravimetric water content, Ea is the activation energy of degradation processes. R and T have their usual meaning.

- For LEACHP, influences of soil water content and temperature are described in a different way. Soil water content is accounted for by assuming that degradation rates are multiplied by a correction factor which first increases from zero (at a matric potential of −3000 kPa) to a value of one for an optimal matric potential zone values (between −300 kPa and a potential corresponding to an air filled porous volume of 8%) and then decreases to

TABLE V Measured values of adsorption coefficients Kd ($Kd_{mean} \pm \sigma$).

Site	*Atrazine*	*Sulcotrione*
Grignon	0.73 ± 0.08	0.28 ± 0.05
Mont St.-Michel	0.69 ± 0.07	0.23 ± 0.05
Roujan	0.75 ± 0.08	

σ: standard deviation from the experimental procedure

TABLE VI Degradation characteristics used for simulations. PRZM: mean degradation rates over the dissipation kinetic period. VARLEACH and LEACHP: values of degradation parameters determined experimentally.

Herbicide	*Site*	*PRZM*		*VARLEACH* $t_{1/2} = A \cdot \omega^{-B}$			*LEACHP*	
		Year	*mean k* d^{-1}	*A* *d*	*B*	*Ea* *kJ/mol*	*Q10*	*k(15°C)* d^{-1}
Atrazine	Grignon							
		1993	0.0462	53	0.71	44700	2	0.0433
		1994	0.0495					
	Mont-St. Michel							
		1993	0.0365	136	0.92	46750	1.95	0.0315
		1994	0.0462					
	Roujan							
		1993	0.0133	4552	2.29	94200	4	0.0182
		1994	0.0129					
Sulcotrione	Grignon							
		1994	0.1733	24	0.94	50950	2.2	0.154
	Mont-St. Michel							
		1994	0.139	272	1.67	51000	2.2	0.116

0.6 at saturation. Influence of soil temperature is described with a Q10 coefficient applied to a degradation rate value corresponding to a reference temperature (taken here as 15°C).

- For PRZM, degradation rates are not allowed to depend on the soil water content and temperature so that the difficulty is to use relevant values for the entire period under study. We have chosen to use a "mean" value calculated with the Walker and Arrhenius formulae using the mean soil water content and the mean soil temperature determined over the period of time corresponding to the dissipation kinetics. This was done for each soil/year/herbicide situation. Values of degradation parameters for the three models are given in Table VI.

The variation of sorption coefficient and degradation rates with depth was not measured. It was described on the basis of their dependence on the soil organic carbon content and the following relationships were used.

- Since for most pesticides the soil organic matter play the main part in sorption processes, it was assumed that sorption coefficients are approximatively proportional to the organic carbon content.[10]
- There are few published data on the variation of degradation rates with depth and no general relation was yet proposed. Then, considering that degradation in the soil is essentially due to microflora activity, it was as-

sumed that degradation rates were proportional to the soil organic matter content as proposed by Jury.[11]

Models were run taking dissipation kinetics in the 0–10 cm layer as output. All simulation were obtained for one year from the date of herbicide application. They were obtained on cropped soils with herbicides applied on the soil surface without incorporation. At Grignon and Roujan, bottom boundary conditions for water and solute transport were those of a free draining profile for the three models while at Mont Saint-Michel for LEACHP, it corresponded to a fixed water table at 1.5 m depth.

RESULTS AND DISCUSSION

The Shape of Simulated Dissipation Kinetics

Mean simulations were obtained with mean values of adsorption coefficients (Table V), of degradation rates for PRZM and of degradation parameters for VARLEACH and LEACHP (Table VI). No numerical fitting was done, only measured or recommended values were used as previously mentioned. It should be emphasized that, beside the fact that numerical fitting would be difficult or impossible because the great number of parameter values to calculate, it does not correspond to our objective. As a matter of fact, what we want to assess is the ability of some models to simulate dissipation kinetics using parameter values which can be routinely measured or estimated. Figures 1 and 2 represent the simulated mean kinetics; residual amounts of herbicide are expressed as percentages of applied amounts.

Visual examination of Figures 1 and 2 shows that dissipation kinetics of atrazine at Roujan (except, perhaps, for VARLEACH in 1993) and at Grignon in 1994 cannot be simulated by the three models. Similarly, this is the case at Mont-Saint Michel for sulcotrione. So, it is possible to distinguish two sets of situations. The first set corresponding to situations for which the three models are not able to describe the general shape of dissipation kinetics: Atrazine/Grignon/1994, atrazine/Roujan/1993 and 1994, sulcotrione/Mont-Saint Michel/1994. The second set is constituted by the other four situations for which the three models describe the dissipation kinetics more or less correctly. A more detailed analysis of these situations can be done tentatively, using statistical indices.[12,13] Three statistical indices were used:

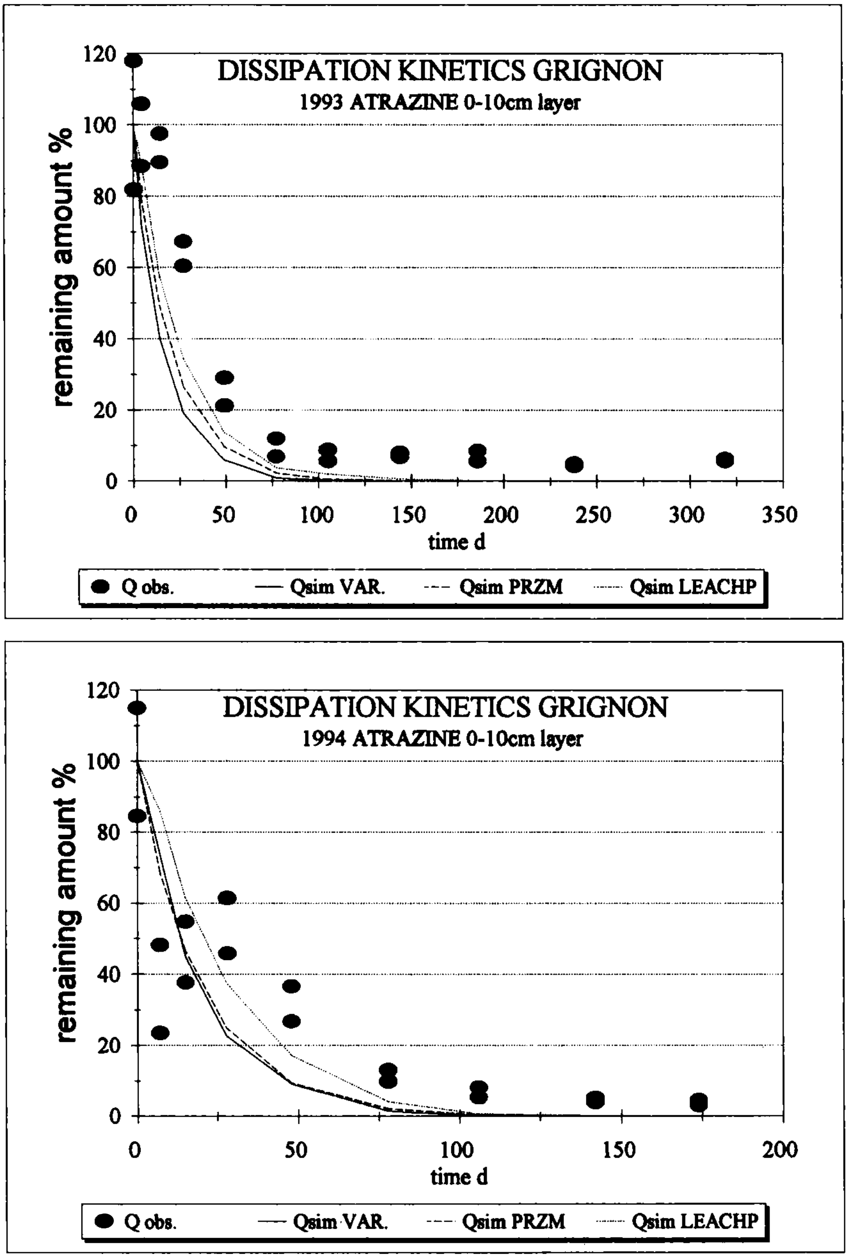
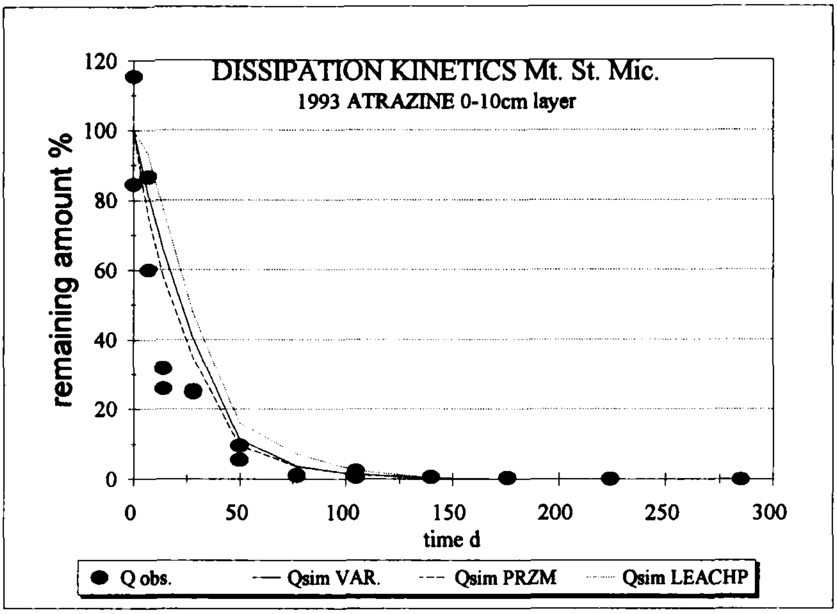


FIGURE 1 (a & b) Dissipation kinetics for atrazine



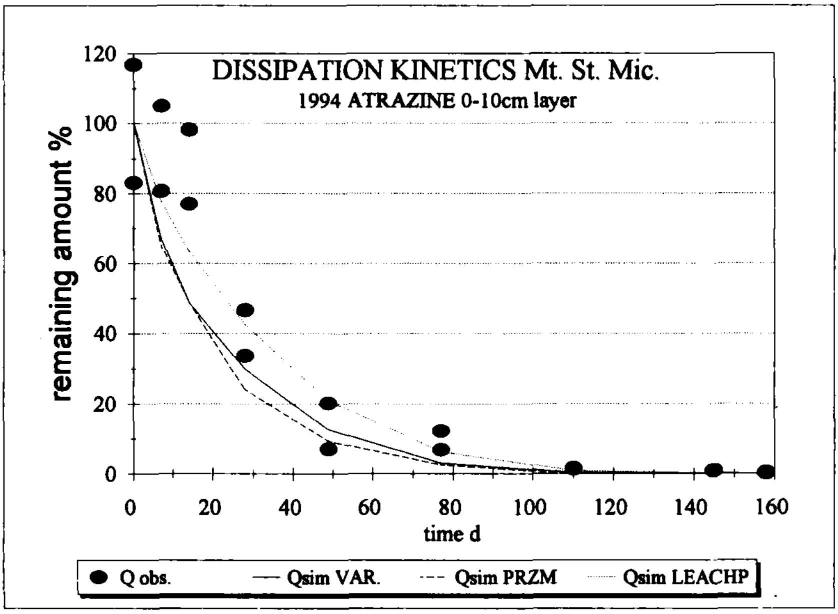


FIGURE 1 (c & d) Dissipation kinetics for atrazine

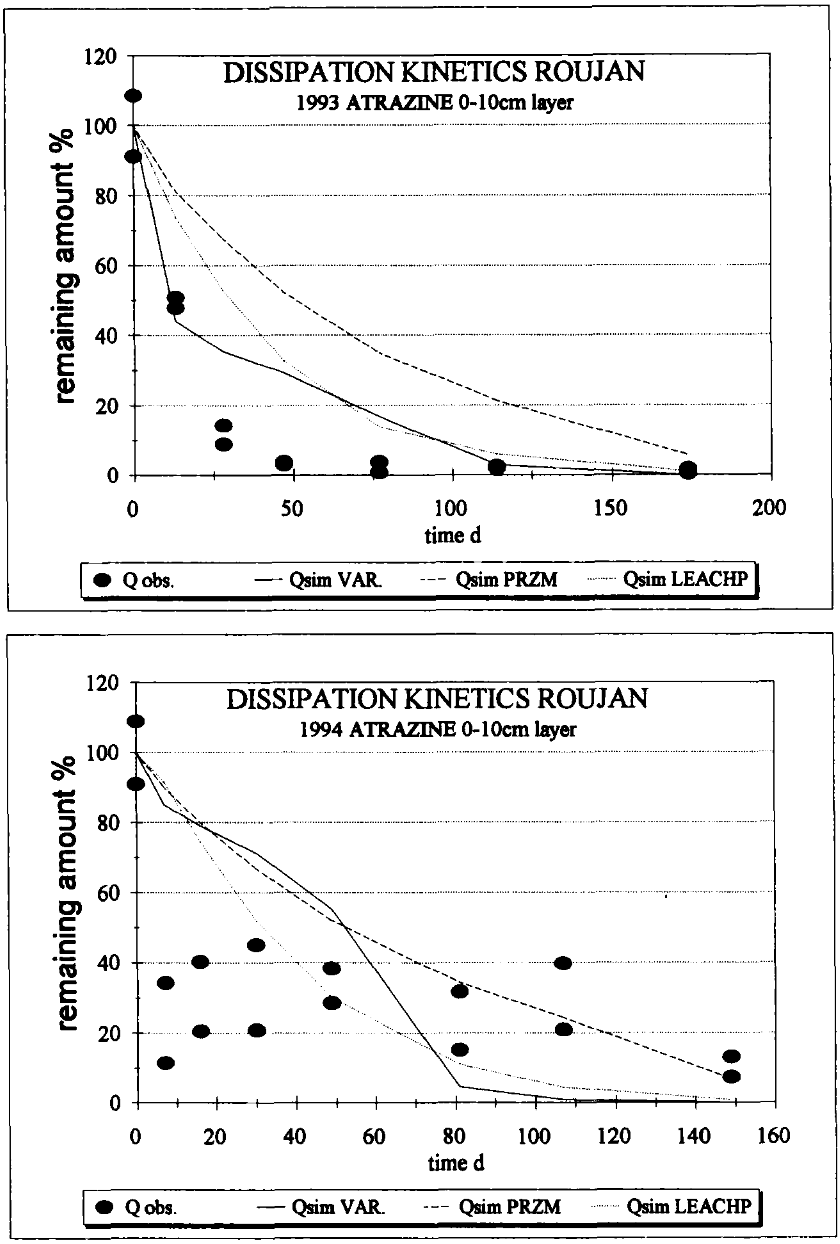


FIGURE 1 (e & f) Dissipation kinetics for atrazine

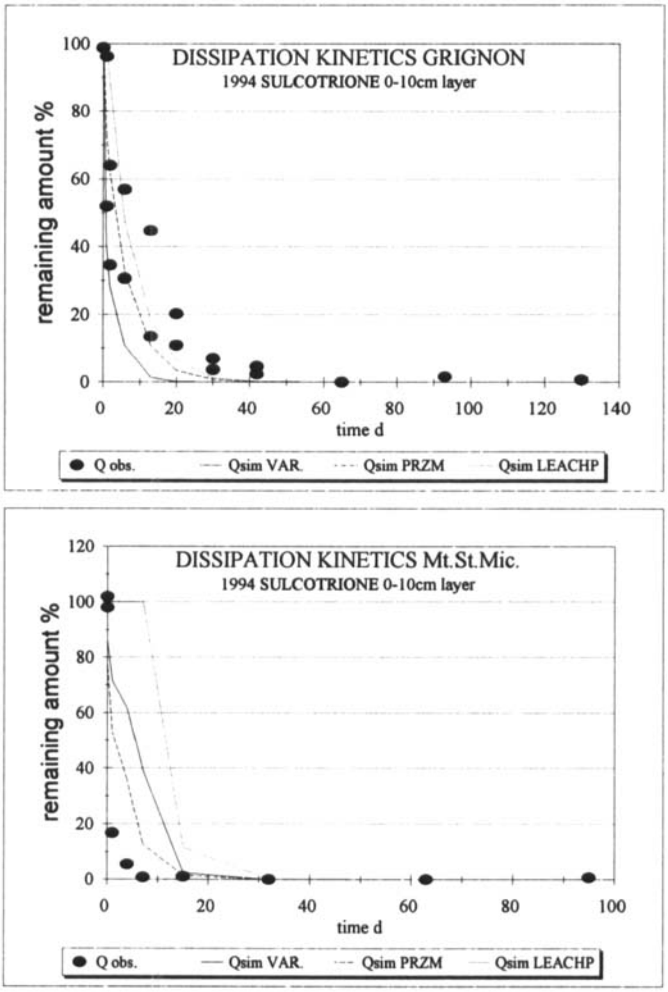


FIGURE 2 Dissipation kinetics for sulcotrione

- the scaled total error: $$TE = \frac{\sum_{i=1}^{N} \|Pi - Oi\|}{\sum_{i=1}^{N} Oi}$$

- the scaled root mean squared error: $$SRMSE = \frac{1}{\bar{O}} \sqrt{\frac{\sum_{i=1}^{N} (Pi - Oi)^2}{N}}$$

and the model efficiency: $$ME = \frac{\sum_{i=1}^{N} (Oi - \bar{O})^2 - \sum_{i=1}^{N} (Pi - Oi)^2}{\sum_{i=1}^{N} (Oi - \bar{O})^2}$$

where Pi and Oi are the simulated (predicted) and observed values, $\bar{O}$ is the mean of observed values and N is the number of observed data.

Calculated values of these three indices are given in Table VII. TE represents the total discrepancy between simulated and observed values. SRMSE is a measure of the spread around the ideal case corresponding to $Pi = Oi, \forall i$. The smaller TE and SMRSE are, the better is the simulation. ME can vary from 1 to $-\infty$. The ideal case is $ME = 1$ which corresponds to $Pi = Oi, \forall i$. It is admitted that when $ME < 0$, the simulation is unacceptably poor.[13]

Figures 1 and 2 together with indexe values (Table VII) lead to the following comments.

-1-Concerning the herbicide/site couple:

- for atrazine at Grignon, the kinetic is better simulated in 1993 than in 1994
- for atrazine at Mont-Saint Michel, the kinetic is better simulated in 1994 than in 1993
- for sulcotrione in 1994, the kinetic is better simulated at Grignon than at Mont-Saint Michel.

-2-Concerning the performance of models

From index values reported in Table VII, it can be said that the quality of simulations is generally not very high. In spite of this, these values allow to rank the models according to their performances which appear to depend on the type of index, on the type of model, on the site and on the herbicide. Frequences of the model's position in the first, second or third place as indicated in Table VIII suggest, at least for the studied situations, that VARLEACH would be the worst model and that PRZM would be the less bad but better than LEACHP. In other words, the following order of decreasing performance may be proposed:

$$\text{PRZM} > \text{LEACHP} > \text{VARLEACH}$$

It is important to note that this kind of discussion should be taken with caution; it cannot be generalized because only three sites and two herbicides have been studied.

TABLE VII Values of statistical indexes

Herbicide	*Site*	*TE*			*SRMSE*			*ME*		
		VARLEACH	*PRZM*	*LEACHP*	*VARLEACH*	*PRZM*	*LEACHP*	*VARLEACH*	*PRZM*	*LEACHP*
Atrazine	Grignon									
	1993	0.57	0.48	0.55	0.78	0.65	0.51	0.51	0.67	0.79
	Mt.St.M									
	1993	0.53	0.43	0.77	0.99	0.78	1.35	0.64	0.77	0.31
	1994	0.37	0.40	0.24	0.59	0.62	0.40	0.75	0.73	0.89
Sulcotrione	Grignon									
	1994	0.62	0.26	0.41	0.85	0.34	0.71	0.45	0.91	0.62

TABLE VIII Number of observed rank 1, 2 and 3 for the three indexes.

Model	*Rank 1*	*Rank 2*	*Rank 3*
PRZM	7	2	3
LEACHP	5	4	3
VARLEACH	0	6	6

It remains now to explain why the shape of dissipation kinetics can be simulated in some situations and not in others. Soil properties do not allow any explanation to be proposed. On the contrary, since degradation and transfers depend on the soil water content and temperature, climatic characteristics must be examined. However, those given in Table III do not lead to any particular explanation, probably because they are too global. To have a more detailed analysis, meteorological data were examined on a decade basis and have shown that only the sum of the difference between precipitation and potential evaporation and transpiration (P-PET) could be interesting (Figure 3). From Figures 1, 2 and 3, it appears that models simulate correctly the shape of dissipation kinetics when this difference is positive or slightly negative during the two first decades approximately, as it is the case for atrazine at Grignon 1993 and Mont-Saint Michel 1994, and for sulcotrione at Grignon 1994. The importance of the first twenty days is understandable because about 80% of the applied herbicides are dissipated during this period. This would mean that simulation may be only possible when the soil does not dry or dry slightly. The explanation could probably be found in the ability of models to describe the degradation rate/soil water content relationship. The reason could be a bad simulation of water transfer and/or the inability of models to take into account the modification of microflora activity when the soil dries too much. As a matter of fact, simulations for conditions such as those of Roujan (south part of France) are not possible. It is also worth noting that observed data are the extractable amounts of herbicide with methanol under given experimental conditions.[4] These amounts may not be the proper values for comparison with simulated results since simulation by numerical models implies that total amounts of residual herbicide are completely extractable, which is known to be unfrequent.

How Simulations Could be Used for Predicting Dissipation Kinetics?

The preceeding discussion has shown that the shape of dissipation kinetics can be simulated in some circumstances. Now, the following question rises: how simulations can be used for predicting purposes? It is important to emphasize that we never discuss fitted curves since all simulations are obtained from measured pesticide parameters and from measured and estimated soil parameters. This

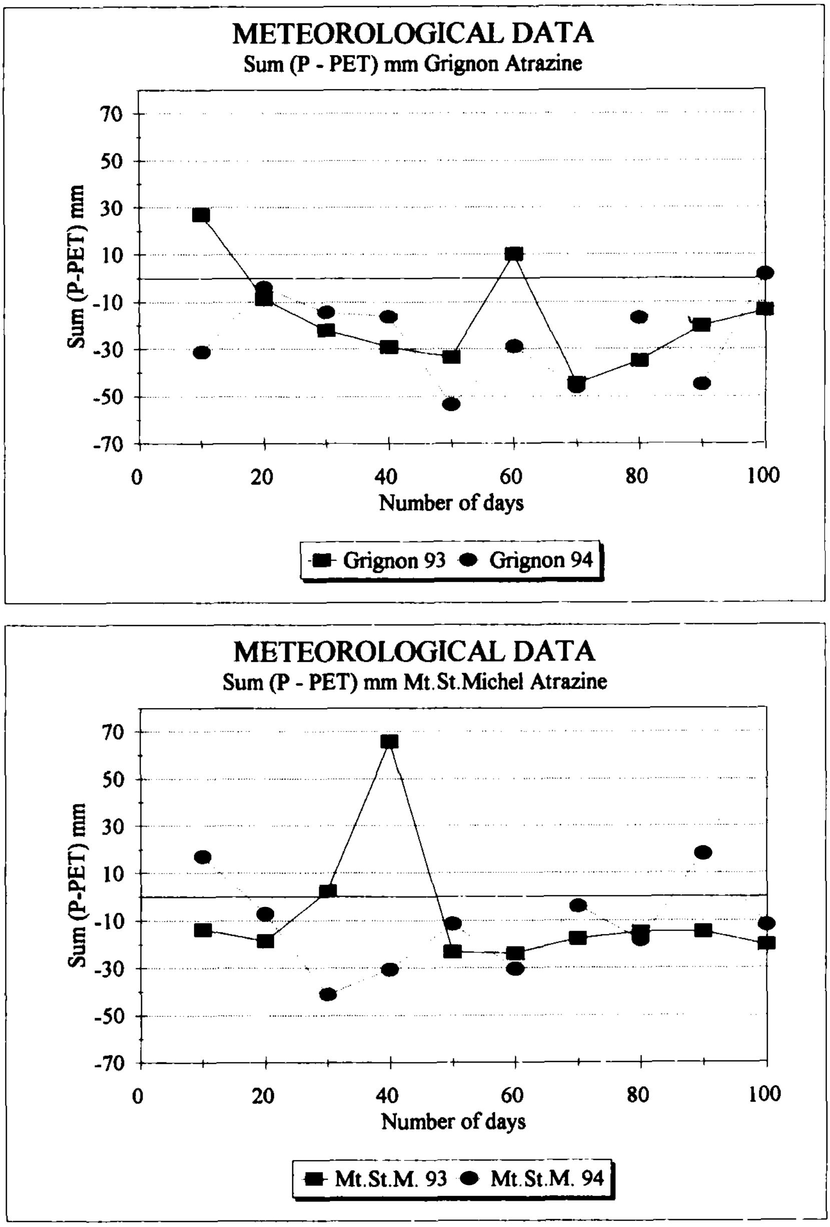
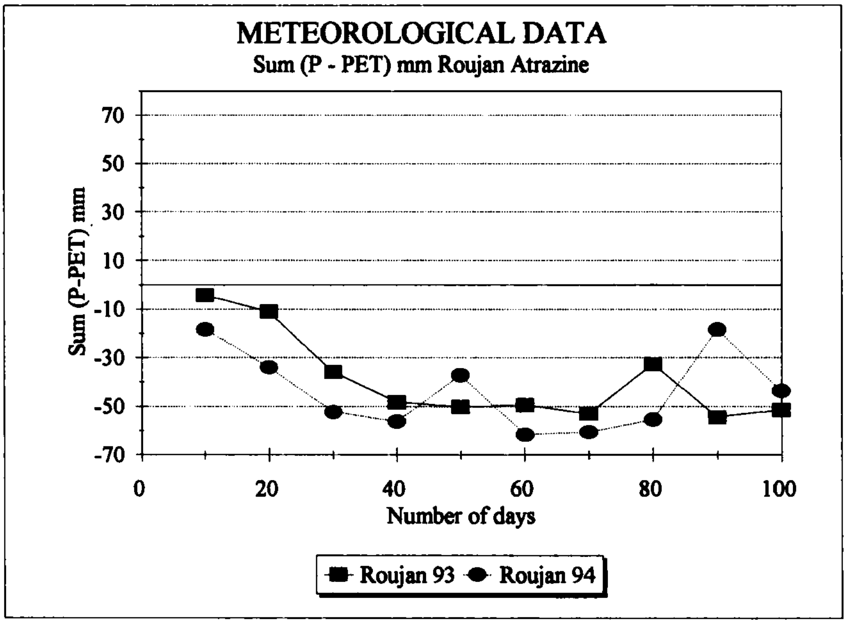


FIGURE 3 (a & b) Decade values of sum (P-PET)



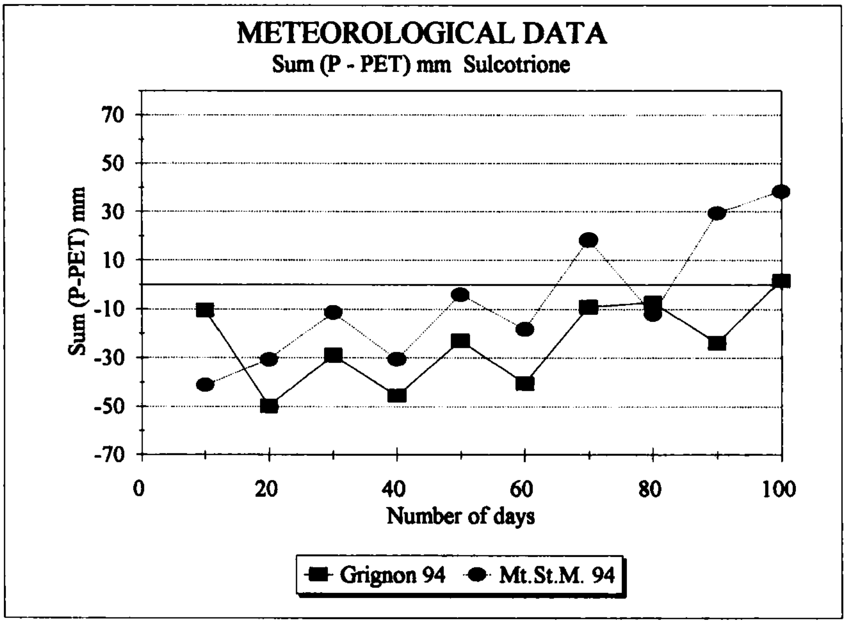


FIGURE 3 (c & d) Decade values of sum (P-PET) approach is followed because model calibration for a given site and a given year does not provide a tool for prediction. To try to answer the question, it is necessary to take into account both experimental and simulation uncertainties. Experimental uncertainty can be estimated by repeating soil sampling and measurements on field soil samples. In this work, for each sampling date, this estimation is roughly given by two data (two micro-lysimeters) for atrazine and by a standard deviation calculated with six data for sulcotrione. Simulation uncertainty can be estimated in the following way. Numerous sensitivity analysis have shown that models are generally very sensitive to variations of sorption coefficients and degradation rates.[14] Variability of values of these parameters is essentially due to a spatial variability which have been shown to be characterized by a coefficient of variation of about 25–30%.[15,16] Accordingly, simulations have been performed for two limiting conditions based on the following values.

- sorption coefficient: $Kd_{maximum} = Kd_{mean} + \Delta Kd$; $Kd_{minimum} = Kd_{mean} - \Delta Kd$
- degradation rate: $k_{maximum} = k_{mean} + \Delta k$; $k_{minimum} = k_{mean} - \Delta k$

were $\Delta Kd = 0.3\ Kd_{mean}$ and $\Delta k = 0.3\ k_{mean}$. Values of Kd_{mean} are given in Table V. For PRZM, k_{mean} values are those calculated on the basis of mean soil temperature and water content (Table VI). For VARLEACH and LEACHP, k_{mean} are calculated with observed mean values of degradation parameters (Table VI) assuming that they are characterized by a coefficient of variation of 30%.

The two limiting conditions are defined as:

- Low Risk conditions (LR) with $Kd_{maximum}$ and $k_{maximum}$
- High Risk conditions (HR) with $Kd_{minimum}$ and $k_{minimum}$

Limiting simulated dissipation kinetics for LR and HR conditions are shown in Figures 4 and 5 for the site of Grignon and Mont Saint-Michel, respectively.

Using LR and HR scenarios leads to domains of simulated values which allows to estimate, at least qualitatively, the possible uncertainties of simulations. With VARLEACH, the simulated zone (between LR and HR curves) does not overlap the observed zone (between observed points) under-estimating the dissipation except for atrazine at Mont Saint-Michel in 1993. Thus, for our studied situations, this model is not well appropriate for predicting dissipation kinetics. PRZM and LEACHP give better simulations and this confirms what has been previously observed. With these two models, simulated zones overlap more or less the observed zone, depending on the site, the year and the herbicide.

The remaining problem is to decide how much simulated curves can differ from simulated ones but it is not a matter of modelling.

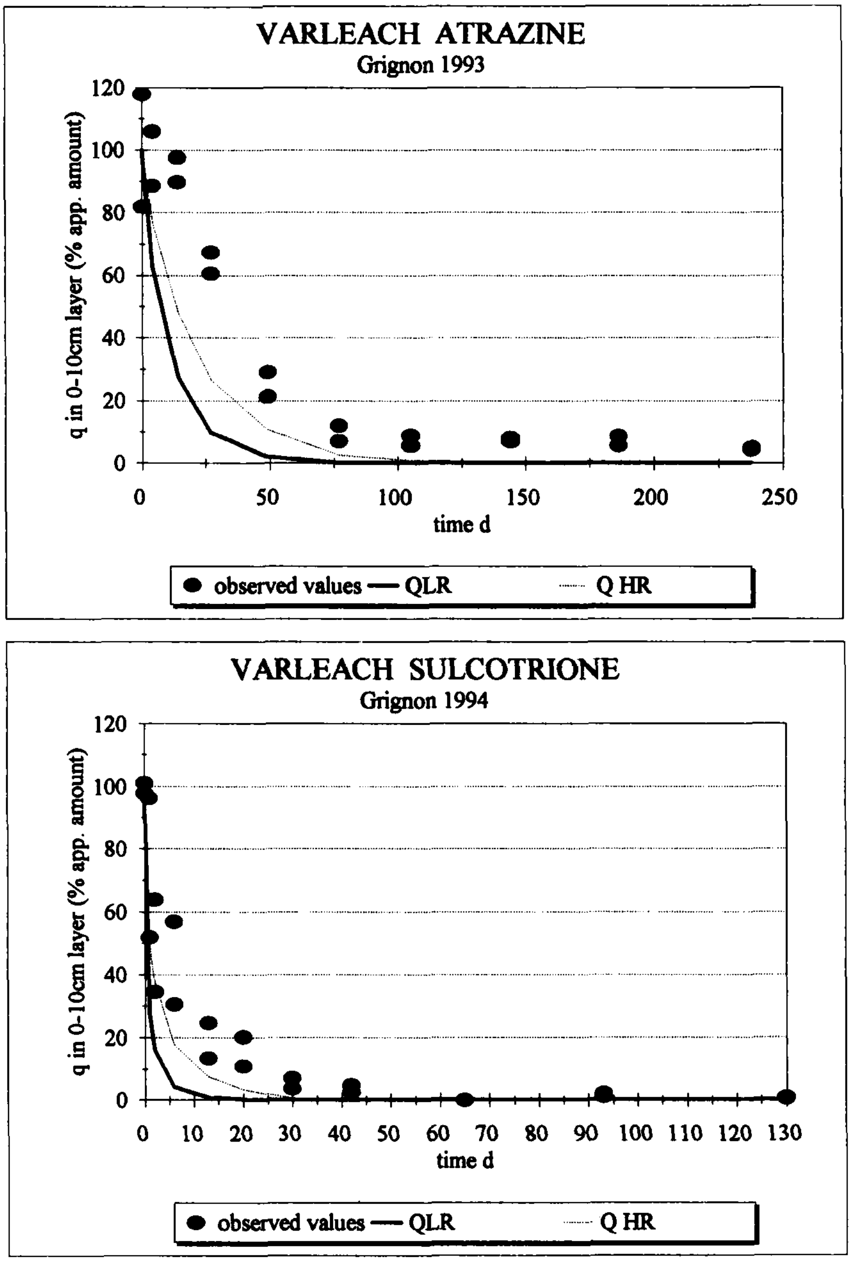


FIGURE 4 (a & b) Simulations for two limiting scenarios; QLR = low risk scenario; QHR = high risk scenario.

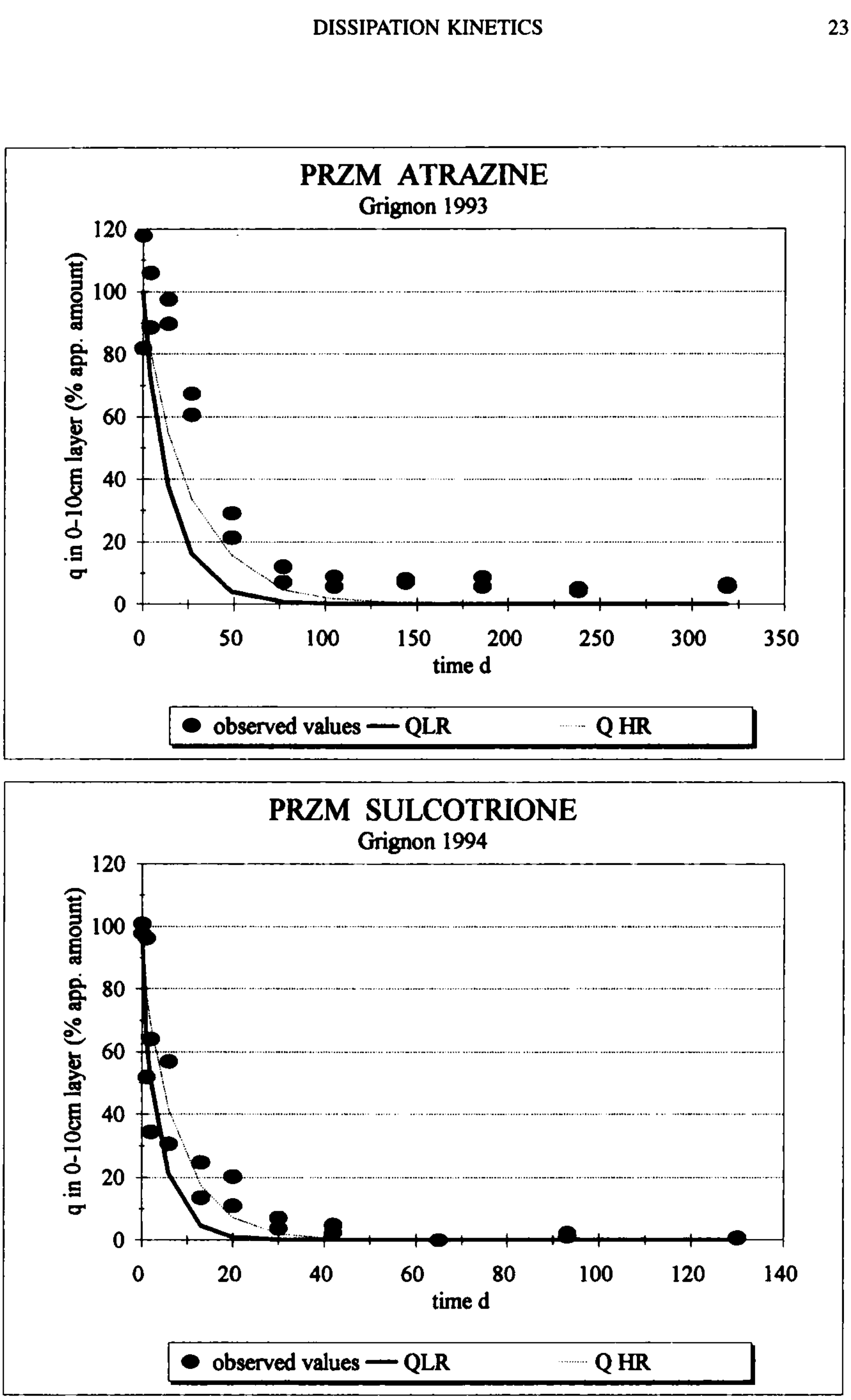
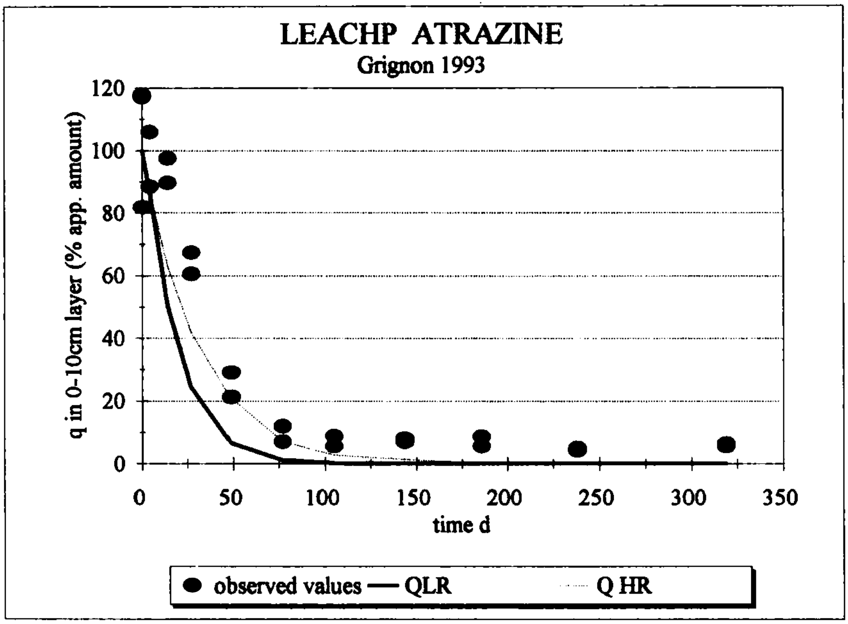


FIGURE 4 (c & d) Simulations for two limiting scenarios; QLR = low risk scenario; QHR = high risk scenario.



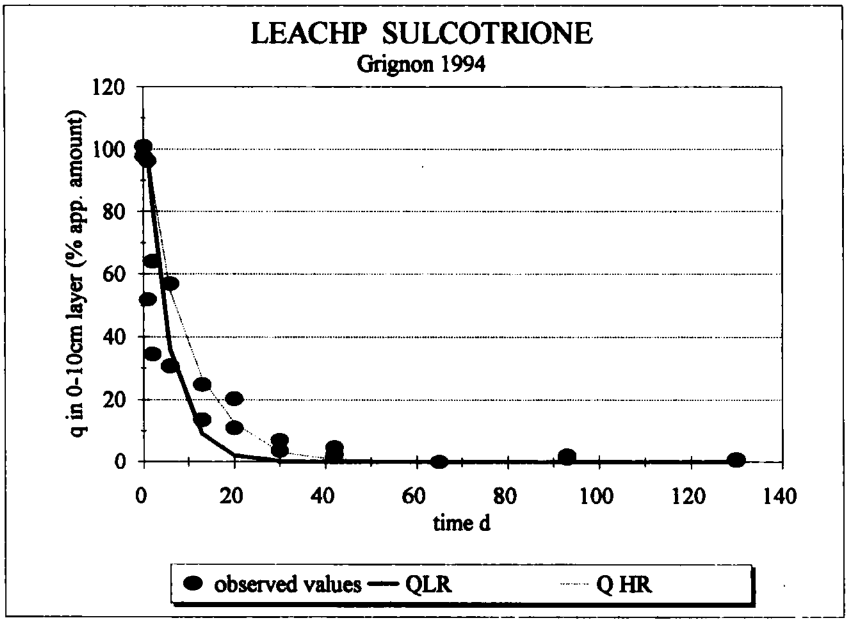


FIGURE 4 (e & f) Simulations for two limiting scenarios; QLR = low risk scenario; QHR = high risk scenario.

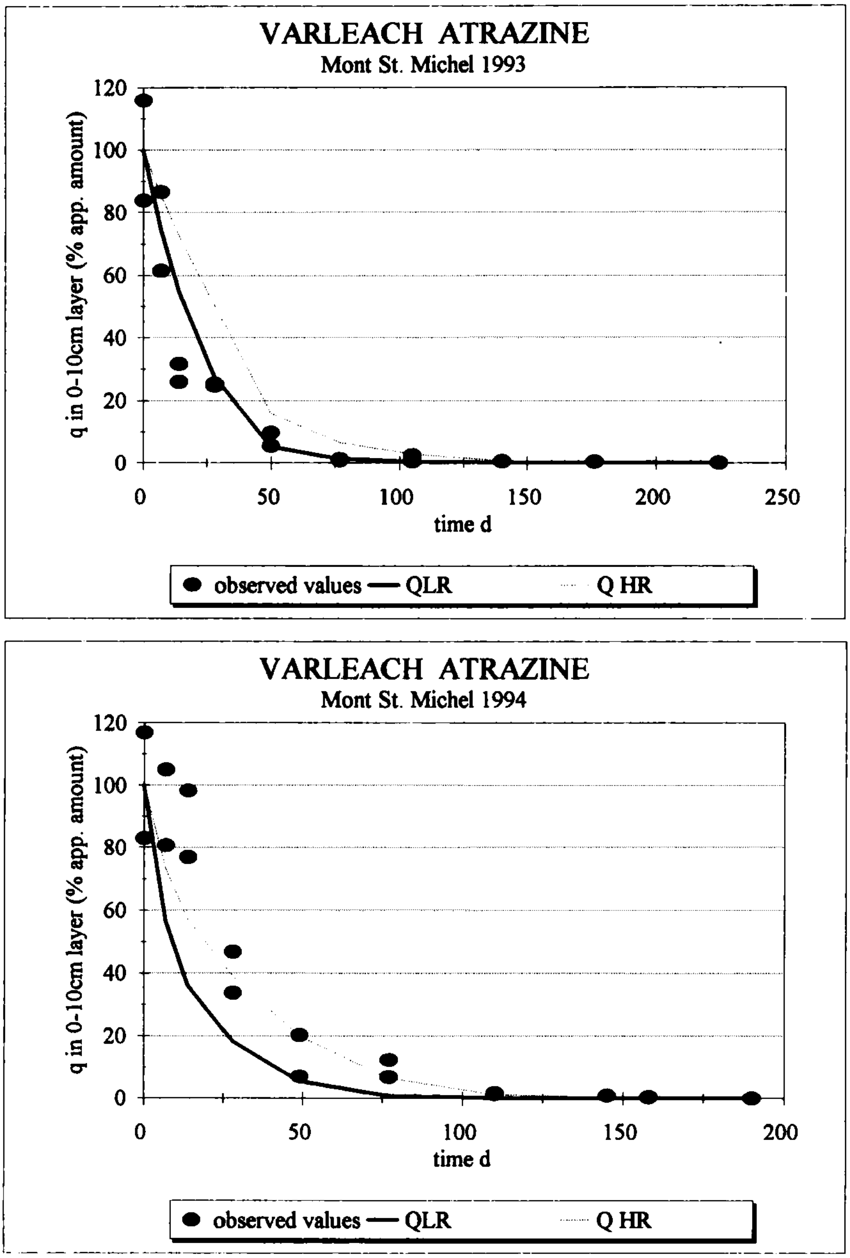
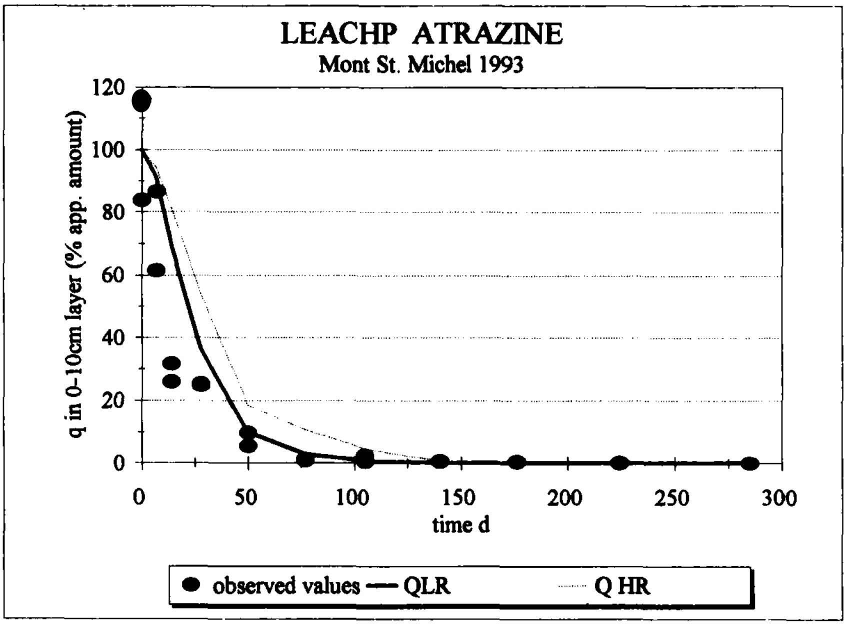


FIGURE 5 (a & b) Simulations for two limiting scenarios; QLR = low risk scenario; QHR = high risk scenario.



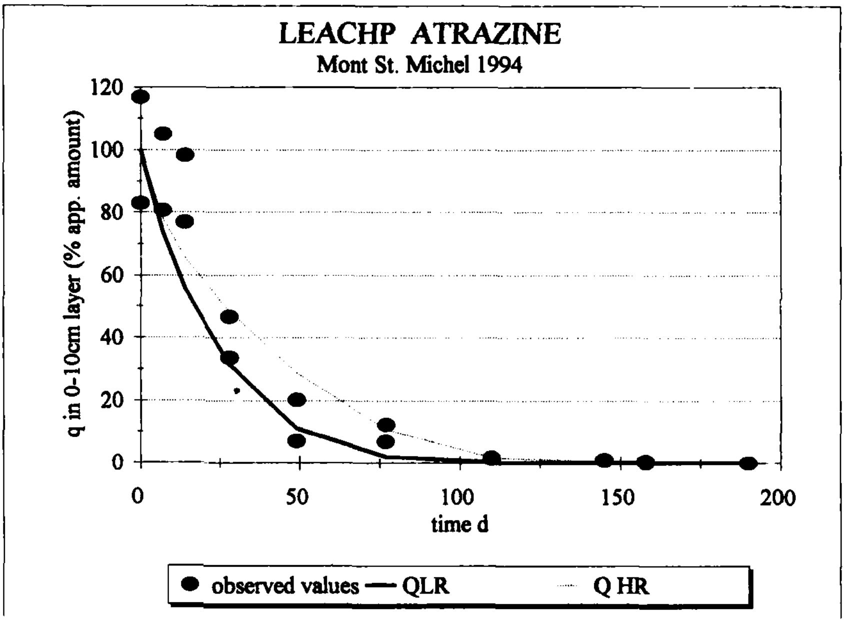
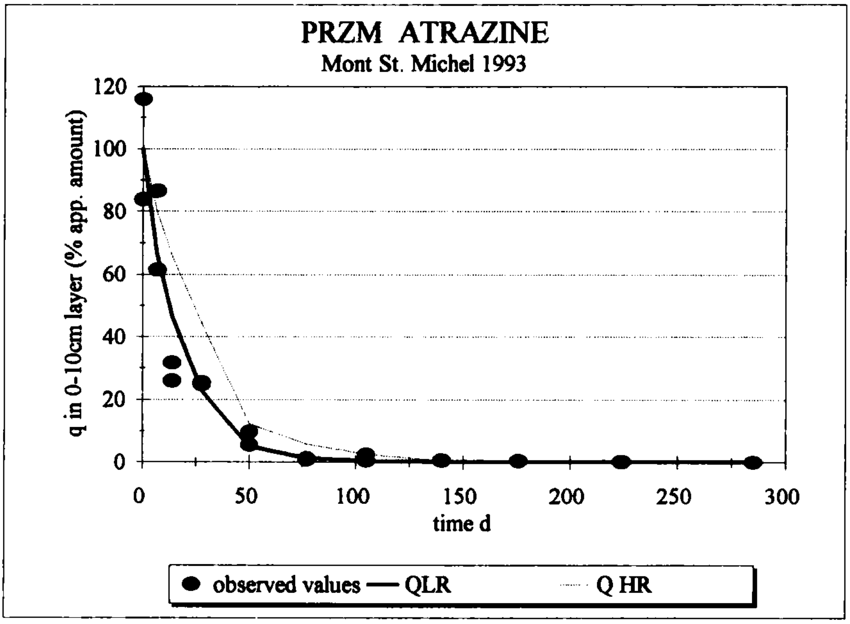


FIGURE 5 (c & d) Simulations for two limiting scenarios; QLR = low risk scenario; QHR = high risk scenario.



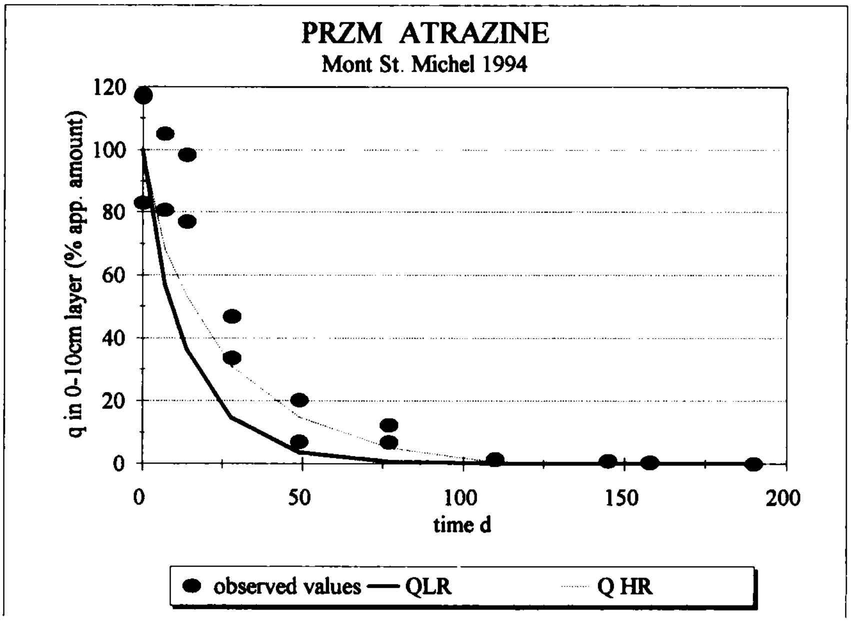


FIGURE 5 (e & f) Simulations for two limiting scenarios; QLR = low risk scenario; QHR = high risk scenario.

CONCLUSION

Numerical models are only able to describe correctly the shape of herbicide dissipation kinetics in a limited number of herbicide/soil/climate situations. This agree with a recent work done by several european laboratories which has shown that about 70% among 80 various pedoclimatic situations were not well simulated.[13] This communication allow to draw attention to several points.

No model is absolutely better than another one but PRZM and LEACHP seem to be more efficient. Taking into account both the performances and the number of input parameters, PRZM seems the more interesting model, at least, for conditions corresponding to situations of this present study. It is worthnoting that model performances may vary with the nature of the herbicide and with the type of pedo-climatic situation.

Prediction seems today a rather difficult exercise but in order to provide useful information, both experimental and simulation uncertainties must be taken into account. The proposed low/high risk scenarios approach provides approximate simulations and could be a basis for prediction.

An interesting point raised by this work is the part played by meteorological conditions, probably in relation to the model ability to describe degradation processes and their dependence towards soil water content and temperature, particularly during the first ten to twenty days of the dissipation period. Improvement of numerical simulation could probably result from better modelling of degradation processes and their variation with climatic conditions. It is also important to note that attention should be given to the simulation of water transfers and to the meaning of extraction procedures used to determine residual amounts. This last point allows to emphasize the benefit which could be obtained by incorporating unextractable residue formation in models which describe the fate of soil applied pesticides.

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