

# **SESSION 4**

## **SORPTION AND MOBILITY (LARGE SCALE)**

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### Field-scale variability of herbicide transport

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#### ABSTRACT

Ninety-nine undisturbed soil columns were collected in order to characterise a 1.8 ha field site with respect to herbicide leaching. All samples were subjected to leaching experiments under steady state water unsaturated flow conditions. The individual breakthrough curves of the applied bromide and the two herbicides isoproturon and terbuthylazine were averaged to obtain large or field-scale signals which were analysed with a stochastic advective modelling approach. Two different manifestations of preferential transport could be distinguished. The analyses revealed that herbicide transport in one part of the field (0.66 ha) was dominated by preferential flow which increased the total leached mass by 350% and 810% of isoproturon and terbuthylazine respectively.

#### INTRODUCTION

The behaviour of pesticides, such as herbicides, in the terrestrial environment is predominantly mediated by the vertical transport characteristics of the organic compounds in soils. To what extent chemicals are leached below a certain soil depth depends on the water flux regime on the one hand and on the adsorption process on the other. Both processes are known to vary considerably in the horizontal plane within field units (Lennartz, 1999). The variation of the water flux, especially in field studies, is often captured by analysing the transport behaviour of non-reactive tracers that are known to travel like water through the soil profile. Following the application of a solute pulse, the assessment of solute transport parameters is made from an analysis of the breakthrough curve (BTC). The application of reactive compounds such as herbicides along with the conservative tracer gives additional insight into the transport system.

The vadoze soil zone has been identified as a transport region that is dominated by multiple non-equilibrium effects. These have been conceptualised with respect to transport with the system of soil water regions of different mobility. In the mobile / immobile soil water approach advective solute transport is limited to the mobile region, while transfer into the immobile fraction is diffusion controlled. Another possible manifestation of transport non-equilibrium is that advection takes place in both, the region of fast and the more slowly flowing water. Solute exchange between regions is neglected. The nature of the dominating flow regime can be identified by model analyses of experimental data.

The objective of this study was twofold. A multiple column leaching test with 99 undisturbed soil samples was conducted to obtain a field-scale view of the herbicide leaching situation by averaging the individual BTCs. A succeeding model analyses on the computed large- or field-



scale BTCs with a stochastic advective-reactive travel time approach was performed aiming at identifying governing non-equilibrium conditions and their effects on herbicide losses.

## METHODS AND MATERIALS

The experimental site Altenholz had a size of 1.8 ha and is located in the vicinity of the city of Kiel in northern Germany (54.4° N, 10° E). The 99 samples were taken at a regular grid with a 15-m spacing. First, sampling started by removing the 5-cm top layer of the soil. Secondly, the stainless steel cylinders (10 cm in length and 5.4 cm in diameter) were slowly inserted vertically into the prepared sampling location. Thirdly, the intact cores were carefully removed from the soil and were sealed with plastic lids for safe transport to the laboratory. Fourthly, crumbed soil surrounding the cores was collected at each sampling location in order to determine additional soil parameters. Soil cores that were not directly used in the leaching experiments were stored at 4° C.

All 99 soil monoliths were subjected to classical displacement tests under unsaturated steady-state flow conditions. The set-up facilitated the simultaneous treatment of 24 samples (Lennartz et al., 1997). Water desaturation of samples was achieved by applying a pressure of -3 kPa at the lower end of the samples which corresponded to natural conditions during the winter period in humid regions. A chemically inert Nylon membrane with an average pore space of 10 µm functioned as a ceramic plate. Herbicide and tracer-free water was supplied at the top of the sample via a sprinkler consisting of a plastic cover preventing evaporation and 4 hypodermic needles. The sprinkler were rotated manually once per day. The chemical composition of the water was adjusted according to naturally occurring rain water. Samples were irrigated at 19-min intervals for 1 s; that resulted in an average water flux density of  $q=0.58 \text{ cm d}^{-1}$ . The established flow regime was chosen in order to represent natural conditions, no bypass flow was expected at the adjusted moderate flux density.

Application solutions were prepared from the formulated commercial products Arelon (Hoechst AG) and Gardoprim 500 (Ciba-Geigy GmbH) containing  $2.42 \text{ mol l}^{-1}$  isoproturon (IPU) and  $2.13 \text{ mol l}^{-1}$  terbuthylazine, respectively, as a suspension. The chemicals were dissolved in a bromide solution ( $12.5 \text{ mmol l}^{-1}$ ) at rates between  $2 \text{ µmol l}^{-1}$  and  $2.05 \text{ µmol l}^{-1}$ . The application solution was freshly prepared for every batch of soil samples and subsequently analysed. Observed minor fluctuations in herbicide concentrations probably resulted from using formulated standard agrochemicals for the preparation of the application solution. Two doses of 0.5 ml each were applied at 19-min intervals with a Hamilton high precision syringe to the surface of the soil samples; this corresponded to an average rate for both herbicides of  $1.6 \text{ kg ha}^{-1}$ .

### Model analyses

The advantage of the stochastic advective-reactive modelling approach is that possible biogeochemical mass transfer and transformation processes that may affect a reactive compound during its transport through the vadoze soil zone can be decoupled from pure advection and the different manifestations of preferential flow and transport. One possible manifestation of non-equilibrium transport conditions is that advection occurs only in the mobile soil water region, whereas the remaining soil water fraction is considered to be stagnant. In this classical mobile / immobile soil water concept diffusional mass transfer between regions is an additional important mechanism for solute transport which is quantified



in terms of a mass transfer coefficient  $\alpha$  [ $T^{-1}$ ]. The total soil water content  $\theta$  is the sum of the mobile  $\theta_m$  and the immobile  $\theta_{im}$  water fraction:  $\theta = \theta_m + \theta_{im}$ .

Another non-equilibrium flow and transport scenario is that the soil water is divided into two fractions and that advection takes place in both regions. The non-equilibrium is caused by significant soil water velocity differences between the two water phases. The soil water content is distributed as  $\theta_1$  (water content in slow flow paths) and  $\theta_2$  (water content in preferential flow paths), so that the total water content is  $\theta = \theta_1 + \theta_2$ . The flow domains are represented as the weighted sum of two log-normal probability density functions (pdf) which is defined by the mean travel times  $\mu_i$  and the variances of  $\ln \mu_i$   $\sigma_i^2$ , with index  $i = 1$  referring to the slow flow paths and index  $i = 2$  referring to the preferential flow paths (Destouni *et al.*, 1994).

## RESULTS AND DISCUSSION

Two general, but different, types of breakthrough situations could be distinguished with the lysimeters (Figure 1). As expected, in over 90 % of all lysimeters, a chromatographic separation of the applied chemicals in the order bromide, isoproturon and terbuthylazine was observed. However, despite the small adjusted water flux rate and water desaturation, all compounds occurred simultaneously in 7 cases, indicating a pronounced preferential transport situation. The simultaneous occurrence of all 3 chemicals was accompanied by an early arrival at the outlet of the columns, providing further evidence for preferential flow. Assuming pure advective-dispersive transport, concentration maxima of non-reactive tracers should occur in the effluent after the exchange of one pore volume. The range of breakthrough times observed in this study reflects the presence of immobile or slowly moving soil water fractions. This phenomenon of immobile water phases reduces the effective flow cross-sectional area, and has been documented previously for unsaturated flow conditions in undisturbed soil columns (e.g. Jardine *et al.*, 1993). Our experimental results confirm that solute transport under unsaturated flow conditions is always faster than expected from the measured flux density and volumetric water content and therefore is not equilibrated.

The bromide mass recovery ranged from 57% to 125% with a mean of 85% and a CV of 15%. Incomplete mass balances of non-reactive solutes as observed in this case are probably related to the fractionating of soil water in mobile and stagnant water phases. During early stages of the leaching tests solute molecules, following a steep concentration gradient, are transported easily into immobile water regions. At later stages when the centre of solute mass has left the column, the concentration gradient from the stagnant fraction towards the convective moving water phase is less pronounced and solute diffusion out of the immobile region is also less effective. This may lead to a solute release from the columns at concentrations below the detection limit ( $0.5 \text{ mg l}^{-1}$  for bromide), so that a fraction of the applied solute mass is washed from the column after sampling has been terminated. An additional reason for incomplete mass balances that has to be taken into account is a possible mechanical change in soil structure during the experimental run because of processes such as internal erosion effects. These mechanical changes may decrease the accessibility of immobile water regions via diffusion during the experimental run. As a consequence, solute transport into the stagnant zone at the beginning of the experiment may occur unhindered while the transport into the opposite direction at later stages of the test is limited.

Twenty columns had an acceptable mass balance of  $100\% \pm 10\%$ . The sampling locations of these samples were located in the south-western part of the field site (Area 2, 1.14 ha). Moreover, these 20 columns, as well as most other columns in Area 2, yielded BTCs with less pronounced preferential flow characteristics than the columns in the remaining north-eastern part (Area 1, 0.66 ha) of the field site. All samples in Area 1 yielded poor bromide mass balance and several of them exhibited bimodal BTCs.

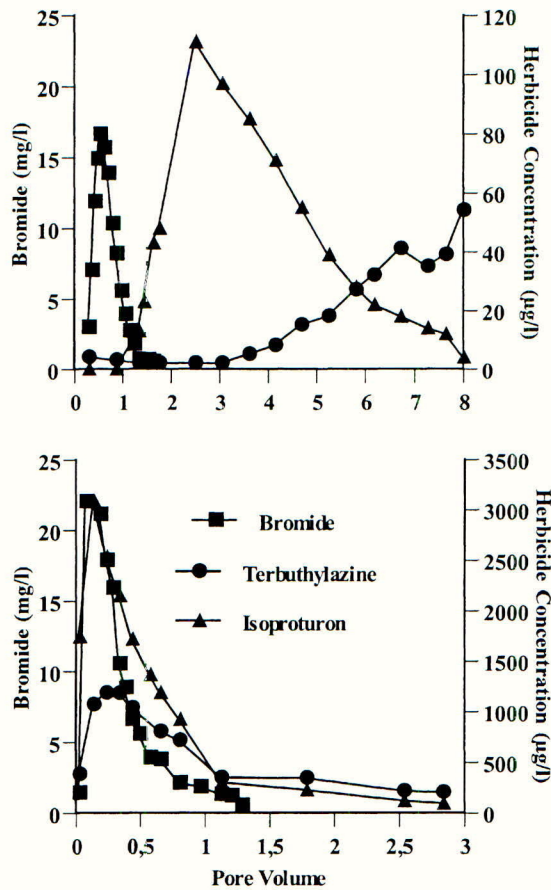


Figure 1. Examples of individual breakthrough behaviour. Top: Classical separation of non-reactive and reactive compounds. Note: Bromide maximum concentration is reached before the exchange of one pore volume. Bottom: Simultaneous occurrence of all three applied solutes in the effluent indicating pronounced preferential flow.

The data set was separated into four sub-sets: Mass balance columns (MBC), Area 1 columns, Area 2 columns, and the entire data set (Area 1 + Area 2). The individual BTCs of the data



sets were summarised by averaging in order to obtain a large or field-scale signal which was subjected to model analyses (Simic *et al.*, 2001).

Examples of the field-scale breakthrough behaviour of bromide and isoproturon are depicted in Figure 2. Whereas the few columns that exhibited an extreme preferential transport regime had obviously only minor effects on the breakthrough behaviour of the conservative compound, they caused a bimodal field-BTC for isoproturon. As the area under the BTCs represents the solute loss it is evident that extreme preferential transport conditions have a great effect on the exported solute mass especially for sorbing compounds.

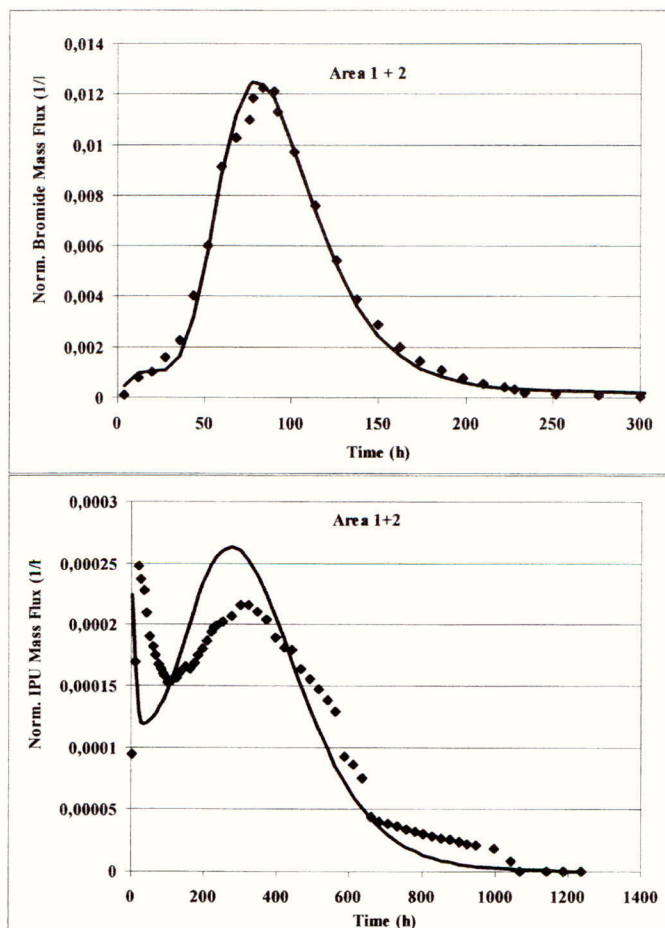


Figure 2. Large- or field-scale bromide (top) and isoproturon (bottom) BTCs as resulting from the averaged 99 individual BTCs representing the entire experimental field site. The solid line indicates the optimised curve assuming two advective flow domains.

The two field-BTCs that were derived from the MBC and from the Area 2 columns could be described best with the mobile/immobile approach while the remaining two large-scale signals required a bimodal function to obtain satisfying optimisation results. The preferential

flow columns of Area 1 had a strong influence on the entire data set causing bimodal BTCs of the reactive compounds (Figure 2). The model analyses showed that two different manifestations of non-equilibrium transport modified the breakthrough behaviour of solutes at one field site. However, the different flow scenarios were spatially separated.

In addition to the analyses with the mobile / immobile and the two advective flow domain approaches large-scale BTCs were computed assuming equilibrium transport conditions in order to estimate non-equilibrium effects on the exported herbicidal mass fraction. Results of model analyses are summarised in Table 1.

Table 1. Modelling results; leached herbicide mass fraction as percentage of (measured) recovered mass with and without consideration of transport non-equilibrium.

	Area 1	Area 2	MBC*	Area 1+2
Isoproturon				
Tot. leached herbicide mass fract. with transport non-equilibrium (% of observed)	99	94	96	97
without transport non-equilibrium (% of observed)	22	46	54	40
Terbutylazine				
Tot. leached herbicide mass fract. with transport non-equilibrium (% of observed)	106	103	100	105
without transport non-equilibrium (% of observed)	11	44	48	31

\* Mass balance columns

The rapid transport at Area 1 increased the total leached mass of isoproturon and terbutylazine by 350% and 810% respectively. At the remaining area of the experimental plot (1.14 ha) immobile water regions caused an increase of the leached mass fraction of 100% and 130% of the respective reactive compounds.

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## Edge field leaching study of metalaxyl-M and its main metabolite

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## ABSTRACT

The study aimed to assess the leaching of the fungicide metalaxyl-M and its main metabolite N-(2,6-dimethylphenyl)-N-(2'-methoxy-acetyl)-alanine under Italian field conditions. The experiment was carried out in an irrigated 1824 m<sup>2</sup> field, cultivated with pepper. The leaching of the compounds were evaluated following a strict field protocol including several chemical and physical measurements in field and laboratory. The parent compound dissipated quickly in the soil (DT<sub>50</sub>=20days) being transformed to the main de-methyl metabolite that is more water soluble. Residues were detected frequently in the soil pore water: the maximum concentration of Metalaxyl-M and its metabolite in soil water were 13.9 µg/litre and 8.6 µg/litre respectively, 31 days after the first treatment, then disappearing slowly in 120 days. However, these residues were not detected in the groundwater 8 m deep during the study of 360 days. Taking into account the spatial field variability of the soil properties, as well the applied dose, the PELMO model has been applied to complement the monitored data and the risk assessment analysis.

## INTRODUCTION

Metalaxyl is a well known systemic fungicide used to control diseases caused by *Peronosporales* in several crops. Recently new formulations with higher biological efficacy have been developed based on the stereoisomer (R) commercially known as Metalaxyl-M (Figure 1). In soil and water the Metalaxyl-M is transformed quickly to its metabolite via oxidation of the methyl group which is more soluble in water (265 g/litre against 26 g/litre of Metalaxyl-M) but also less persistent in soil. Zadra *et al.*, (2001) have measured a faster soil dissipation of the stereoisomer (R) compared to the racemic mixture.

However, looking at the chemical properties of the a.i. a common question may arise: is the metabolite a potential leacher ?



Figure 1. Metalaxyl-M (DL-N-(2,6-dimethylphenyl)-N-(2'-methoxy-acetyl)-alanine-methylester) (left) and its metabolite (DL-N-(2,6-dimethylphenyl)-N-(2'-methoxy-acetyl)-alanine) (right).

The pesticide European directive 91/414/EEC has focused attention on this environmental process affecting water quality. For groundwater quality the measurement of the pesticide leaching in field conditions is the main issue. The method described by the SETAC and EPPO provides an experimental design that does not cover the spatial & temporal diversity of the environmental processes influencing the pesticide fate.

In this paper we report the methodology adopted to measure the leaching of the above a.i. and its metabolite at the field scale and also assess their hazard to the groundwater in Italy.

## METHODS AND MATERIALS

### Field study

The study protocol applied followed that of Capri *et al.*, (2000), modified for outdoor conditions. Briefly, the field is representative of the typical use of the compound studied and of the normal agricultural practice; it is an irrigated 1824 m<sup>2</sup> plot cultivated with pepper sited in Piacenza (44.92 N; 9.73 E). Unsaturated zone and soil properties were measured and sampling was carried out through the collection of continuous cores down to the shallow groundwater (8 m depth). The soil is deep about 1 m and above an old and deep gravel bed river which is very permeable. Soil is loamy (Vertisol xeric FAO taxonomy) with an uniform vertical mass distribution in texture (about 45 % silt and 33 % clay) and pH (about 8); organic matter decrease from 1.2 % to 0.2 % from the top soil to 120 cm depth.

Pesticide was applied along the crop lines on the 7th June and the 26th June in post emergence of the pepper crop as commercial formulation Ridomil 480EC Gold at 0.134 g/m<sup>2</sup> and 0.109 g/m<sup>2</sup> in the first and second application respectively. The crop was irrigated via drip irrigation every week starting from the plant transplanting (total irrigation 230 mm). Pesticide application and crop interception was measured using paper traps. Unsaturated zone as well the pesticide mobility was investigated by means of soil samples collected in the top soil (0-30 cm divided in 3 layers 10 cm each) and soil-water suction cup installed below the root zone at 60 cm depth: sampling followed a schedule over a time frame of 180 days after the pesticide application. Additional sampling was also done after the main irrigation and precipitation. The groundwater quality in the saturated zone was monitored by means of sampling carried out after the main precipitations and monthly for 1 year after the pesticide application (Figure 2).

### Extraction and pesticide analysis

Soil and water samples were extracted with methanol and aqueous buffer solution of pH 10. Metalaxil-M was partitioned from this solution into dichloromethane. The organic phase was brought to dryness and the residues were cleaned up by alumina column chromatography. The aqueous phase was acidified with hydrochloric acid and the metabolite was partitioned into dichloromethane. The organic phase was evaporated, the residues were methylated with diazometane and then were cleaned up by alumina column chromatography. Quantification of both Metalaxil-M and metabolite residues was achieved by GC-MS using selected ion monitoring. The limit of detection was 0.01 mg/kg for both a.i. in soil, 0.10 µg/l for Metalaxil-M and 0.20 µg/litre for the metabolite in water.



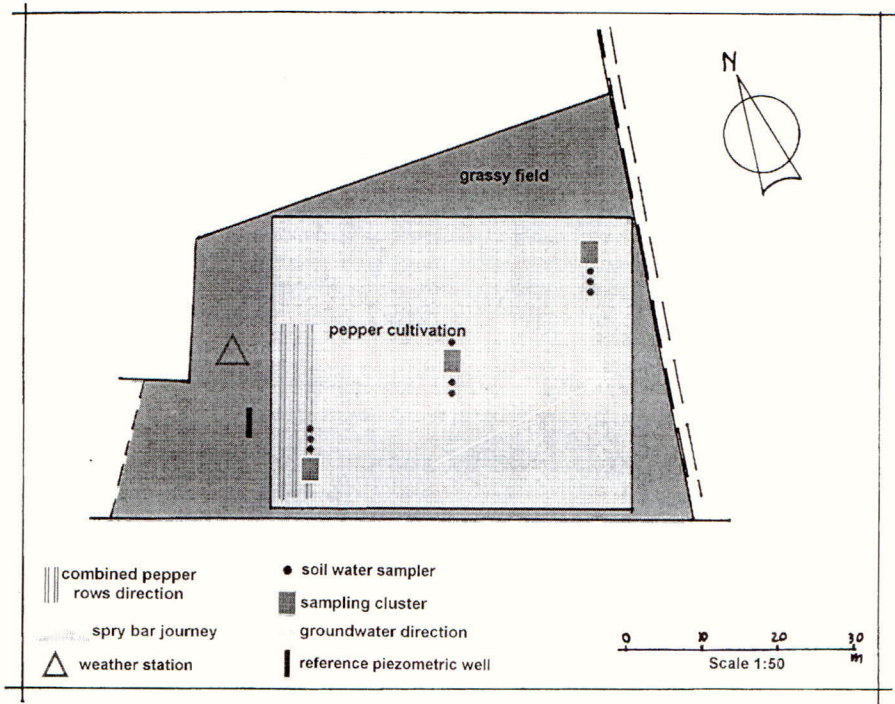


Figure 2. The experimental field.

### Data analysis

Measurement of the pesticide leaching in the field studies can show high spatial variability due to the variability of the soil properties such as organic matter, texture and microbial biomass as well variability of the pesticide application (Vischetti *et al.*, 1997). Geostatistics was the technique used to characterize the spatial variability (Gamma Design Software, 1992) for some of the main properties.

To assess the leaching of the pesticides to the groundwater two different strategies were used: a stochastic approach and the FOCUS methodology (FOCUS, 2000). The former was realised by means of Monte Carlo approach with a sample size equal to 64 obtained considering 80% of occurrence probability, 20 % of unoccurrence probability, 90 % confidential interval (Zewei, 2001) and changing randomly the value of some model input (Table 1); furthermore FOCUS approach with 20-years simulation in the "scenario Piacenza was applied. Both strategies were not used for validating the models but to obtain data that were not measured in the field such as the outflow concentration below one meter of soil depth and the soil water fluxes.

## RESULTS

### Pesticide persistence in the soil-water system

A high percentage of the pesticide applied was intercepted by the crop (about 50%) and the load to the soil surface was varying along the field: the semi variance was not significant for the different models (spherical, exponential, linear, linear to sill, gaussian).

Metalaxyl-M was transformed to the metabolite which was detectable in the top soil from the first sampling after the application. Maximum soil concentration of both Metalaxyl-M and metabolite was measured three days after the second application (0.45 mg/kg and 0.033 mg/kg respectively). The DT50 in soil, assuming a first order kinetic, is about 2 weeks for both compounds. However, residue of the pesticide persisted in the soil for some weeks, but after 272 days no residues were detectable in the soil (Figure 3).

Table 1. Parameter assumption in the Monte Carlo approach. Between the brackets the value for the metabolite.

Input	Distribution Type	Minimum Value	Maximum value	Mean	Standard deviation
Applied dose (g/m <sup>2</sup> )	Normal			0.361	0.189
Koc (ml/g)	Uniform	109.8 (61.0)	1122.0 (695.1)		
Organic Carbon (%)	Lognormal			0.491	0.048
Dissipation time (days)	Uniform	19.5 (10.4)	86.9 (36.4)		
Sand top soil (%)	Normal			17.92	2.23
Silt top soil (%)	Normal			47.11	1.29
Bulk density (kg/l)	Normal			1.44	0.005

Metalaxyl-M and its metabolite were detected mainly in the top soil (Figure 3) but were measured in the soil-water at 60 cm depth (Figure 4): in the first 130 days after the application pesticide residue were measured in soil pore water with maximum concentration of 14 µg/litre and 8 µg/litre for the Metalaxyl-M and the metabolite respectively. Movement may be due to the high water input used in the field as irrigation.

Both compounds were not detected in the groundwater for one year after the application although an estimated water recharge > 200 mm had occurred due to irrigation.

Table 2. Descriptive statistic of the model outputs obtained after three years of simulation.

	Metalaxyl-M		Metabolite	
	g/ha	µg/litre	g/ha	µg/litre
Mean	0.0019	0.0005	0.0092	0.0026
Std dev	0.0133	0.0038	0.0369	0.0103
90° perc.tile	0.0010	0	0.0096	0.0030



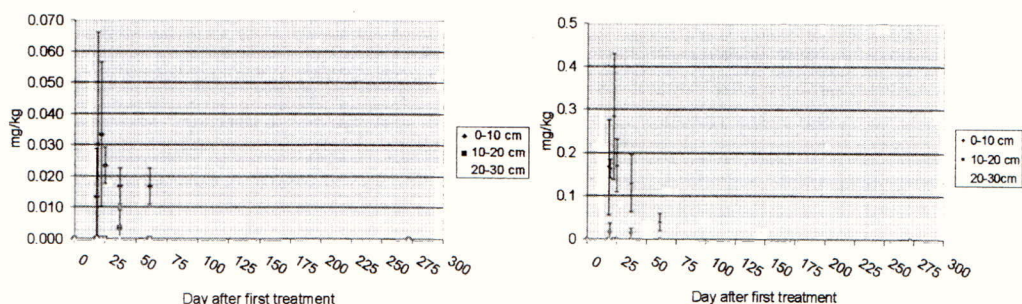


Figure 3. Metalaxyl-M (right) and metabolite dissipation in soil at different depth (left).

### Actual and potential leaching assessment

Both pesticide and metabolite may not leach to the bottom of the unsaturated zone in the field test site although they are slightly persistent and mobile in the root soil zone. However, the detection of residue at 60 cm depth, in only a few samples, from this field test suggest groundwater contamination is unlikely to be significant

Results of the probabilistic assessment, that included all the possible combinations of conditions that we can find, indicate that water concentration below 1 meter will be always below the limit required by 91/414/EEC ( $<0.1 \mu\text{g}/\text{litre}$ ) after two consecutive years of application (Table 2). This was also confirmed when the Piacenza scenario of the FOCUS was applied (Boesten *et al.*, 2000) per 20 years

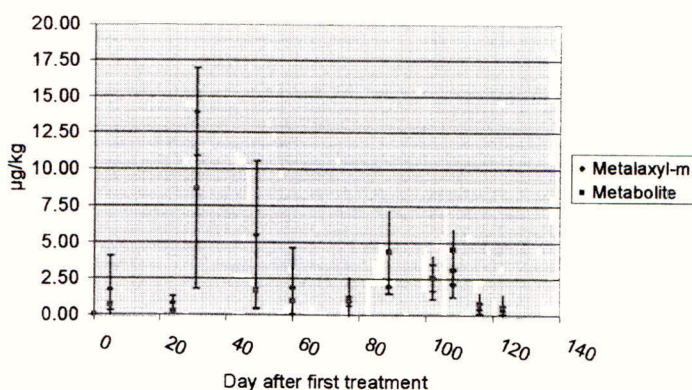


Figure 4. Metalaxyl-M and metabolite dissipation in soil-water.

The leaching of both a.i. and metabolite after the normal agricultural uses is mitigated throughout a combination of different factors but the low application dose and the plant interception play an important role.

The results reported confirm that deterministic and probabilistic model application which is integrated with the measurement carried in the field can assess the pesticide hazard to contaminate the groundwater. Furthermore, as the model application included the spatial variability of the input measured in the field or estimated, the output obtained will include the uncertainty associated itself with the predictions.

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