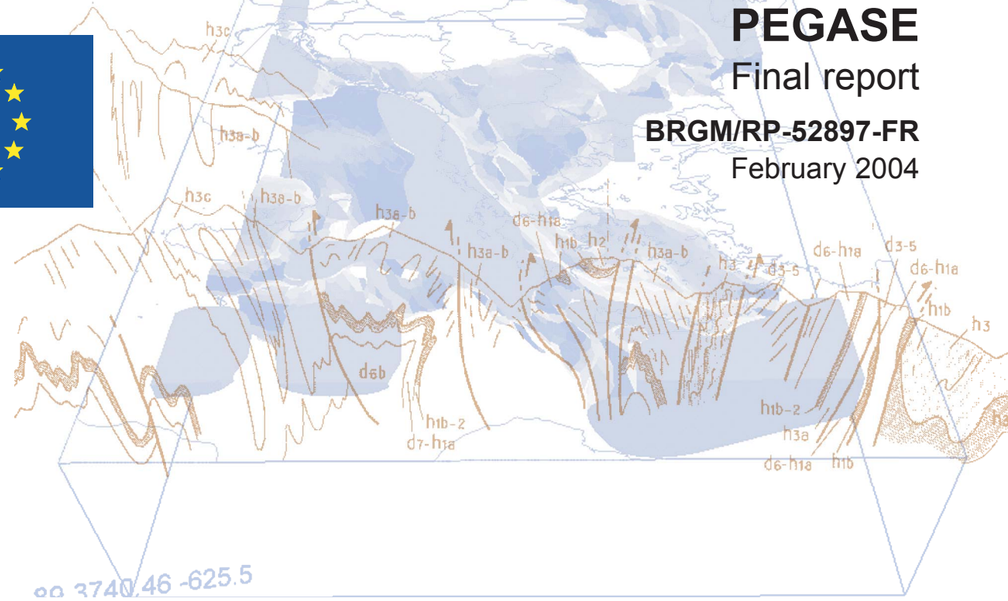
Public document

Pesticides in European Groundwaters: detailed study of representative Aquifers and Simulation of possible Evolution scenarios

PEGASE

Final report

BRGM/RP-52897-FR
February 2004



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Geoscience for a sustainable Earth
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within the 5th Framework Programme
EU contract number: EVK1-CT1999-00028

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Executive summary for policy- and decision-makers

- Pesticides have been repeatedly measured in groundwater at concentrations in excess of the thresholds set by the EU directive 91/414. The potential contamination of European potable water supplies by contaminants is a **major concern to the Public** and is being addressed by the European Union through the **Water Framework Directive**.

- The **PEGASE project funded by the European Commission** (Pesticides in European Groundwaters: detailed study of representative Aquifers and Simulation of possible Evolution scenarios; EU contract number EVK1-CT1999-00028) aimed at:

  1. **Monitoring the presence of pesticides** in a number of representative aquifers;
  2. **Elucidating processes involved in the transport of pesticides** from the soil surface to and in groundwater;
  3. and **Developing advanced tools** (mathematical modelling tools, but also socio-economic instruments) supporting the management of pesticide usage with regard to the sustainable management of groundwater (GW) quality.

- The 42-month project involved a total of **11 partners from 8 European countries**. Monitoring activities were undertaken at different scales (from plot to catchment scale) for six aquifers representative of European GW resources. A total of 10 modelling tools which were refined within PEGASE were evaluated against the monitoring data collected. Finally, results of a socio-economic analysis were integrated into a deliberation support tool ('PEG@SE') which helps the various stakeholders to (re)formulate their expectations with regard to the management of water resources.

- A number of PEGASE research findings have a direct relevance to current policy initiatives, notably the **Water Framework Directive** and the **Daughter Groundwater Directive**.

  - The **strong variability in pesticide concentrations measured in groundwater**, which translated into differences in neighbouring piezometers and significant variations in concentrations from one sampling date to the other, is of importance with regard to the design of monitoring activities aimed at assessing the chemical status of water resources within the scope of the Water Framework Directive.
  - Laboratory experiments undertaken in the project suggest that there is a **significant potential for degradation of selected pesticides in aerobic aquifers**. This natural remediation process has rarely been reported before and could form the basis of a long-term management strategy for groundwater quality.
  - Finally, a range of advanced modelling tools enabling the simulation of the fate of pesticides from the soil surface to and in the groundwater have been developed. Although further evaluation of the models is required, they offer great expectations with regard to their use as groundwater quality management tools.

- Further information about the data collected in the field, the models used within PEGASE, the PEG@SE deliberation tool and the overall project and its results can be obtained by visiting the PEGASE web site at **http://www.brgm.fr/pegase**.

Executive summary for EU citizens

- The transport of the pesticides from the soil surface to and in groundwater was monitored in six aquifers representative of European groundwater resources (2 in France, 1 in Germany, 1 in Switzerland, 1 in Denmark and 1 in the Netherlands). Results show that there is a potential for a rapid transport of pesticides to depth under specific conditions. The pattern of detection of pesticides in groundwater varied according to the compound and the aquifer considered. Where detection occured, it was limited to the first few weeks following application to agricultural crops whereas in some others, the compound was detected throughout the monitoring periods.

- Mathematical tools enabling the simulation of pesticide fate from the soil surface to and in groundwater were developed or improved within the scope of the project. The models were tested against the data collected at the various study sites. Although further validation work is required, the integrated models used in the project, which allow the simulation of pesticide fate from the soil surface to and in groundwater, have the potential to be used as management tools to ensure the long-term protection of European groundwater resources.

- A socio-economic analysis was undertaken to understand the expectations of various stakeholders with regard to the long-term management of groundwater quality. A deliberation support tool known as 'PEGASE' was developed to help create a bridge between scientific and non-scientific knowledge, integrating technical, scientific and social information in a single framework. The system was evaluated through interactive demonstrations in schools, universities and local authorities and proved a useful tool in helping users in formulating their expectations with regard to water quality.

- Further information about the data collected in the field, the models used within PEGASE, the PEG@SE deliberation tool and the overall project and its results can be obtained by visiting the PEGASE web site at **http://www.brgm.fr/pegase**.

Extended executive summary

The presence of pesticides at concentrations exceeding the EU drinking water limit has been reported in many aquifers used for drinking water supplies in Europe. The **PEGASE** research project (Pesticides in European Groundwaters: detailed study of representative Aquifers and Simulation of possible Evolution scenarios; EU contract number EU contract EVK1-CT1999-00028) was funded by the European Commission to: i) **investigate pesticide contamination** in a number of representative aquifers; ii) **elucidate transport processes** from the soil surface to and in groundwater; and iii) **develop advanced tools** (deterministic mathematical models, but also socio-economic instruments) supporting the management of pesticide usage with regard to the sustainable management of groundwater (GW) quality.

Six contrasted aquifers representative of European GW resources (from a sandy aquifer with a GW table <2 m below ground level to a 50 km^2 karst aquifer with GW at >10 m depth) **were extensively monitored for water and pesticide fluxes for up to three years**. The six study areas were Brévilles (Normandy region, France), Les Trois Fontaines (Centre region, France), Zwischenscholle (North Rhine - Westfalia, Germany), Roswinkel (Drente region, The Netherlands), Martigny (Valay, Switzerland) and Havdrup (Sealand, Denmark). The intensity of data collection was adjusted according to the aquifers and variables monitored. Data collected included information on soils, land use, climate, pesticide usage, hydrogeology and geology. Knowledge about the transport of water and pesticides in soil and in the unsaturated and saturated zones was obtained through i) field leaching experiments in soil; ii) soil and subsoil coring; and iii) sampling of groundwater at various locations and depths. In addition, laboratory studies were conducted on **sorption and degradation of five pesticides** in batch systems **with solids recovered from the saturated zone of five aquifers**. The monitoring exercise demonstrated that i) there is a potential for significant and rapid transport of selected pesticides to depth under unfavourable climatic conditions (*i.e*. significant rainfall events shortly after application); ii) except for selected compounds which were found throughout the year (*e.g.* atrazine, deethylatrazine), detections of pesticides in groundwater were generally limited to a few weeks following application; and iii) concentrations of pesticides in aquifers are very variable in space and time. The laboratory studies revealed that a significant degradation of MCPP and isoproturon in samples of aerobic saturated zone occurred. Redox conditions were found to influence potentials for sorption and degradation.

Mechanistic or semi-empirical tools were developed for the modelling of pesticide contamination in GW at various spatial scales. Approaches investigated included the refinement of a screening tool (PESTGW) and 1D root zone models (MACRO and ANSWERS), the addition of pesticide fate and crop subroutines in integrated models (thereby allowing the prediction of pesticide fate in the soil-unsaturated zone-saturated zone continuum; MARTHE, TRACE and POWER) and the coupling of different models (TRACE+3DLEWASTE, MACRO+FRAC3DVS, MACRO+MODFLOW, ANSWERS+ MODFLOW). The numerics of the models were upgraded within the framework of the project, which allows the future deployment of advanced modelling activities, such as automated calibration against field data or sensitivity and uncertainty analyses.

The majority of the new modelling tools developed within the project were **applied to reference case studies, numerical solutions or to the datasets collected as part of the project**. First investigations demonstrated that new subroutines had been correctly implemented in the models. The large inter-annual and spatial variability in pesticide concentrations noted at most study sites was difficult to reproduce with the models in some instances. Inadequate simulation of field data by models was generally attributed to i) the lack of long-term spatialized information on pesticide application practices in the catchments; ii) the lack of spatialized information on the structure and properties of the unsaturated and saturated zones; and iii) the inability of most models to account for preferential flow processes. **Overall, the use of integrated models enabling the simulation of pesticide fate in the soil and in the subsoil in 1, 2 or 3 dimensions was considered to be more appropriate** than combinations of root zone and groundwater models **for assessing the transfer of pesticides from the soil surface to and in groundwater.** Still, the modelling work undertaken within the project confirmed the challenging nature of simulating water and pesticide fluxes in the root zone - unsaturated zone - saturated zone continuum.

Alternative management scenarios to ensure the sustainability of groundwater in relation to quality issues were developed on the basis of the driving forces and solutions envisaged for pesticide management strategies. These scenarios were implemented within a software tool referred to as 'PEG@SE'. The system is designed to **create a bridge between scientific and non-scientific knowledge, integrating technical, scientific and social information in a single tool**. The system has been evaluated through interactive demonstrations in schools, universities and local authorities and proved a useful tool in helping users in formulating their expectations with regard to water quality.

A number of PEGASE research findings have a **direct relevance to current policy initiatives**, notably the Water Framework Directive and the Daughter Groundwater Directive. The strong variability in pesticide concentrations measured in groundwater, which translated into differences in neighbouring piezometers and significant variations in concentrations from one sampling date to the other, is of importance with regard to the design of monitoring activities aimed at assessing the chemical status of water resources within the scope of the Water Framework Directive. Laboratory experiments undertaken in the project suggested that there is a significant potential for degradation of selected pesticides in aerobic aquifers. This natural remediation process has rarely been reported before and could form the basis of a long-term management strategy for groundwater quality. Finally, a range of advanced modelling tools enabling the simulation of the fate of pesticides from the soil surface to and in the groundwater have been developed. Although further evaluation of the models is required, they offer great expectations with regard to their use as groundwater quality management tools.

A total of four **priority research needs** have been identified. First, there is a need for additional information on the distribution of pesticides in the unsaturated and saturated zones. A number of recommendations with regard to sampling schemes and data collection have been made to support the design of future groundwater monitoring activities. Secondly, laboratory experiments undertaken within the project have revealed that there is a significant potential for pesticide degradation in the unsaturated and saturated zones depending on redox conditions of the aquifer and the nature of the pesticide. These innovative results deserve further investigation as they could lead to a better understanding of the functioning of the aquifer with regard to pesticide

contamination and the development of remediation strategies. Thirdly, there is a need to undertake further research into the application of integrated models which can simulate water transport and pesticide fluxes from the soil surface to and in the groundwater. Finally, an aspect which should be researched is the connection between preferential flow phenomena in soil and flow processes in the unsaturated and saturated zones. The significant contribution of preferential flow to the presence of pesticides at the bottom of soil profiles has been established, but little is known about the fate of these 'hot spots' in the deeper environment and hence the overall contribution of preferential flow phenomena to the contamination of European aquifers by pesticides.

Further information about the data collected in the field, the models used within PEGASE, the PEG@SE deliberation tool and the overall project and its results can be obtained by visiting the PEGASE web site at **http://www.brgm.fr/pegase**.

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Project web site

The project web site can be visited at: **www.brgm.fr/pegase**.

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Introduction

Groundwater provides a significant proportion of drinking water in European Member States, from 25 % in Spain to as much as 99 % in Denmark, and the protection of groundwater resources is therefore considered a major priority in Europe. This recently translated in the release of the European Water Framework Directive (2000/60/EC) which aims at ensuring that good chemical status of groundwater resources is achieved throughout Europe. Contamination of aquifers by crop protection products (or 'pesticides') at levels exceeding legal thresholds set by the EU directive 91/414 (EEC, 1991) has been reported on many occasions throughout Europe (*e.g.* IUPAC, 1987; Leistra & Boesten, 1989; Clark *et al.,* 1996; Carter *et al.,* 1997) and large scale monitoring campaigns are undertaken in Member States to study the magnitude of the contamination and its evolution (*e.g.* IFEN, 2002). A significant body of research has been conducted in the last 30 years to describe and simulate the transport of pesticides in soil (FOCUS, 1995; 2000; Vanclooster *et al.,* 2000). This has resulted in the development of a breadth of mathematical tools of varying complexity (Mills & Leonard, 1984; Carsel *et al.,* 1985; Rao *et al.,* 1985; Jury *et al.,* 1986; Nofziger & Hornsby, 1986; Jarvis *et al.,* 1991; Hutson & Wagenet, 1992; Knisel *et al.,* 1992; RZWQM team, 1992; Grochulska & Kladivko, 1994; Tiktak *et al.,* 2000). The specific focus on the soil compartment of the research on the environmental fate of pesticides is mainly due to the facts that i) sorption and degradation, two processes known to be key to the overall fate of pesticides in the environment (Walker, 1987; Wauchope *et al.,* 2002), mostly take place in soil where organic matter provides sorbing surfaces and microbial degrading populations are most active; and ii) risk assessment activities to assess the risk of groundwater contamination by pesticides within the context of the registration of products in the EU have been and are still based on an evaluation of pesticide leaching at 1-m depth (FOCUS, 2000). The underlying assumption in the assessments undertaken is that groundwater is unlikely to be affected by pesticides at concentrations exceeding legal thresholds if those concentrations are not encountered at a shallow depth. Little research has been conducted on the fate and behaviour of pesticides once they have leached through the soil and below the root zone.

Water flow and contaminant transport in groundwater are notoriously difficult to study because i) the time lag between an input of a contaminant at the soil surface and the resulting contamination in an aquifer is often in the order of several years or decades; ii) the quality of groundwater at a particular point is dependent on that at other depths, e.g. in soil or the deeper vadose zone; iii) a local groundwater contamination can originate from an input of a contaminant in areas situated at a significant distance from the monitoring point; and iv) gaining access to groundwater for sampling purposes requires in many cases technologies and tools which are difficult to set up and which are costly to maintain. As a result, investigations on pesticide fate at the aquifer scale are scarce and the tendency has been to isolate the various processes which control the fate of pesticides and to investigate them separately. For instance, pesticide sorption and degradation studies have been carried out using water and solids retrieved from aquifers (Bröholm *et al.,* 2001a; Clay *et al*., 1997; Johnson *et al.,* 1998, 2000; Moreau & Mouvet, 1997; Nordmeyer *et al.,* 1992; Toräng *et al*., 2003; Tuxen *et al*., 2002), but the relevance to the field behaviour of these results obtained under laboratory conditions is questionable. Studies on pesticide fate at the scale of the aquifer which have been reported in the literature usually consisted in monitoring of seasonal variations of pesticide concentrations in the groundwater only (Barbash *et al*., 2001; Cerejeira *et al*., 2003; Hill *et al*., 1996; Jayachandran *et al*., 1994; Pasquarell and Boyer, 1996) or in the unsaturated and saturated zones (Johnson *et al.,* 2001). Some small scale (< 1 km) and short-term (< 1 year) monitoring experiments following the injection of pesticides in aquifers have also been reported (Agertved *et al.,*

1992; Bröholm *et al.,* 2001 b; Rugge *et al.,* 2002; Springer & Bair, 1998; Widmer & Spalding, 1995).

From a modelling perspective, the problem of coupled modelling of exchange of water and pesticides between the atmosphere, the soil and the groundwater at the aquifer scale has received little attention given its complexity and lack of validation data. Although numerous 1D models for the transport of water and pesticides in soil and a significant number of 3D models for water flow in aquifers have been developed and evaluated, a bridge between the two different categories of models and the two scientific communities remains to be built. Two approaches for the simulation of pesticide fate from the soil surface to and in the groundwater can be foreseen: i) coupling root zone models and groundwater models; and ii) extending the capabilities of groundwater models by adding a description of processes affecting pesticide fate, effectively turning them in versatile integrated models capable of simulating the fate of pesticides in the root, unsaturated and saturated zones.

The PEGASE project was designed by 11 research institutes from 8 European countries to i) characterise the presence and transfer of pesticides from the soil surface to groundwater in a number of locations representative of European aquifers; ii) elucidate processes involved in the transport of pesticides from the soil surface to and in groundwater; and iii) develop advanced tools (mathematical modelling tools, but also socio-economic instruments) supporting the management of pesticide usage with regard to the sustainable management of groundwater quality. The extensive monitoring and characterisation of water flow and pesticide transport, which covered the root, unsaturated and saturated zones, supported the development, refinement and evaluation of the modelling tools. Finally, results of a socio-economic analysis were integrated into the development of a deliberation support tool ('PEG@SE') which helps the various stakeholders involved in groundwater quality to (re)formulate their expectations with regard to the management of water resources.

The present report describes the work undertaken within the scope of the PEGASE project, presents the results obtained and discusses their implications within the context of the sustainable management of the quality of groundwater resources. For readability purposes, the present report is structured in four chapters containing sections formatted as short scientific papers. The name of the contributing group is provided on the section heading and a summary is provided at the end of each section to help the reader get an overview of the work undertaken and the results obtained.

Chapter 1 reports on the field monitoring activities at the six study sites and on the laboratory experiments undertaken on soil and subsoil samples extracted at the various sites. Chapter 2 presents the development or refinement of modelling tools to allow the simulation of water transport and pesticide fate from the soil surface to and in the groundwater. Chapter 3 reports on the evaluation of the modelling tools against analytical solutions, reference datasets or experimental data collected within the scope of the project. Finally, chapter 4 reports on the socio-economic analysis undertaken and the development of PEG@SE, a deliberation support tool amalgamating scientific and socio-economic information. Additional information on PEGASE can be accessed through the project web site at www.brgm.fr/pegase.

Chapter 1 -

Monitoring of pesticide fate in the soil-unsaturated zone-saturated zone continuum

A significant objective of the PEGASE project was to generate data regarding the transfer of pesticides to groundwater and in the groundwater itself. The aims were two-fold: i) to understand processes leading to contamination of water resources; and ii) to generate datasets suitable for the development, refinement and evaluation of numerical tools. Six contrasted aquifers representative of European GW resources were extensively monitored for water and pesticide fluxes for up to three years. Monitoring activities for estimating the transfer of pesticides from the soil surface to and in the groundwater included the collection of samples of soil and of the subsoil, sampling of groundwater through piezometers and collection of spring water, groundwater tracing experiments, field leaching experiments and injection of pesticides into an aquifer. In addition, a detailed characterisation of the sites in terms of climate, agricultural and pesticide application practices, soil, subsoil material and hydrogeology was undertaken. Sorption and degradation properties of pesticides play an important role in determining their environmental fate and these properties were established in the laboratory for the five main compounds which were monitored at the study sites. Data to be collected were reviewed by modellers at an early stage and throughout the project to ensure their suitability to support subsequent modelling activities within PEGASE.

The sites were selected to represent a wide range of catchment size and agricultural, soil and subsoil characteristics. The six study areas were Brévilles (Normandy region, France; sandy aquifer overlaid by limestone with GW between 0 and 40 m bgl – below ground level), Les Trois Fontaines (Centre region, France; karst aquifer with GW > 10 m bgl), Zwischenscholle (North Rhine - Westfalia, Germany; sandy/gravel aquifer with GW table around 8 m bgl), Roswinkel (Drente region, The Netherlands; sandy aquifer with GW < 2 m bgl), Martigny (Valay, Switzerland; alluvial aquifer with GW table around 2 m bgl) and Havdrup (Sealand, Denmark; sandy aquifer overlaid by fractured moraine clay soil with GW table around 2 m bgl). Their location within Europe is displayed on Figure 1. Table 1 provides a summary of the data collection effort for each of the sites which were studied.

Monitoring activities and main results obtained for the six sites are presented below.

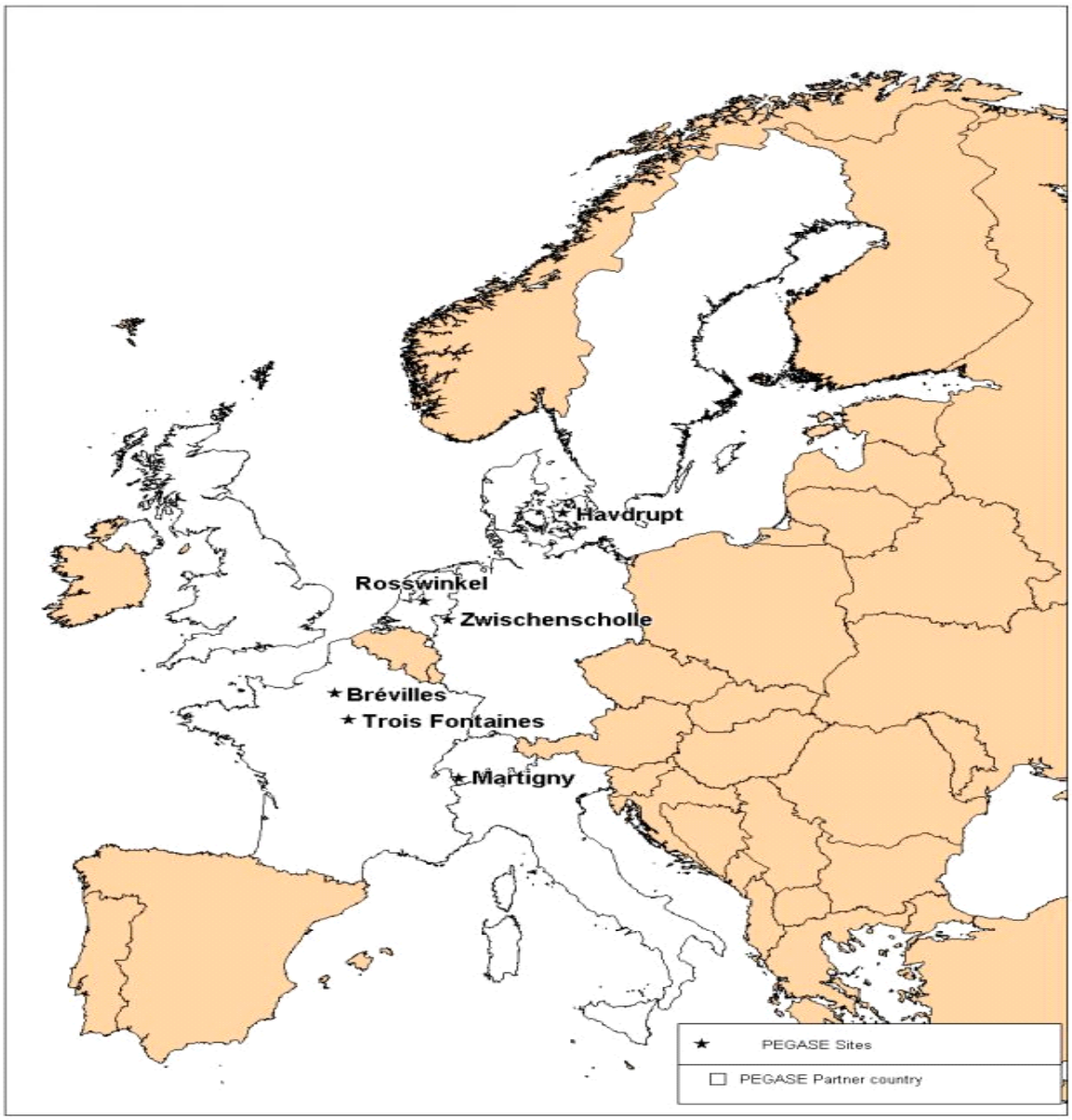


Fig. 1 - Location of the six study sites in Europe.

Table 1 - Summary table showing the main activities undertaken on the six study sites within the scope of PEGASE.

	Brévilles	Les Trois Fontaines	Zwischenscholle	Roswinkel	Martigny	Havdrup
Country	France	France	Germany	The Netherlands	Switzerland	Denmark
Catchment size	3 km^2	50 km^2	21 km^2	-	Study area: 4 km^2	10 ha
Subsoil material	Limestone overlaying a sandy aquifer	Chalk	Sand and gravel	Sandy aquifer	Sandy alluvial aquifer	Clay and sand
Pesticides monitored	Acetochlor and two of its metabolites (ethanesulfonic acid and oxanilic acid), isoproturon and two of its metabolites (monomethyl and didesmethyl-isoproturon), atrazine and two of its metabolites (deethylatrazine and deisopropylatrazine), chlortoluron	isoproturon and two of its metabolites (monomethyl and didesmethyl-isoproturon), atrazine and two of its metabolites (deethylatrazine and deisopropylatrazine), diuron	atrazine and two of its metabolites (deethylatrazine and deisopropylatrazine), simazine, diuron, isoproturon, terbuthylazine	Carbofuran, oxamyl	Atrazine, terbuthylazine, simazine, deethylatrazine, isoproturon, diuron	MCPP, metsulfuron-methyl, prochloraz
Field leaching experiments (root zone)	4 experiments with acetochlor, its metabolites and a tracer on different soil types in contrasted climatic conditions	No	Krauthausen: terbuthylazine, isoproturon, metolachlor and pendimetaline	Yes with carbofuran, oxamyl and a tracer	1 experiment with atrazine, isoproturon and tracers (4 replicated plots)	Yes, with bromide
Monitoring at the catchment outlet	Yes	Yes	No	No	No	No
# of piezometers or boreholes (maximum depth)	7 piezometers (45 m)	Not within PEGASE	350 boreholes (31 m)	83 piezometers (5 m)	13 piezometers (4 m)	80 piezometers (16 m)
Groundwater tracing experiments	Yes	Not within PEGASE	No	Yes	No	Yes
Coring of subsoil material	Yes, to 40 m	Not within PEGASE	Yes	Yes	Yes	Yes
Other activities	Pumping tests Geophysics Tritium measurements Information on land use over the last 20 years					Injection of pesticides in the saturated zone

1. BRÉVILLES [BRGM]

The monitoring site is located at Montreuil-sur-Epte, 70 km west of Paris, on the border of two French regions (Normandy and Ile-de-France). The Brévilles spring was used by the 350 inhabitants of the village for their drinking water supply until atrazine was found in concentrations exceeding legal thresholds and use of the spring was discontinued in 2002. In an effort to reduce contamination of the spring by atrazine, acetochlor, an alternative to atrazine for the control of weeds in maize, was used by farmers on the catchment. First applications of acetochlor in May 2000 coincided with the start of the pesticide monitoring exercise, thereby providing a unique opportunity to study pesticide detections in a context of product substitution. Additional factors supporting the selection of this particular catchment included: i) the expected small size of the hydrogeological catchment (a few km^2); ii) the small number of farmers on the catchment; and iii) the sandy nature of the geological material of the aquifer, which suggested that the aquifer was porous and homogeneous and therefore represented a relatively simple hydrogeological case.

1.1. Material and methods

1.1.1. Catchment characterization

- ***Soils***

A soil map of the catchment was drawn on the basis on 270 auger samples and nine soil pits through collaboration with INRA. Fifteen representative horizons were distinguished based on grain size distribution, percentage of stones and topographic position in the landscape. Hydraulic properties for each of the 15 horizons were determined in the laboratory.

Two experimental plots representing contrasting soil conditions were instrumented over two successive cropping seasons (different plots each year) with TDR and temperature probes to a depth of 1 m to monitor variations in water content and temperature.

- ***Unsaturated zone***

Samples of the unsaturated zone –which was >30 m in some instances– were retrieved during drilling campaigns (8 piezometers and 6 specific drilling exercises). Samples were taken every 50 cm and described from a geological perspective. Tritium measurements were done in four profiles to estimate a mean velocity of water in the unsaturated zone. Hydraulic properties were measured in the laboratory or estimated through the determination of the porosity distribution (mercury injections). Geophysical measurements (Protonic magnetic resonance which allows the location of the top of the water table) were performed throughout the catchment to help building a piezometric map of the area.

- ***Saturated zone***

Eight piezometers, seven of which were situated in the suspected hydrogeological catchment area, were drilled and instrumented. Monitoring took place on a two-weekly

basis from the winter of 2000. Pumping tests in the piezometers provided estimates of the transmissivity of the aquifer, but did not allow the computation of its storage coefficient.

- ***Other data***

The topography, which was known from a 1:25,000 IGN (National Geographic Institute) map, was fine-tuned through field measurements. This supported the building of a Digital Elevation Model with a centimetric precision. A field campaign was made by a geologist to determine the bottom and upper limits of the aquifer. Meteorological data were available from different locations in the vicinity of the catchment. In addition, two rain gauges were installed in the catchment to obtain local rainfall data. A gauging station located 200 metres downstream from the Brévilles spring was installed to estimate the diffuse outlet of the aquifer.

1.1.2. Fate of acetochlor and its main metabolites

- ***Field leaching experiments***

The risk of leaching of acetochlor and its two major metabolites (ethanesulfonic acid, ESA; oxanilic acid, OA) to groundwater was investigated through field leaching experiments in a luvisol and a calcisol/calcasol over two 12-month monitoring periods (agricultural seasons 2000 and 2001).

The experiment was carried out both years on two different 100 × 70 m maize plots (sub-sets of agricultural fields with surface areas >10 ha). Each experimental plot was divided into four subplots. Acetochlor (commercial formulation) was applied at an application rate of 2,000 g/ha prior to emergence by the farmers. This was the first instance that acetochlor had been applied to these fields. An aqueous solution of KBr was sprayed onto the plots a few minutes before application of the pesticide to allow the tracing of water movement through the soil. Forty aluminium cups were placed in each plot to determine the heterogeneity of the bromide and pesticide applications.

Soil cores were collected before application of the herbicide and six or five times after application in 2000 and 2001, respectively. Four replicates were taken from each subplot during each sampling, thus giving a total of 16 cores per plot per sampling. Sampling was carried out using a 10-cm-diameter percussion corer to a depth of 1.0 m or less. The presence of a shallow limestone substratum prevented the coring to 1-m depth in some instances. The cores were sent to the laboratory. Outer layers were removed and the resulting cores were cut into segments corresponding to depth intervals of 0-5, 5-10, 10-20, 20-30 cm, etc. Each sample was dried at 40 °C for 3 days then ground to 2 mm. A composite sample was made for each layer by mixing equal weights of the 16 individual samples. This composite sample was used for pesticide determinations whereas analyses for bromide were done on each of the 16 individual samples.

1.1.3. Water quality monitoring

Sampling campaigns were conducted on a monthly basis in seven piezometers from March 2001 and twice a month at the spring from October 1999. Atrazine, DEA, DIA,

isoproturon and its metabolites (monomethyl/didesmethyl-isoproturon), chlortoluron, acetochlor and its metabolites (ESA and OA) were analysed. Sampling in the piezometers was done after pumping to allow the stabilisation of physico-chemical parameters of the groundwater such as pH and conductivity.

Major anions and cations were analysed at the same time as pesticides. This information can be used to help identifying mechanisms leading to aquifer recharge.

1.2. Results

1.2.1. Hydrogeologic basin

Delineation of the geometry of the aquifer was based on geophysical and geological data. The hydrogeologic basin of the spring was determined on the basis of:

- geophysical investigations using Protonic Magnetic Resonance;
- a substratum map (the structure of the anticline was studied in detail for a gas storage project in 2001);
- and a piezometric map.

Montreuil-sur-Epte is located on the left bank of the Epte Valley, at the foot of a tilted plateau composed of tertiary material: a carbonaceous formation from Lutetian age, locally overlaid by lacustrine limestones and sandstones from Bartonian age. Quaternary sediments are present in the form of silts on the plateau and colluvions at the foot of hills.

The spring basin is part of a plateau, tilted westwards, which forms an independent hydrogeological system, delineated on the western side by the Epte Valley, on the north and south by two tributaries of the Epte River, and on the east by a crest line.

The top of the Sparnacian clays is showing a depression, centred 1 km SE of Montreuil, *i.e.* approximately 500 m south of the hydrometric station. Within the hydrogeological basin, the dips of the layers converge towards this depression. The fault system breaks the slope on the west flank of the anticline.

The top of the Cuise sands shows the same pattern. The bottom of the Lutetian formation is not an impervious layer, although it may be semi-pervious by places, where green clays are accumulated.

The hydrogeological basin is limited by a fault, direction NW-SE, on its eastern boundary. The throw of this fault being around 20 m, the upper compartment raises sparnacian clays in front of Cuise sands, thus constituting a hydrogeological barrier.

A 50-year series of rainfall data was obtained by aggregating data from Beauvais (45 km north of the basin; 1950-1988), Bray-et-Lû (5 km south of the basin; 1988-2001), Buhy (250 m to the north of the basin; 1993-2001) and two local rain gauges. The 15-year annual average rainfall (01/10/88-30/09/02) was 762 mm/year. There was 113 days of rainfall per year on average over the same period. The largest rainfall event occurred on 26 July 2001 (47.2 mm).

The discharge measured at the spring was corrected for surface runoff. It should be noted that surface runoff was low due to high retention capacity of a number of soils. Moreover, most of the runoff is intercepted by roads which carry runoff water out of the basin.

- ***Soils***

A highly detailed soil map with a total of 25 classes was built (Fig. 2). A simplified soil map with four classes was also drawn for modelling purposes. The simplified classes were Luvisol (the deepest soils), Calcosol and Calcisol (shallower stony and calcareous or calcic soils) and Colluvisol (remanied soils). The dominant units in the area were Luvisol and Calcosol/Calcisol. Luvisols hold soils whose dominant characteristic is a marked textural differentiation within the soil profile, with the surface horizon being depleted of clay and with accumulation of clay in the subsurface. The Reference Soil Group of the Calcisols accommodates soils in which there is substantial secondary accumulation of lime. Calcisols are common in calcareous parent materials.

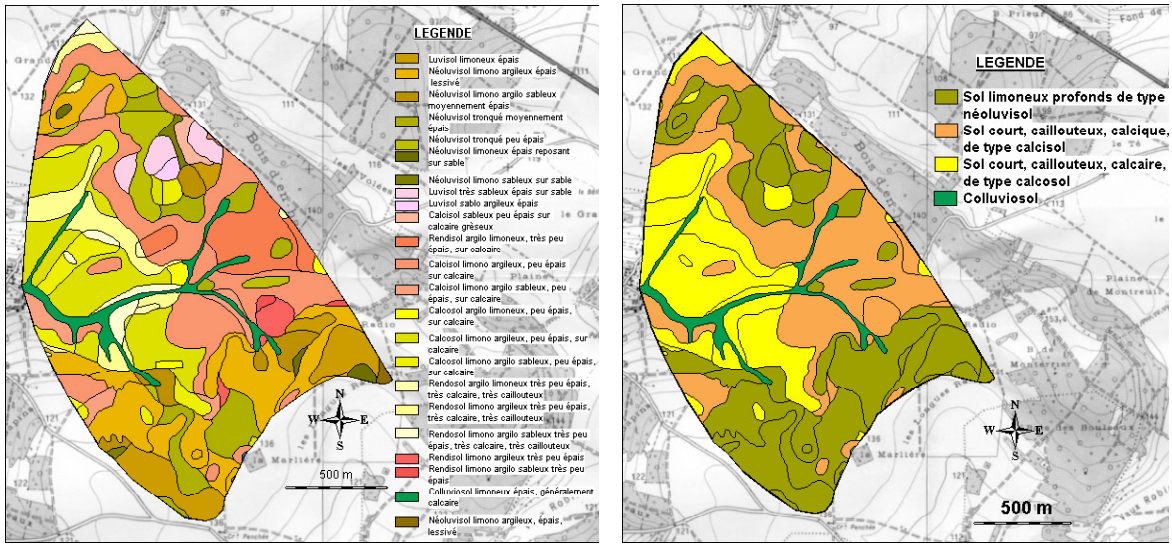


Fig. 2 - Soil maps for the Brévilles catchment (left: comprehensive; right: simplified).

- ***Unsaturated zone***

Some of the water retention curves obtained for unsaturated materials (Lutetian limestone) showed a high variability between triplicates and between samples from different depths (Fig. 3). The velocity of the water could thus vary significantly within a given vertical profile and between several points located throughout the basin.

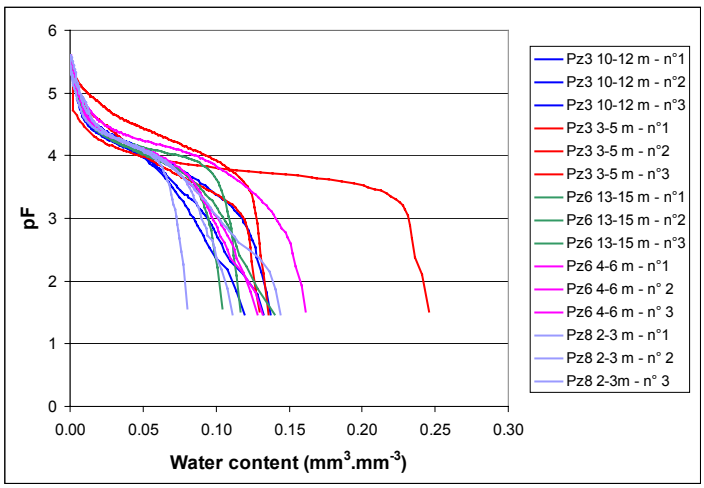


Fig. 3 - Examples of water retention curves obtained for some limestone samples.

Tritium profiles showed various shapes (Fig. 4). Some profiles (Pz3 and 5) consisted of a unique and rather symmetrical peak, while others (Pz2 and 6) showed several peaks.

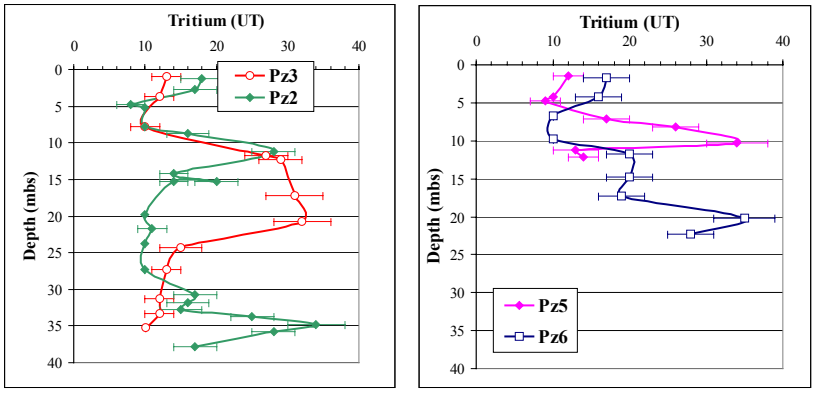


Fig. 4 - Tritium profiles obtained for the unsaturated zone of 4 piezometers.

- ***Saturated zone***

Pumping tests provided estimates of the transmissivity values of the aquifer (Table 2). Values in the vicinity of the spring were larger by about an order of magnitude compared to those estimated for the upstream area.

Table 2 - Transmissivity values for the eight piezometers.

	Pz2	Pz3	Pz4	Pz5	Pz6	Pz7	P8
T (m^2/s)	$2.\ 10^{-4}$ to $6.\ 10^{-4}$	$3.\ 10^{-4}$ to $4.\ 10^{-4}$	$1.5\ 10^{-3}$ to $2.5\ 10^{-3}$	$2.\ 10^{-3}$	10^{-3} to $1.3\ 10^{-3}$	$4.\ 10^{-3}$	$4.\ 10^{-3}$

For a specific piezometer, the permeability appeared to be higher in the upper part of the aquifer compared to the lower formations.

Piezometric heads in the piezometers have increased continuously since February 2001 (Fig. 5). Variations reached 1.4 m in the upper part of the basin and ca. 20 cm near the spring. The increase was particularly marked at the beginning of the study (between February and September 2001).

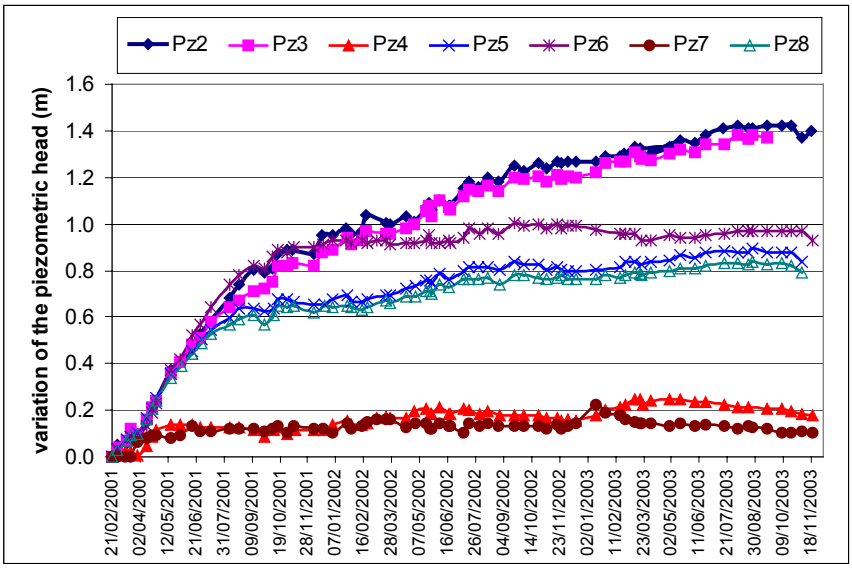


Fig. 5 - Variation of the piezometric head in the various piezometers since February 2001.

1.2.2. Fate of acetochlor and its main metabolites

In the field leaching experiments, degradation products were detected in the soil samples very soon after application in both years (acetochlor dissipation constants were less than 7 and 5 days in 2000 and 2001, respectively), indicating a rapid onset of acetochlor degradation. Acetochlor was still detected 344 days after application although it should be noted that < 1 % of the dose applied was present as the parent in the soil profile after a few months. Acetochlor and its two metabolites were detected below the 0-10 cm surface horizon in both soils and years.

The amounts recovered, expressed as percentages of the average applied dose of acetochlor, were determined for acetochlor, ESA, OA and the sum of all three compounds over the first 70 cm of the profile. Concentrations below the limit of quantification were taken as zero. The ratio between ESA and OA varied with time and the soil considered (data not shown). Acetochlor metabolites were found to be more persistent in 2001 than in 2000 (Fig. 6).

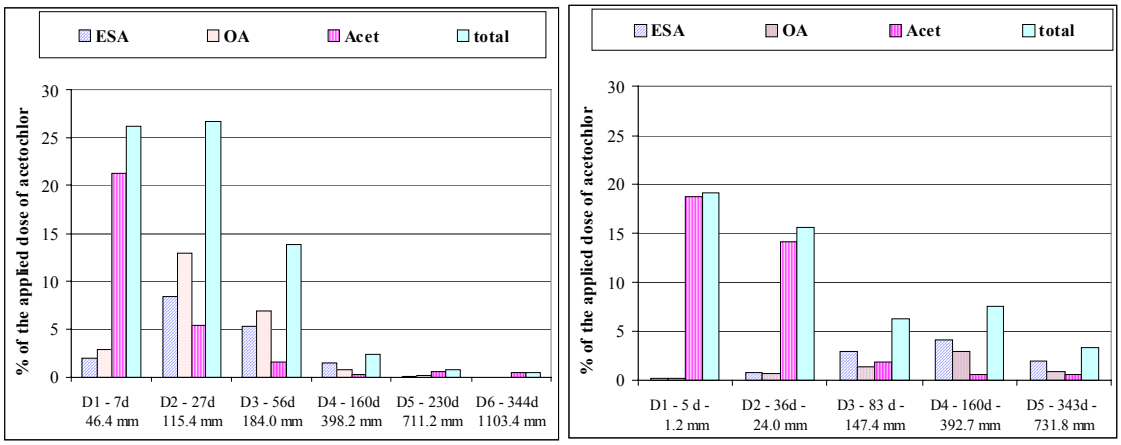


Fig. 6 - Recovery rates (expressed as a % of the average applied doses acetochlor) of ESA (ethanesulfonic acid), OA (oxanilic acid), acetochlor (Acet) and total ESA+OA+Acet in the luvisol on dates (days after application) corresponding to different cumulative rainfall values for 2000 (left) and 2001 (right).

1.2.3. Water quality

Atrazine and deethylatrazine were systematically detected at the spring even though the last application of atrazine in the catchment occurred in April 1999. The time series of concentrations at the spring (Fig. 7) showed significant variations of atrazine and deethylatrazine concentrations over rather shorts periods of time especially at the beginning of the study. Isoproturon and chlortoluron were detected on a few occasions only and detections were made at the time of application (end of February).

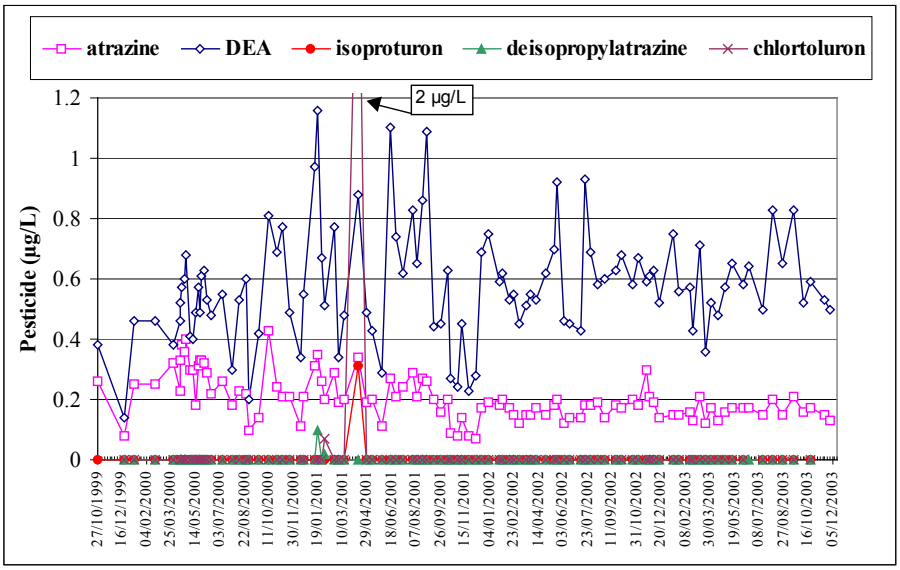


Fig. 7 - Time series of pesticides concentrations (µg/l) in water from the Brévilles spring.

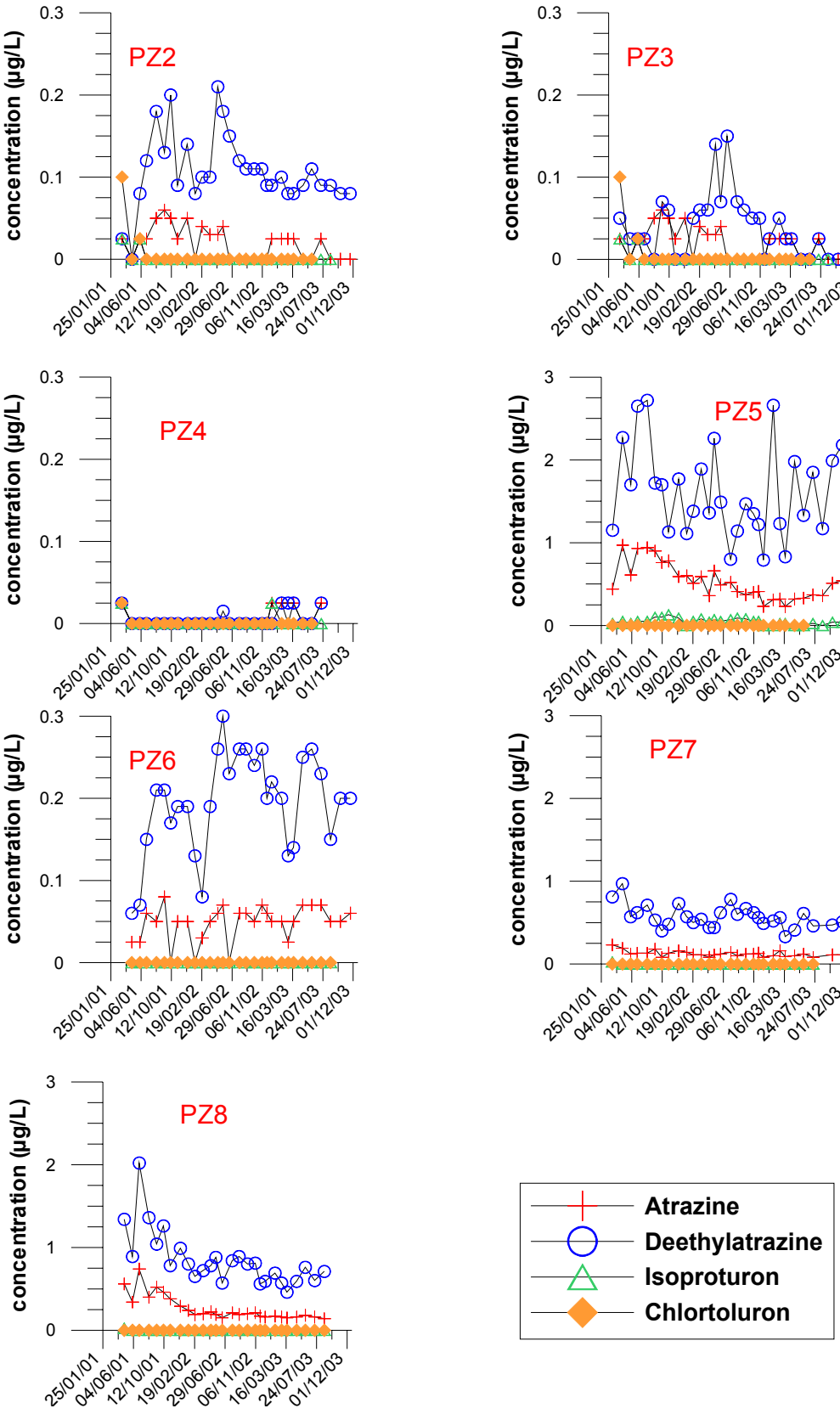


Fig. 8 - Time series of pesticides concentrations in 7 piezometers sampled monthly since February 2001.

Pesticides concentrations were found to be very variable between the various piezometers. For instance, no detection was made in Pz4 whereas concentrations up to several µg/l were noted in Pz5. Trends were found to vary between the different piezometers.

To date, acetochlor and its two metabolites have not been detected in groundwater except in one sample at the spring and one in a piezometer. Concentrations were very low and these detections could not be confirmed after a second analysis.

1.3. Discussion

1.3.1. Functioning of the catchment

The very rainy period in 2000 and the very dry and hot period which started in the spring of 2003 had little impact on the flow and the piezometric levels. The small variations noted in the spring flow and the lack of significant change in piezometric heads are typical of buffered environments, the unsaturated zone acting as a big reservoir.

Even though the limestone is highly fractured, a high fraction of water could be slowly transferred to the groundwater. The tritium data confirm this hypothesis as several peaks were detected in the unsaturated zone, which is a good indication of very heterogeneous infiltration rates. The hydrodynamics of the system are hence more complex than initially anticipated. A simplified model of the system would be difficult to obtain given the significant heterogeneity in soils and in the subsoil.

1.3.2. Fate of pesticides

Monitoring of acetochlor and its metabolites ESA and OA was undertaken in a luvisol and calcisol during two 12-month monitoring periods. The rapid onset of degradation observed in situ was confirmed by the laboratory experiments on both soils. This result is in agreement with literature data (Feng, 1991; Vaughan *et al.,* 1999). The rapid dissipation of acetochlor and its two metabolites suggests the occurrence of leaching, secondary degradation and the formation of bound residues. It is however impossible to determine the relative magnitude of each of these processes with precision. Still, the greater persistence of the three products in 2001 could be due to reduced leaching resulting from smaller rainfall and higher potential evapotranspiration in 2001 compared to 2000.

Significant improvements in the lowering of detection limits for these three compounds compared to typical levels of detection reported in the literature have enabled a much more detailed follow-up of the fate of these products, especially in the deeper soil layers. Leaching of the parent molecule and its metabolites ESA and OA was demonstrated by their detection in the deeper layers. This observation is in contradiction with previous works (Konda & Pásztor, 2001), but confirms the hypothesis suggested by Balinova (1997) and Zheng & Ye (2002) that acetochlor has the potential to be leached to groundwater. Although acetochlor has been detected in groundwater (Kalkhoff *et al*., 1998; Kolpin *et al*., 1998) and, in some cases, the first year of application (Kolpin *et al*., 1996), acetochlor was not detected at our site. Possible

reasons for non-detection include: i) the presence of acetochlor concentrations lower than the limit of detection due to fast degradation and the limited part of the catchment which was treated (<10 %); ii) the distance between areas of application and the spring (all the plots treated are located in the upstream of the catchment); iii) the fact that the time for acetochlor to be transferred to groundwater resources may be larger than the 3-year PEGASE monitoring period.

The systematic detection of atrazine and deethylatrazine suggests the existence of a stock of these compounds in the soil and/or in the unsaturated zone with regular releases in response to water infiltration. The marked peaks at the beginning of the time series (until December 2001) corresponded to very rainy period which have probably induced high recharge events. Although atrazine has not been applied to the site since 1999, the compound and its metabolites are likely to be still detected in the years to come given i) the persistence of the parent compound; ii) likely stocks in the soil and/or in the unsaturated zone; and iii) the slow hydrological response of the aquifer. This result is in agreement with observations reported by Tappe *et al.* (2002) concerning several aquifers in Germany.

1.4. Summary

The catchment of the Brévilles spring was studied in detail in terms of soil, geology and hydrogeology. Water levels and pesticide concentrations were monitored at the spring and in seven piezometers over a three-year period. In addition, two leaching experiments were undertaken over two 12-month monitoring periods in contrasting soil types to study the fate of acetochlor in soil. Results suggest that the hydrogeological nature of the catchment is more complex than anticipated. The high variability in soils and the subsoil mean that the system cannot be easily simplified. Results of the pesticide monitoring activities suggest that atrazine and its metabolites are likely to be detected at the spring for a significant amount of time even though the last application of the compound on the catchment occurred in 1999.

2. LES TROIS FONTAINES [BRGM]

The study site referred to as “Les Trois Fontaines” is located at Saint-Loup-de-Gonois, 120 km south-east of Paris. The main outlet of the catchment is a group of springs tapped for the adduction of several villages. The catchment has been studied for several years before the PEGASE project was initiated and the limits of the catchment and the hydrodynamic functioning are fairly well-known. Previous studies have shown a contamination of the aquifer by pesticides (triazines in particular). The geological material is chalk, which is abundant in France and other European Countries (*e.g.* in the UK). Selection of this particular catchment was based on: i) the earlier investigative work carried out; ii) the large size of the catchment (50 km^2); iii) the nature of the aquifer material; and iv) the established contamination of the water resource.

2.1. Material and methods

2.1.1. Flow at the spring

A new gauging station was installed in November 2000 to measure the flow leaving the catchment. A Venturi channel of 15 m length was built to provide a laminar flow and obtain reliable measurements. Calibration of the new equipment was carried out using manual gauging readings. An automatic data logger allowing the collection of hourly data was also installed. The site was visited once a month to check the installation. Contacts were established with the water company utilising the spring to correct readings for volumes pumped.

2.1.2. Piezometric map

An extensive measurement campaign was carried out in March 2003 to establish a new piezometric map of the catchment. This particular period was selected on the basis of the monitoring of water levels in a well located in the middle of the catchment (Fig. 9). The period corresponded to high water levels which had not been observed for several years. A total of 201 data points were collected throughout the catchment which provides a thorough coverage of the catchment.

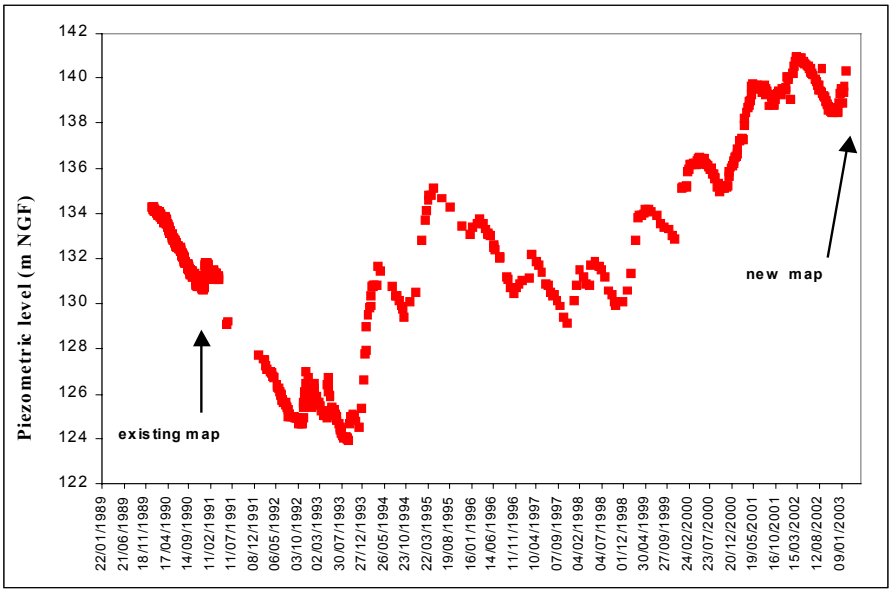


Fig. 9 - Piezometric levels observed weekly in a well located in the middle of the Trois Fontaines' catchment.

2.1.3. Pesticide concentrations

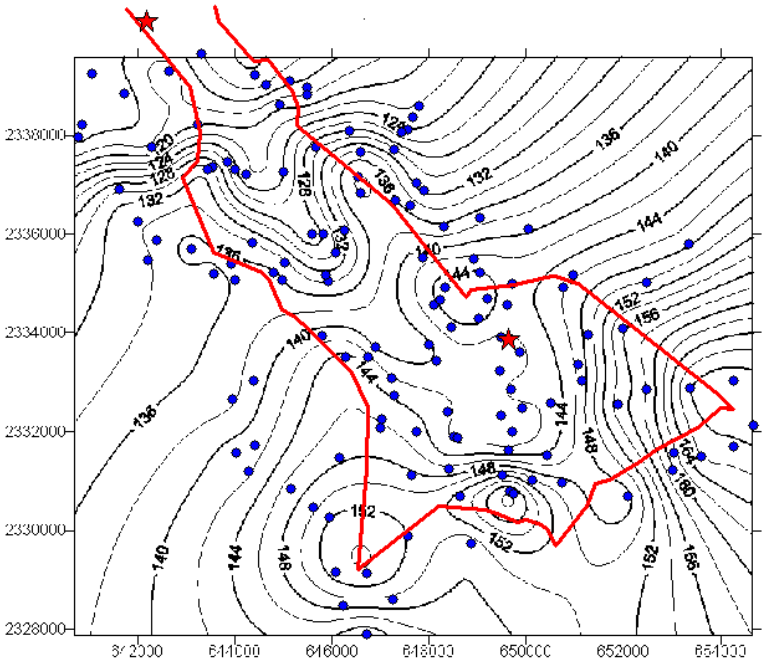
Sampling campaigns were conducted at least three times per month at the spring from March 2000. Atrazine and its metabolites (DEA, DIA), isoproturon and its metabolites (monomethyl/didesmethyl-isoproturon) and diuron were analysed in the samples. Sampling occurred directly at the spring without resorting to any pumping. Major anions

and cations were also analysed in the samples and act as indicators to identify mechanisms responsible for the recharge of the aquifer (Lasne, 1992; Baran, 1999).

2.2. Results

2.2.1. Hydrogeologic basin

Measurements of piezometric levels in 201 locations throughout the catchment allowed the drawing of a detailed piezometric map (Fig. 10). A clear drainage axis corresponding to areas with high permeability could be identified on the map. These areas are typical of karstic areas. Zones of higher piezometric levels corresponding to regions of the aquifer with low permeability constituted the limits of the basin.



(blue dots correspond to real measurements; the red line indicates the limits of the basin; the red star in the upper left corner of the figure indicates the Trois Fontaines spring which is the outlet of the catchment; the red star in the middle of the figure indicates the well where piezometric levels have been monitored on a weekly basis).

Fig. 10 - Piezometric map established in March 2003.

The piezometric levels measured in March 2003 were compared to those measured in September 1990. The differences are reported in Figure 11. Differences varied from a few centimetres to a maximum of 10 metres depending on the location in the catchment. In general, the largest variations were observed in areas with a high permeability. Conversely, the lower variations corresponded to areas with a low permeability.

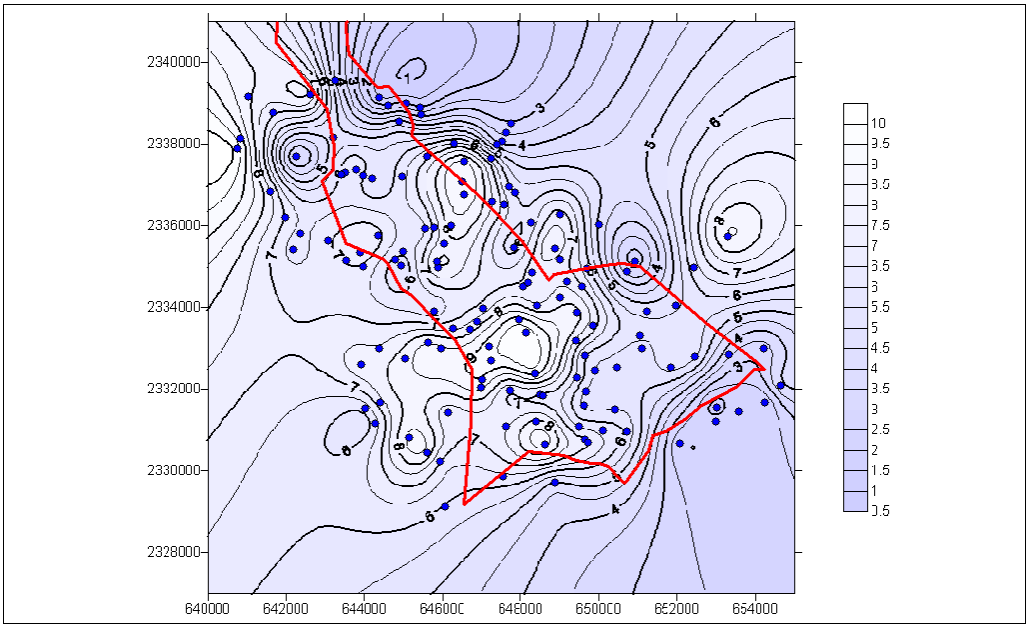


Fig. 11 - Variations of the piezometric level (in meters) between September 1990 and March 2003.

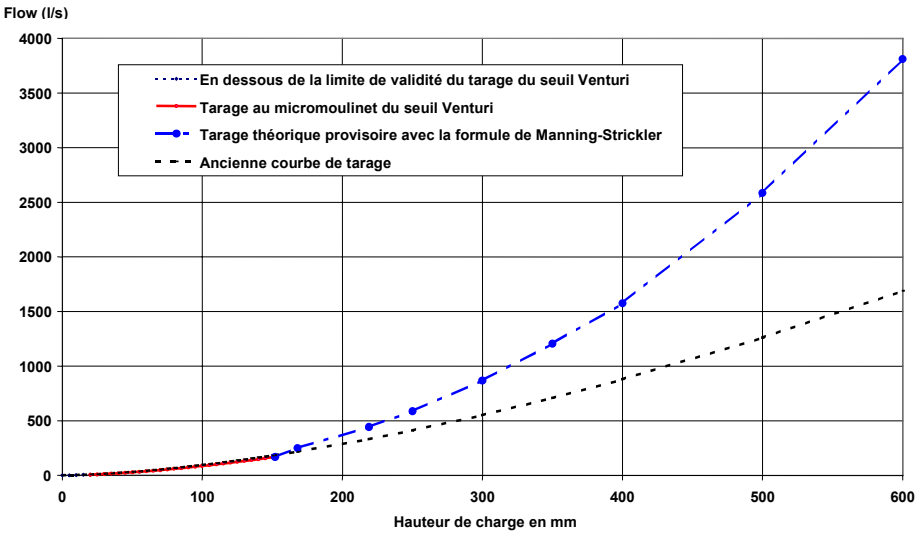


Fig. 12 - Calibration of the relationship between hydraulic head and flow in the Venturi channel. The old calibration curve is in black while revised curves are in red and blue.

Manual checks on the automatic gauging station revealed two malfunctions. First, a time drift was noted and after 3 years, the time-lag between the real time and the time registered by the device was 2.25 hours. Secondly, a drift in the measurements themselves was observed. Corrections to the values recorded cannot be easily implemented as the drift is not constant and non linear.

Several manual gaugings were made to verify and modify the calibration curve deducted from the geometry of the sill and the Ventury channel. The shift was found to be rather large for flow values exceeded 250 l/s, but this range of values was rarely observed at the spring.

2.2.2. Pesticide concentrations

The concentrations of pesticides in the spring are presented in Figure 13. Diuron was never detected in the first year and the analysis for this compound was therefore discontinued in the rest of the study. Diuron was not used by the farmers on this catchment, but by a petroleum company which weeded several metres of concrete around their wells. Deisopropylatrazine was detected in a few samples only (5 and 10 March 2003, 6 and 15 October 2003) and the small concentrations involved prevented quantification. In contrast, atrazine and deethylatrazine (DEA) were almost always detected. The average concentrations were between 0.05 and 0.1 µg/l for atrazine and > 0.1 µg/l for DEA. Isoproturon was detected in several samples, usually during the winter. The compound was also detected at the beginning of the spring. Values in excess of 0.1 µg/l were sometimes observed.

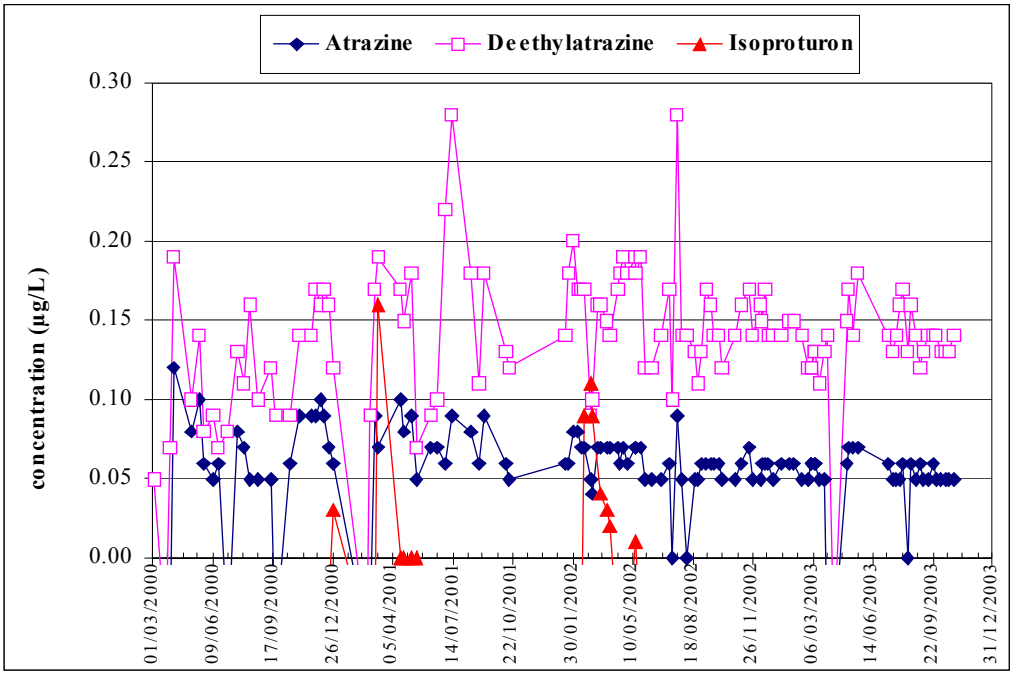


Fig. 13 - Time series of pesticides concentrations (µg/l) in the Trois-Fontaines' spring.

2.3. Discussion

2.3.1. Functioning of the catchment

The new piezometric map confirmed that i) the limits of the catchment which has a size of 50 km^2, ii) groundwater flow routes have developed independent of surface topography, iii) areas with different hydraulic gradients resulting from permeability

differences exist in the catchment. A clear drainage axis was noted from the upstream to the spring (SE-NW direction). This axis corresponds to an area in which the water flow is increased in response to significant chalk dissolution. Previous dye tracing tests have shown velocities of several metres per hour in some parts of the saturated zone (Lasne, 1992), which is in line with the present observations. At the opposite, the piezometric hills display a lower permeability due to a limited dissolution of the chalk.

Compared to 1990, the piezometric levels in 2003 have increased from a few decimetres (0.5 m) to several meters (10 m) depending on the location in the catchment. The largest increase corresponded to areas with high permeability.

The hydraulic functioning of the catchment may have changed in a matter of 13 years in response to the rise in piezometric levels. Some features (limits of the basin, drainage axis) were found to be identical while others (*e.g.* piezometric levels) changed significantly in particular locations. Groundwater may follow two distinct flow paths in karst formations (diffuse and channelled transport). The ratio between these two types of flow may have been altered between the two study periods. It should be noted that this would affect the transport of contaminants as well. Some flow channels may be further activated by the increased piezometric level.

2.3.2. Pesticide fate

Time series of isoproturon, atrazine and deethylatrazine were significantly different (Fig. 13). Isoproturon was detected in a few samples only while atrazine was almost always detected. It is interesting to note that the quantities of isoproturon applied on the catchment are theoretically larger than those of atrazine, maize and cereals representing 15 and 50 % of the cropped area, respectively. Differences may therefore be attributed to differences in physico-chemical properties between the two compounds. Atrazine is known to be more persistent than isoproturon. The minimum and maximum DT50 values are 38-170 and 12-33 days for atrazine and isoproturon, respectively (Agritox, 2001). Moreover the potential for sorption is somewhat larger for isoproturon compared to atrazine (observed range for Koc: 38-170 l/kg for atrazine; 36-241 l/kg for isoproturon). Trends in sorption and degradation for the two compounds may explain the higher mobility of atrazine. Pasquarell & Boyer (1996) have distinguished several categories of pesticides on the basis of time series of concentration measured at a karstic spring. They concluded that difference in leaching potential due to specific pesticide properties have a strong influence on pesticide detections and concentrations.

The hydrodynamic conditions may also have a significant influence on the shape of the time series of concentrations. Rapid flow through fissures in the chalk can transport water quickly directly to the spring. This fast moving water is likely to contain pesticides at concentrations exceeding those for the more diffuse flow. Even if the volume of rapid flow is low compared to the diffuse flow, these fast inputs are likely to lead to peaks in the time series of concentrations. Contribution of this fast flowing channelling resulted in the detection of isoproturon at the spring in response to the first rainfall events following application.

The phenomenon was less obvious for atrazine as the signal of the compound is likely to be more continuous. Pesticides peaks have been observed during discharge events in other karstic systems (Libra *et al.,* 1987). The authors attributed the peaks to surface

water runoff and rapid flow through fissures. The systematic detection of atrazine and DEA can be explained by a greater persistence of atrazine and suggests that pesticides can be transported by diffuse flow (and not exclusively through fissure flow).

The high variability in the measured concentrations justified the use of a high spatial and temporal resolution monitoring of water and pesticide fluxes, as suggested by Ryan & Meiman (1996).

2.4. Summary

Data on water and pesticide fluxes were collected at Les Trois Fontaines within the scope of PEGASE. These data together with those collected within the scope of earlier studies at the site constitute a rather unique dataset. Pesticides detections and concentrations in the spring water were found to be dependent on the specific physico-chemical properties of the compounds and on the hydraulic functioning of the catchment. Rapid flows through high velocity areas resulting from the dissolution of the chalk lead to large concentrations of isoproturon at the spring when significant rainfall events were encountered shortly after application. In contrast, atrazine was detected throughout the year. The more continuous signal observed for this compound was attributed to diffuse flow, in contrast to isoproturon for which channelled flow was assumed to be dominating. The high variability in water and pesticide fluxes on the catchment justifies the adoption of a high spatial and temporal monitoring campaign.

3. ZWISCHENSCHOLLE [FZJ]

The Jülicher 'Zwischenscholle' test area (21 km^2) is located in North Rhine – Westfalia (Germany). It is situated in the Lower Rhine Embayment. The Lower Rhine Embayment is divided into several parts by mainly southeast-northwest directed faults. The 'Zwischenscholle' area is bounded by the Rurscholle on the southwest and the Erftscholle on the northeast. The bounding faults are called Rurrand fault and Rursprung. The Zwischenscholle area is lowered against the Erftscholle, but lifted against the Rurscholle. The area is characterized by forest and agricultural land use (Fig. 14). The western part, which includes the FZJ research centre area, is mainly covered by deciduous forest. The eastern part is dominated by agricultural land use. The typical crop rotation is sugar beet - winter wheat. Minor crops are maize, potatoes and oat. Urban regions in the area are small villages (Stetternich, Hambach, Niederzier, Krauthausen and Selgersdorf), a network of smaller or larger motorways and the area of the research centre.

The first (unconfined or semi confined) aquifer consists of Quaternary Rhine and Maas sand and gravel sediments (Klosterman, 1992). The base of the aquifer is built by the Reuver clay. The aquifer thickness varies from a few meters in the southwest to 35 m in the northeast. The main groundwater flow direction is from southwest to northeast. The first aquifer is in direct contact with small local creeks and the Rur river. Regions with leakage effects from the lower confined aquifer (between 45 and 120 m thick) are found on the Rurrand fault. The Rurrand fault is assumed to be a natural no flux boundary, whereas the Rursprung fault shows a hydraulic connection between the Zwischenscholle area and the Rurscholle area. The southern part of the area is used

by the research centre for the pumping of drinking water from shallow wells. For this purpose, two water supply wells are used. The total amount of water withdrawn by these two wells is 33,000 m^3/y.

The following text describes the pre-processing of the input data collected at the site to generate a dataset for the modelling of pesticide fate on the 'Zwischenscholle' test site. The main focus is on the calculation of the potential evapotranspiration, on the application of pedotransfer functions to derive the soil hydraulic properties and on the spatio-temporal interpolation of groundwater levels used as vertical boundary conditions. Concentrations of five pesticides (atrazine, simazine, diuron, isoproturon and terbuthylazine) monitored in wells prior and during the PEGASE project were included in the dataset.

3.1. Material and methods

To calculate daily evapotranspiration, daily time series of radiation, air temperatures, air humidity, wind speed and precipitation were obtained for the period 1/12/1983-31/11/1993. All of these parameters were measured at the meteorological tower in the UFZ research centre. Potential evapotranspiration was calculated using the FAO Penman/Monteith approach (Smith *et al.*, 1996). Not all parameters were available during some periods and the simplified approaches of Makkink or Hamon were used in these instances to complete the time series on potential evapotranspiration.

In order to derive the soil hydraulic parameters from the textural properties and porosity of the 1:5,000 soil map, the pedotransfer functions (PTF) of Rawls & Brakensiek (1985) were used. Because these PTF calculate the parameters according to the Brooks and Corey approach, the pore size index λ [-] and the bubbling pressure Ψ_b [L] were transformed to the Mualem/Van Genuchten (Van Genuchten, 1980) parameters n [-] and α [cm^{-1}] by using the following relationships:

$$\alpha = \psi_b^{-1}$$
$$n = 1 + \lambda$$

In order to take the coarse fraction (> 2 mm) into account, PTFs of Brakensiek & Rawls (1994) were also applied. The volumetric coarse fraction Z_2 [L^3 L^{-3}] was first calculated from the density of quartz ρ_s [M L^{-3}], the dry bulk density of the soil ρ_b [M L^{-3}] and the gravimetric coarse fraction Z_1 [M M^{-1}]:

$$Z_2 = \frac{\rho_b}{\rho_s Z_1}$$

The modification of the volumetric water contents (θ_s and θ_r) according to the volumetric coarse fraction is given by:

$$W_{vt} = W_{v<2}(1 - Z_2)$$

where W_{vt} [L^3 L^{-3}] is the modified water content of the total soil and $W_{v<2}$ [L^3 L^{-3}] is the water content of the soil matrix only. The saturated hydraulic conductivity of the soil K_s

[L/T] influenced by the coarse fraction is calculated from the gravimetric coarse fraction and the saturated hydraulic conductivity of the matrix K_m [L/T]:

$$1 - Z_1 = \frac{K_m}{K_s}$$

The relation between porosity ϕ [L^3 L^{-3}] and bulk density is given by:

$$\phi = 1 - \frac{\rho_b}{\rho_s}$$

This relation was used to calculate the porosity from the bulk density classes of the 1:5,000 soil map.

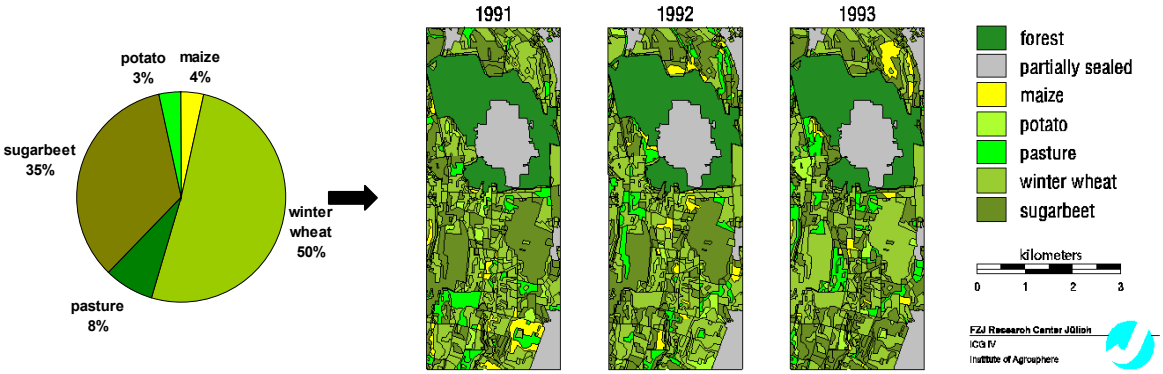
A temporal interpolation was initially carried out to calculate the groundwater levels which are necessary for the definition of the vertical boundary conditions. For a fixed time step interval of 30 days, the groundwater level of every available well was linearly interpolated from the measurements of available dates. In a second step, the spatial interpolation for the 30-day intervals was done using the point dataset generated from the temporal interpolation by applying the inverse distance weighting method (IDW). The output was a raster of the groundwater levels at the grid size chosen for the hydraulic model. The last step was the extraction of the grid cells relevant for the boundary conditions.

Interviews with farmers were carried out to generate information on the spatial distribution of land use in the test area. As this did not provide a complete map of land use for each year, a stochastic distribution approach was adopted. The land use fraction of every crop was first calculated from the interview data. The land parcel boundaries were then digitized and the forest and built up areas (partially sealed surface) were identified. The land use of these areas was fixed for the whole period 1983-1993. The remaining area (arable land) was used for the stochastic spatial distribution of crops which reproduced the calculated land use fractions.

3.2. Results

Figure 14 shows the results of the procedure used for generating stochastic spatial distribution of crops for the period extending from 1991 to 1993. The interviews with the farmers were also used to fix the dates of sowing, harvest and pesticide applications. The rate of application for every compound was taken from the guidelines provided by the local farmers authority. The timing and amount of application was thus linked to the land use, which was stochastically generated.

Figure 15 shows the spatial distribution of soil types on the ‘Zwischenscholle’ test site. Every spatial unit was attributed to one of the 122 representative soil profiles. Even for the areas with ‘no soil type’, data on texture, organic carbon and coarse fraction was available for pedogenetic soil horizons. For these areas, a single soil type could not be attributed during the soil survey due to the heterogeneity of soils in this spatial unit.



The diagram on the left shows the average fraction of the crops between 1983 and 1993, the right side shows the stochastically generated land use maps for 3 years.

Fig. 14 - Spatial distribution of crops.

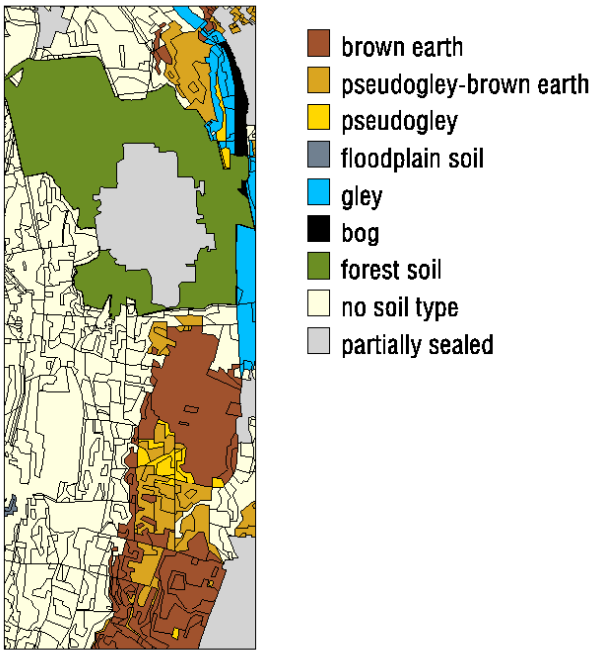


Fig. 15 - Soil map at 1:5,000 according to the German soil classification.

The results of the PTFs are shown in Figure 16. Mualem/Van Genuchten parameters were derived for every horizon of the representative soil profiles. The broad range of soil hydraulic properties is visible, although loamy textured soils predominate, resulting in a rather slow decrease of soil moisture with decrease in pressure head and moderate air entry values. The low saturation water contents are mostly found at the bottom of the soil profiles due to large amounts of coarse fractions (gravel). The saturated hydraulic conductivities cover a range of roughly four orders of magnitude.

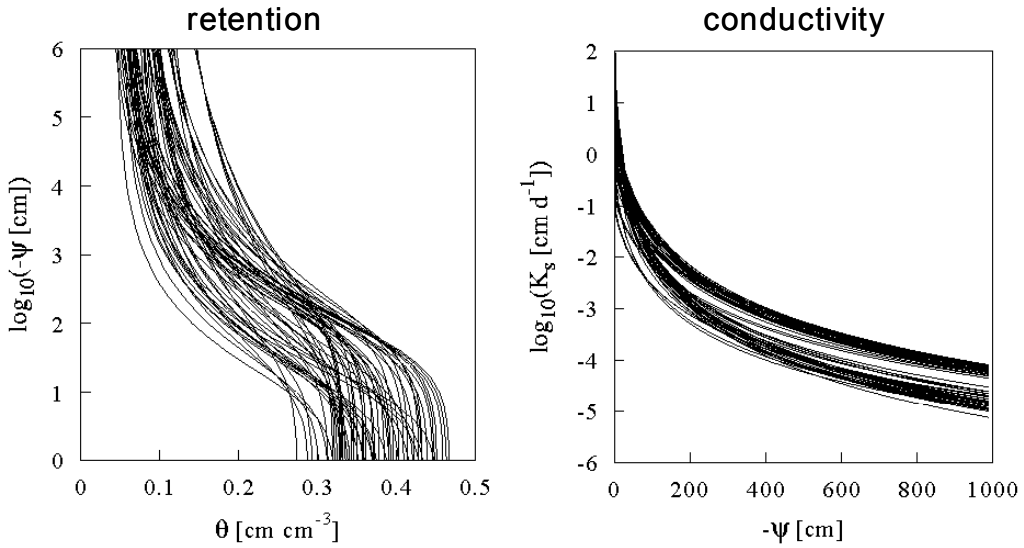


Fig. 16 - Conductivity and retention functions according to Mualem/Van Genuchten (Van Genuchten, 1980) for the 293 horizons of the 122 soil profiles.

For the estimation of the hydrogeological situation, data of about 350 boreholes were analysed. These data were used to calculate mean properties of the aquifer, such as porosity and saturated hydraulic conductivity. In addition, the borehole data were used to define the position of soil and aquifer layers necessary for the model geometry. The base of the uppermost aquifer is the Reuver clay. This aquifer base was interpolated from the point data on boreholes (for details on this procedure; see Jahn, 2002).

As shown in Figure 17, the base of the upper aquifer is closer to the surface near the river Rur (cross section AA'). In the north-western direction, the main trend is also an increase of aquifer thickness (cross section BB'). The geometry of the upper boundary was given by a digital elevation model.

An example of an interpolated groundwater level is given in Figure 18. The main groundwater flow direction is northwest. This groundwater level calculated for the first date at the beginning of the simulation period was taken as initial condition for the hydraulic model after spatial transformation.

The mean precipitation measured at the meteorological tower for the model period 12/1983-11/1993 was 712 mm/y. Single events were up to 55 mm/d (see Fig. 19). The mean of potential evapotranspiration for the simulation period was 559 mm/y. The occurrence of negative potential evapotranspirations (see Fig. 19) was linked to the method used for their estimation. Only the Penman/Monteith approach yielded negative potential evapotranspiration due to negative radiation balances. In these instances, the process of evapotranspiration is reverted and thawing occurs. The amounts of thawing were rather small and insignificant in terms of annual water balances. With regard to long-term water balance, the mean difference between precipitation and potential evapotranspiration on an annual basis is 153 mm/y, which can be taken as the minimum groundwater recharge.

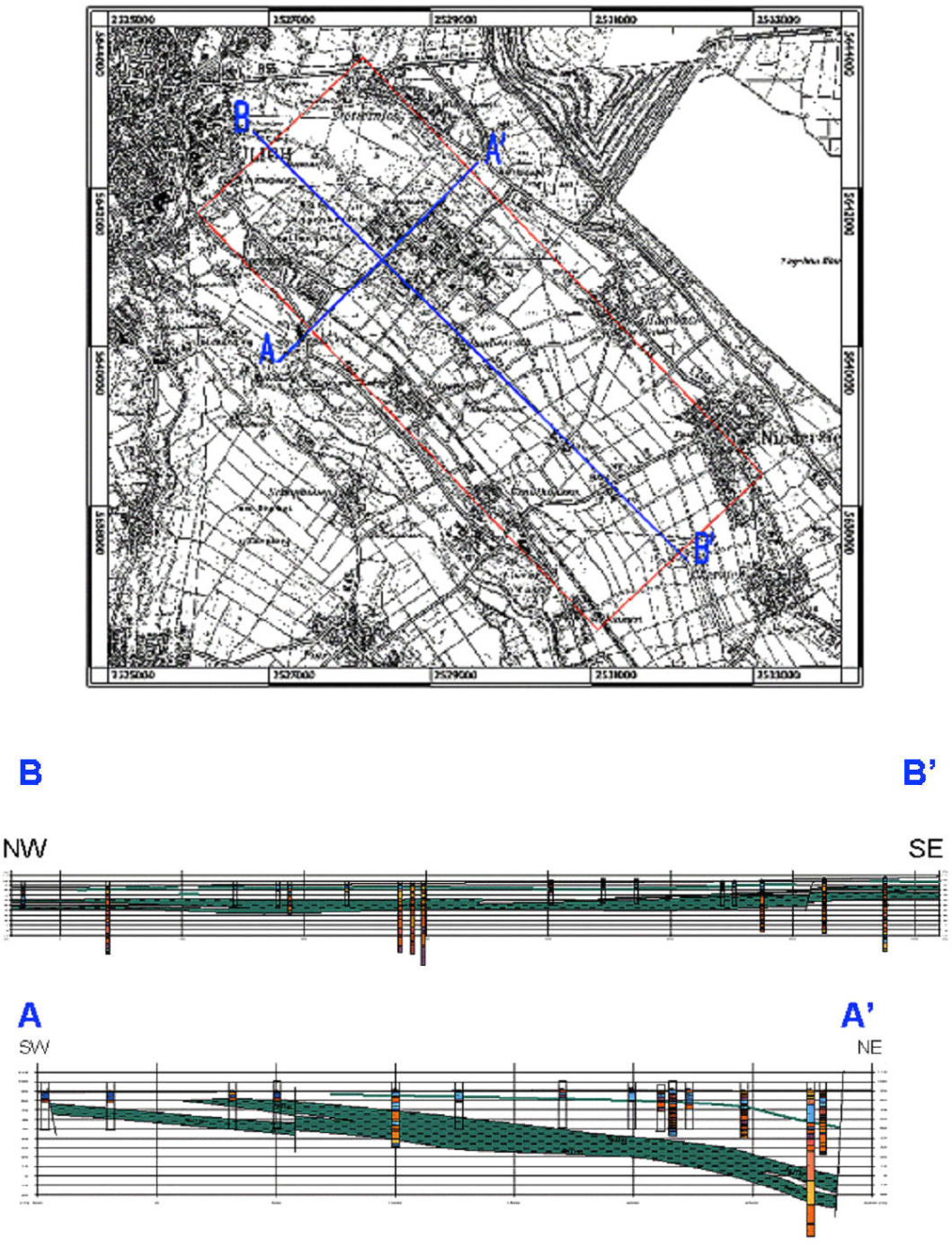


Fig. 17 - Cross sections of the hydrogeological model.

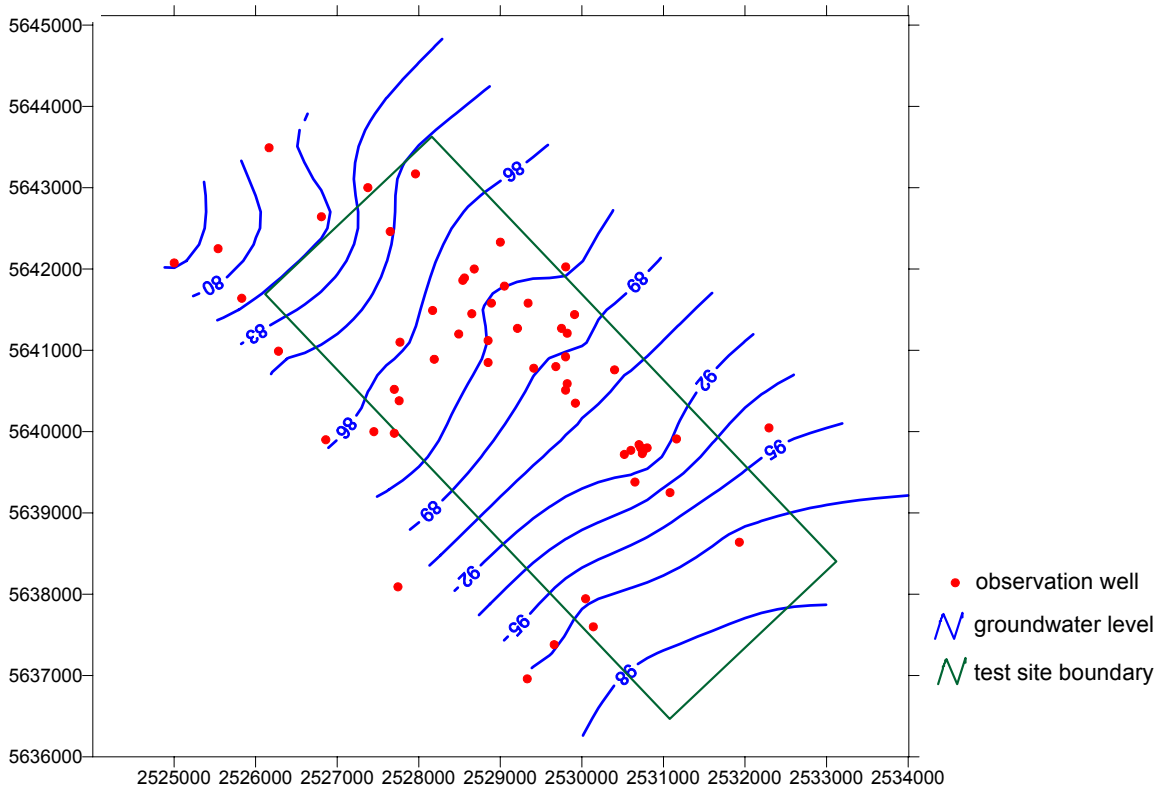
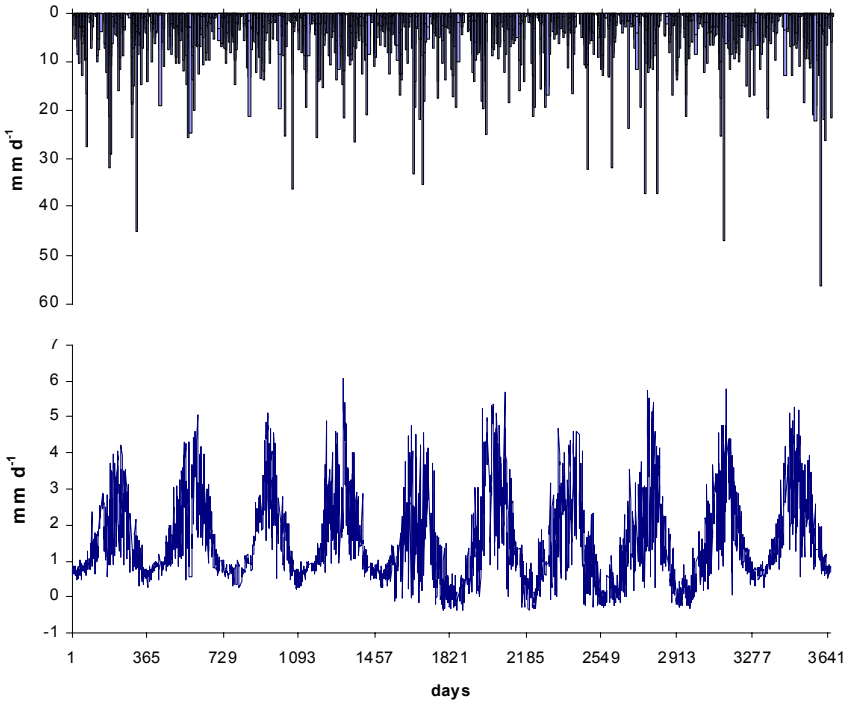


Fig. 18 - Interpolation of the groundwater levels [m above sea level] for 1/12/1983.



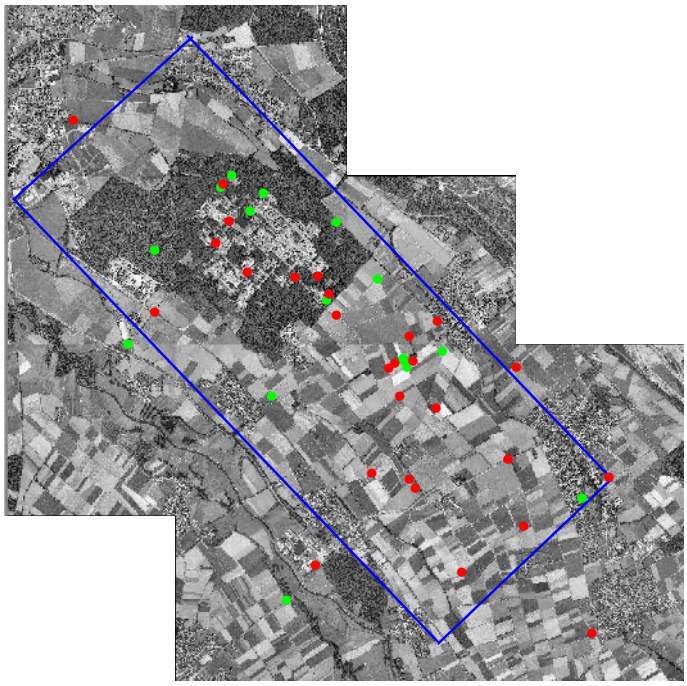
upper graph: precipitation, lower graph: potential evapotranspiration for grass using Penman/Monteith, Makkink or Hamon.

Fig. 19 - Meteorological data: 1 December 1983 to 30 November 1993.

Because of the near surface groundwater and the predominating agricultural land use at the test site ‘Zwischenscholle’, the presence of pesticides in the groundwater was very likely. Between 1990 and 2003, seven sampling campaigns on pesticides in wells were undertaken. The screening analysis included atrazine and two of its metabolites, simazine, diuron, isoproturon and terbuthylazine. A total of 42 wells were monitored although not all of these wells were continuously monitored.

Between 2000 and 2003, the monitoring was intensified and between 8 and 32 wells were screened for pesticides in five campaigns. From a total of 42 wells sampled between 1990 and 2003, 27 revealed pesticide concentrations above the detection limit of 0.05 µg/l (see Fig. 20). Roughly 2/3 of samples taken showed measurable amounts of pesticides. The wells with pesticides did not show any specific spatial structure. Pesticides were found in wells located in the area of the research centre, in the neighbouring forest and on the arable land (see Fig. 20).

The largest pesticide concentration (11.8 µg/l, see Table 3) found during the monitoring time was for isoproturon (IPU) in well ‘822951’ in 2002. The concentration the next year was 1.84 µg/l. Compared to *e.g.* atrazine, isoproturon was detected in a small number of wells and at small concentrations. The large concentration detected in one well only might thus be the result of a point source rather than the result of diffusive inputs from agricultural practice.



green: no pesticide concentrations above 0.05 µg/l were found,
red: pesticides were detected.

Fig. 20 - Location of the wells monitored for pesticide screening 1990-2003.

In a single campaign, atrazine was found above the detection limit of 0.5 µg/l in roughly 1/3 of the wells sampled. Rather large concentrations of atrazine were detected in 2002. The metabolite deethylatrazine was also found in roughly 1/3 of wells sampled. Deisopropylatrazine showed similar concentrations as deethylatrazine. Deisopropylatrazine is a metabolite of both atrazine and simazine and was rarely found on the test site 'Zwischenscholle'. Diuron was also rarely found, while terbuthylazine was never detected in any well between 2000 and 2003.

3.3. Discussion

The numerous data collected at the Zwischenscholle test area were manipulated to facilitate the generation of a dataset for subsequent model evaluation. The 'Zwischenscholle' dataset contains a well-defined vertical boundary condition for the groundwater levels based on a dense dataset of groundwater level data. The high spatial density of wells allowed the computation of a well-defined spatio-temporal boundary condition for the groundwater. The biggest drawback was probably the large uncertainty involved in the time-variable spatial pattern of land use and pesticide application. It seems rather impossible to improve the data through additional interviews. The biggest potential to upgrade the land use data, and thus the pesticide application information, might come from the application of remote sensing techniques.

Table 3 - Pesticide concentrations in groundwater at test site Zwischenscholle (mean = mean of samples with concentrations exceeding the detection limit).

date	concentration [µg/l] and number of samples	atrazine	deethyl-atrazine	deiso-propyl-atrazine	simazine	diuron	IPU	terbuthyl-azine
Jan. 2000	mean	0.14	0.06	0.07	0.28	0.08	-	-
	minimum	0.08	0.06	0.07	0.12	0.08	-	-
	maximum	0.2	0.06	0.07	0.43	0.08	-	-
	# above detection-limit	2	1	1	2	1	0	0
	# total analysed	13	13	13	13	13	13	0
May 2000	mean	0.12	0.08	0.09	0.24	-	0.08	-
	minimum	0.05	0.05	0.08	0.11	-	0.07	-
	maximum	0.24	0.12	0.11	0.36	-	0.08	-
	# above detection-limit	8	6	3	2	0	2	0
	# total analysed	17	17	17	13	0	4	0
Winter 2001	mean	0.11	0.07	0.07	0.26	0.13	-	-
	minimum	0.08	0.05	0.07	0.12	0.13	-	-
	maximum	0.16	0.1	0.07	0.39	0.13	-	-
	# above detection-limit	3	4	1	2	1	0	0
	# total analysed	8	8	8	8	8	8	8
2002	mean	0.27	0.08	0.11	0.16	0.06	11.8	-
	minimum	0.05	0.05	0.07	0.09	0.06	11.8	-
	maximum	1.99	0.11	0.14	0.34	0.06	11.8	-
	# above detection-limit	10	9	2	5	1	1	0
	# total analysed	32	32	32	32	32	32	32
July 2003	mean	0.19	0.06	0.06	0.13	0.17	1.84	-
	minimum	0.05	0.05	0.06	0.05	0.17	1.84	-
	maximum	1.55	0.08	0.06	0.24	0.17	1.84	-
	# above detection-limit	13	12	1	3	1	1	0
	# total analysed	32	32	32	32	32	32	32

The daily time series of potential evapotranspiration and precipitation from 1/12/1983 to 31/11/1993 cover a broad range of meteorological conditions, with very wet years (*e.g.* years 1 and 5) and long dry periods (*e.g.* during year 3). The extension of this time series up to 2003 is desirable given that model predictions could be compared to pesticide concentrations measured between 2000 and 2003.

The monitoring of pesticides clearly showed the presence of significant concentrations of several compounds in the uppermost aquifer. The occurrence of atrazine and its metabolites, as well as the concentrations detected for simazine and isoproturon justify the need for modelling to be undertaken to further the understanding of the transport of these compounds.

3.4. Summary

A dataset was generated at the 'Zwischenscholle' test site. The dataset can be used for model evaluation and scenario development exercises. The 'Zwischenscholle' dataset contains spatial and/or temporal information on meteorological time series, land use, soils, aquifer properties and groundwater levels. The different methods aimed at transforming the raw data (measurements and maps) into model input parameters were described. The time-variable spatial patterns of crops and pesticide application were stochastically generated while the high spatial density of wells allowed the generation of a well-defined vertical boundary condition for the groundwater.

The pesticide monitoring campaigns for atrazine, deethylatrazine, deisopropylatrazine, simazine, diuron, isoproturon and terbuthylazine revealed the possible effects of the combination of a near surface groundwater with an intense agricultural use. Between 1990 and 2003, 27 out of the 42 wells analysed showed pesticide concentrations above the detection limit of 0.05 µg/l. Significant concentrations were detected for atrazine and its metabolites, for simazine and for isoproturon. For the latter, this might be the result of a point source.

4. ROSWINKEL [ALTERRA]

The following section presents the experimental set-up and associated methods used at the Roswinkel field site. No information on the actual results of the monitoring campaign and on the modelling work undertaken with PEARL and HYDRUS was provided by Alterra for the present final report. Reports describing the work undertaken will be produced and circulated by Alterra in due course.

4.1. Experimental field

The field was located at near the village Roswinkel (Boetse weg) in the province Drente in the NE of the Netherlands. The coordinates are: X = 266.900, Y = 540.100 (North Latitude 52° 09' 22.2", East Latitude 5° 23' 15.5"). The altitude above see level is 13 m. Following the Dutch classification it is a 'veldpodzol' with code Hn21 gt VI in the Pleistocene sand district, or a podzol (FAO soil classification) developed in a medium fine cover sand. Information on soil properties for the different layers is given in Table 4.

Table 4 - Soil properties of the soil layers.

Layer NR	Depth (cm)	pH-KCL	pH-H2O	Org. Matter (g/100g)	Org. C (g/100g)	$CaCO_3$ (g/100g)	Particle size composition (µm) (% of mineral fraction)							
							0-2	2-16	16-50	50-105	105-150	150-210	210-300	300-2000
1 *	0-20	4.5	5.2	4.9	3.24	0.0	3.2	2.0	6.5	33.2	25.6	16.7	8.1	4.7
2 *	30-40	4.7	5.7	1.7	0.93	0.0	2.6	0.4	5.0	34.3	26.9	19.0	8.4	3.4
3 *	60-100	5.0	6.1	0.3	0.12	0.0	2.2	0.3	2.0	31.1	27.6	20.6	10.7	5.5
4 b)	0-30	4.4	5.2	4.3	3.26	0.0	4.0	0.9	7.5	33.2	25.2	17.1	7.8	4.3
5 b)	50-70	4.8	6.1	0.6	0.25	0.0	1.8	0.3	3.2	36.9	28.8	18.7	7.2	3.1

* mix of soil samples (volumetric) from 16 soil columns taken at 8 May 2000 (sampling for blanks).
b) samples collected on 18 September 2000, on a strip along the SE side of the field at 40 sites for 0-25 cm and at four sites for the 50-70 cm layer.

The experimental field was 0.2 ha and was part of a much larger field (300 x 100 m). The experimental field started at about 13 m away from border with a road (WSW side) to avoid possible effects of damage of soil structure by heavy machines in the past. The NW side of the field was bordered by a ditch which was filled up in the past. A 20 m wide strip (24 plant rows = about the width of the field sprayer used) of 100 m long was selected for spraying with the test compounds. In the middle, three rows were demolished resulting in a driving lane for activities like spraying, sampling and irrigation.

The total field was planted with potatoes (for starch, variety Kanjer) at 20 April 2000, row distance 0.75 m. On 8 May, ridges were further build up with a five row tractor mounted ridger (manufacturer, Plat). Due to rainfall during the days before, soil was rather wet and the ridging resulted in very cloddy surfaces, which would hinder an equal deposition of the spray liquid and consequently led to an irregular spread of the test compounds. In the evening, after the soil surface had dried somewhat, it was decided to treat the experimental field with a fine toothed weed harrow. The effect of the cultivation was moderated with respect to reducing the cloddy surface and led to more tracks and so to reduced space to do soil samplings on undisturbed ridge/furrow sites.

On 8 and 9 May 2000, six filter tubes were installed to measure the groundwater table (periodically and continuously) at different sites. A cluster of 64 groundwater sampling tubes was installed in a narrow grid that would enable to show possible spatial variability in leaching behaviour below the groundwater table. These tubes were also used to withdraw groundwater samples to follow possible degradation of carbofuran in the saturated zone. The 2.5 cm wide PVC tubes were installed by drilling holes with an Edelman auger to the desired depth. The sand subsoil was carefully collected in flat bowls and replaced around the installed tubes and tamped down to simulate natural packing of the soil material around the tubes. All work was done from a bridge construction over the test plot to avoid damage on the ridge/furrow surface of the field and compaction by footsteps. For soil sampling purposes the field was imaginarily split up into 4 sectors (A, B, C, D) of 24 m long each, with a 4 m stripe between the sectors B and C. The height of all sampling tubes, the groundwater monitoring tubes and the soil surface around the tubes was measured with a levelling instrument against one fixed point.

4.2. Application of bromide and test compounds

The chemicals were applied with a tractor mounted, 21 m wide field boom sprayer (marque; Sieger) provided with 42, Lechler LU 05 nozzles. Before spraying, the flow rate from the individual nozzles was measured at a spray pressure of 2.5 bar (250 kPa). The average flow rate was 1.74 l/min, CV 4.4 %, n = 16. The speed of the sprayer could not be set low enough to spray the desired high volume rate (1,000 l/ha for the bromide solution). Subsequently it was decided to apply the spray solutions for KBr and the pesticides in two sprayings, which would also improve equal areic distribution. The actual driving speed of the sprayer was measured during spraying by recording the time (stop watch) over 24 m stripes. A very constant speed of 3.38 km/h (CV < 1 %) was observed. This speed resulted in an computed areic spray volume of 617 l/ha and with two sprayings, 1,234 l/ha.

On 10 May 2000, the pesticides carbofuran and oxamyl were applied between 10.30 and 10.45 h and thereafter the tracer KBr (11.00-1.15 h). The weather conditions were sunny with a very weak wind (with an angle of 30° on direction of ridges) during spraying. Boom height above the ridges was between 60-80 cm. Both aspects provided good conditions for an equal distribution of the spray liquid on the ridges without 'spray shadows' at the downwind side of the ridges. Sub samples (100 ml) of the spray solutions were taken (from the outer nozzle) at the start of spraying, after about 20 m spraying and at the end to control the estimated concentrations in the spray liquid. The aqueous samples were stored at 5°C for 40 days before they were analysed.

Carbofuran was applied as the formulated product (lc) Curater-vloeibaar® (Bayer), containing 200 g/l carbofuran (2,3-dihydro-2,2 dimethylbenzofuran-7-yl methyl-carbamate). 6 L of the product was added to a total volume of water of 320 l resulting in an estimated concentration of 3.75 g/l carbofuran (measured 3.77 g/l, sd 0.17, n=3, is 101 % of estimated concentration). Oxamyl was applied as the formulated product (sc) Vydate-SL®(DuPont), containing 240 g/l oxamyl (Methyl-N',N'-dimethyl-N-[methyl-carbamoyl)oxyl-1- thio-1-oxamimidate). 10 L of the product was added to the same tank content as for carbofuran. The estimated concentration of oxamyl in the spray liquid was 7.5 g/l (measured 6.64,sd 1.19, n = 3, is 89 % of estimated concentration). Dose of carbofuran was 4.63 kg/ha and for oxamyl 9.25 kg/ha, based on the nominal concentrations in the spray liquid and a liquid dose 1,234 L/ha. The 11 % lower concentration of oxamyl measured in the spray liquid may be caused by the longer storage time, of which the first day was at room temperature. Oxamyl has high hydrolysis rates at pH above 7, degradation during storage of the spray liquid is probably the reason for the lower concentration measured.

The spray liquid for potassium bromide (KBr) was prepared by pre-dissolving 25 kg KBr (= 16.8 kg Br) in 250 l water, held in plastic containers. To this water, 1.5 kg of the tracer 2,6-difluor benzoic acid (2,6-DFBZ, Acros) was also added. The total contents of the containers were pumped into the sprayer tank and the tank content was filled up to about 320 L. The estimated concentration of Br in the tank solution was 52.45 g/l (measured 53.6 g/l, sd 1.7, n = 3, is 102 % of estimated concentration). Dose of Br was 64.7 kg/ha, based on the nominal concentration in the spray liquid.

4.3. Irrigation procedures

To assure clear downward water movement during the first months, surplus rainfall was applied by sprinkler irrigation. The system consisted of a winch draught installation (PerrotT Roller Car, Perrot Regnerbau CALW) equipped with a single sprinkler. The car was driven by a water turbine and the driving speed could be staples installed from 10 to 50 m/h. The diameter of the sprayed circle was about 25 m. The roller car track was always in the middle of the central driving lane. The spray tracks started 12 m before both ends of the experimental field to ensure full overlap and so an equal distribution. The distribution of the irrigation water was traced with 24 rain gauges (household type, 50 cm^2 apertures). They were placed in two rows, at 15 m from the borders at the SW side and NE side of the field. The outer gauges were about 6 m away from the centre of the central driving lane and so comprised the area utilized for soil core samplings and the special plot with groundwater sampling tubes and the test site with TDR measurements. The rain gauge for continuous registration of precipitation was also within this area and so measured the precipitation (and intensity) by the irrigation.

The dates and times when sprinkler irrigation was performed, are summarised in Table 5, together with the averages of the measured rainfall by the 24 rain gauges and the distribution. The majority of the irrigations were done in the evening and during night when wind speed was very low or there was no wind at all. During windy periods, the spray pattern became dislocated, resulting in a less even distribution. This was the case with the irrigation on 8 July, resulting in a less equal length wise distribution in the field and also at right angles to the central driving lane. At 10 May, irrigation was started at 11.30 h, shortly after application of the pesticides. Due to too high wind speed, irrigation was stopped after 1 h and was continued in the evening at 21.00 h when wind speed was much lower and an equal distribution was observed.

Table 5 - Dates with sprinkling irrigations and results measured precipitation with two rows of 12 rain gauges each, rows 15 m inside the indicated borders of the field.

Start	Stop	Average all 24 gauges (mm)	SW border side		NE border side	
Date; time	Date; time		Average (mm)	sd (mm)	Average (mm)	sd (mm)
10-05; 21.00	11-05; 05.00	7.8	8.1	1.6	7.8	1.6
19-05; 22.30	20-05; 12.30	18.8	17.5	2.2	20.1	1.7
30-05; 18.00	31-05; 05.00	10	12.7	0.9	10	0
31-05; 05.30	31-05; 16.00	16	13.6	1.9	16	1.1
08-06; 21.30	09-06; 09.00	15.8	21	2.6	15.8	4.1
09-06; 19.30	09-06; 08.30	19.9	15	0.4	19.9	0.8
22-06; 22.00	23-06; 05.30	9.3	11.3	1.2	9.2	1
23-06; 06.00	23-06; 14.00	13.9	10.8	1.1	13.9	1
	Sub total		*110*		*112.7*	
23-06; 19.45	24-06; 09.00	24.3	24.3	2.8	*)	
	Total	135.8	134		137.0	

* no measurements done at 23-06-01.

4.4. Monitoring of groundwater level and soil temperature

Four filters for manual monitoring of the phreatic groundwater level were placed around the experimental field and one in the centre. The tubes were provided with a 1 m long filter placed at 4-5 m depth. Another three tubes were placed to 3 m depth and were slitted over 2 m length. They were used for continuous registration of the groundwater level by pressure sensors and data loggers. After installation was completed at 11 May, the height of all groundwater tubes and soil surfaces around the tubes were measured with a levelling instrument against one reference level, being the head of the groundwater tube 95 m depth in the centre of the field. The soil level at this spot was also the highest of the field.

4.5. Sampling of soil profiles

An overview of the soil sampling times, including the corresponding days after application, is given in Table 6. For sampling purposes the four sectors of 24 m long were imaginarily split up into 12 subplots of 2 m x 8.5 m and numbered $A_{1\text{-}12}$, $B_{1\text{-}12}$ etc. At each sampling time, pairs of soil cores (one at the top of the ridge and one in the furrow) were taken from a sub-plot at two bands situated 1.5 to 2.5 m away from the central driving lane. One pair was taken at the NW side (left) from the central driving lane and the other pair at the other side (SE). So, each sampling time delivered 16 pairs of soil cores. The sub-plots to be sampled at each time were selected randomly before the start of the experiment.

A special steel corer was used to collect soil cores in PVC tubes (liners) of 1.2 m long and 9.64 cm inner diameter. The steel core tube was provided with a sharp cutting ring with an inner diameter of 9.4 cm. The slightly larger diameter of the PVC liner and its smooth surface resulted in only a small compaction of the soil core (on average 1.0 cm with a maximum of 3 cm). The outer diameter of the cutting ring had a 1.0 cm larger diameter than the steel tube itself, to reduce friction between soil and tube wall during pressing the corer into the soil. The PVC liner was sticked between the cutting ring end and a removable head of the steel tube. The steel corer tube was pressed into the soil with a hydraulic excavator to a depth of 70 to 120 cm. The corer was pulled up after exchanging the flat head by a head with a welded ring on it for easy connecting a chain. During pulling up of the corer, air pressure was applied at the lower end of the cutting ring via a 4 mm copper tube, which was mounted on the outside of the steel core tube. This hindered slipping out (part) of the soil core when it was pulled up. Subsequently the corer was put in a horizontal position. The part of the soil core that was inside the cutting ring was pressed into the PVC liner, which was then pulled out of the steel core tube. The PVC liners with the soil cores were capped airtight at both ends and transported in a horizontal position to the lab, where the cores were split up (within one to three days) and samples for analyses were combined.

The intention was to sample always to 1.0 m depth but the compactness of the sand subsoil restricted sometimes deeper penetration of the corer, due to too low weight of the excavator used at the first samplings. At the last sampling on 18 September 2000, groundwater had raised with the result that the lower part (about 0.5 m) of a series of soil columns slipped out of the corer. Soil samples for moisture determination and chemical analysis of the 50-70, 70-90 and 90-120 cm layer were then collected with an Edelman auger. A hole was drilled to the upper level of the layer with an Edelman

auger 11 cm diameter. Next, soil was removed with a smaller (6 cm) auger to the lower level of the layer to be sampled.

Table 6 - Sampling dates of soil and groundwater and performed analysis.

Sampling date	Days post application	Analysis performed in soil			Analysis performed in groundwater	
		Moisture content	Bromide	Carbofuran	Bromide	Carbofuran
8-5-00	-2	+	b	b	b	b
10-5-00	0.25	+	+	+		
29-5-00	19	+	+	+		
13-7-00	94	+	+	+		
18-9-00	131	+	+	+		

B = blank sample.

The sampling at 10 May 2000, shortly after spraying of the test chemicals, were done with a split-tube auger. This auger was 0.3 m long and the inner diameter of the cutting ring was 9.5 cm, the inner diameter of the split tube was 0.3 cm more than that of the cutting ring to avoid compression of the soil column. The auger was pressed or hammered into the soil to 20 cm depth. Subsequently, the auger was carefully dug out and put in a horizontal position. One half of the steel tube was then removed and the soil core was sliced up into two section of 5 cm and one of 10 cm (lower end). These samplings were done to measure the initial concentration and distribution in depth in the topsoil most accurately.

4.6. Treatment of soil samples in the laboratory

After each sampling time, the 32 soil cores collected in the PVC liners were sliced up in the lab (maximum three days storage at 18 to 23 °C). The PVC tube was placed in a horizontal position in a mold and the wall was carved on both sides. The upper half of the liner was then removed and 10 cm sections were marked with a sharp knife. The upper end of the mark stick was fixed with the soil surface in the PVC tube (visually averaged). No correction was made for the lowering (on average 1 cm) of the soil surface inside the column during field sampling. Sometimes the initial soil surface in the soil columns of the ridges had to be estimated by reconstruction of the soil in the top (upper 5 to 10 cm), because the soil mass flowed out in the PVC tube, due to the horizontal position when the soil was dried out or loose by recent cultivation.

The pre-marked soil core was sliced up into 10 cm long sections with a thin blade (round shaped as the column at one side), always starting at the lower end of the soil column to avoid contamination. The wet condition of the soil allowed us to cut fairly exact slices, that kept their form during careful further handling. The total weight of each section was noted immediately to avoid evaporation of water. Subsequently, the core section was put in a vertical position and the centre was cut out with a sharp thin cutting tube (inner diameter 7.5 cm). This core centre was taken for preparing samples for analyses of the test chemicals, because it can be expected that this part is not contaminated by handling during sampling in the field and in the lab. The soil of the outer part of the core section was used to determine the moisture content by drying to constant weight at 105 °C. From the total wet weight of the 10 cm section and the moisture content of its outer part, the volume fraction of liquid and the dry bulk density

were calculated. A centre core could not always be taken from the upper 20 cm layer because of the loose structure and dryer condition. Part of the mixed soil mass within that core section was then separated for analyses. This method is acceptable because these layers have low risks for inter-contamination (high initial contents).

For each sampling time, all 10 cm core sections of the 32 soil columns were analysed individually for moisture content and bromide content. For cost reduction, all soil columns per sampling time were not analysed individually for the pesticides. The corresponding layers of the four soil cores taken at each section were combined to do one analysis. A 100 g sub sample of each of the four pre-mixed centre core sections were put in a plastic bag that was blown up and the soil was vigorously mixed by tumbling. A sub sample (100 g) was then taken for analysis of the pesticides. The remainder of the mixed sample was stored at -25 °C for (delayed) analyses or possibly re-analysis.

The soil samples collected with the short split-tube auger on 10 May (directly after spraying) were analysed the day after collection. The samples of the 5 cm and 10 cm core sections were first mixed well in the plastic bag wherein the total soil mass was transferred in the field. The total wet mass was weighed for determination of the soil bulk density and sub samples were then taken for moisture determination and analysis of bromide. For cost reduction, a mix sample of four samples (per layer) per sector was prepared for analysis of carbofuran and oxamyl. This was done in a similar way as described before for the sections of the tall soil columns.

4.7. Crop sampling

Crop was sampled at 10 July, 18 September and 24 November. At 10 July and 18 September, on each of the four sectors (A, B, C, D) plants were removed at three spots (2 m row length at each spot). For each sector, all leaves and potatoes (including mean root) were combined to one sample (15 to 18 plants per sector taken from 3 * 2 m * 0.75 m = 4.5 m^2) for determination of dry matter production and bromide uptake by the crop. From each plant one to two potatoes (depending on size) were taken and combined to one sample for bromide analysis per sector. Total weight of fresh leaves and potato tubers (including the separate sample for bromide) was determined. Before weighing, potatoes were rinsed with a water yet to remove soil. The leaves were chopped and put into a box. Sub samples (about 0.75 kg) of the leaves were taken then with a sharp corer for determination of the moisture content and bromide content. The special tuber samples were cut into sections. Leaf and tuber samples were dried to constant weight at 105 °C and the samples stored at -25 °C until analysis for bromide. The determined moisture contents were used to calculate the total dry mass yield per m^2 soil.

At 24 November, little leaves remained and only tubers were collected randomly over the field and combined to one sample. A second sample was collected near the spot with the groundwater sampling tubes.

4.8. Bromide analysis

- ***Soil extraction***

The soil from each 10 cm (centre) core section was mixed in a blown up plastic bag and about 45 g moist soil was put in a centrifuge tube together with 45 cm^3 $CaCl_2$ (0.01 mol/l). The tube was capped and shaken (175 min^{-1}) for 1 h and the supernatant liquid partly brought into a polyethylene flask and stored at 5 °C until analysis. Before HPLC analysis about 2 cm^3 of the supernatant was filtered over a 0.45 µm filter (FP030/20, Schleicher & Schüll).

- ***Crop extraction***

The dried leave and tuber samples (see section 2.9.) were pulverised with a cross mill (SK 100 Comfort, Retsch) provided with a 1 mm bottom sieve and well mixed. Sub samples (about 5 g) were dried at 105 °C and 2.5 to 5 g transferred to 100 cm^3 flasks and 50 cm^3 0.01 M HCl was added and the mixture cooked for 10 min. The flask were filled up with 0.01 M HCl until they contained 100 cm^3 (weight basis). After standing overnight, the liquid was filtered (0.45 µm filter (FP030/20, Schleicher & Schüll) to prepare the sample for HPLC analysis.

The extraction efficiency from only tubers was tested in duplicate by adding 500 mg bromide (with 1 cm^3 water) to 3.5 g dried potato samples collected at 24 November. Recovery was 38 and 57 %. The reason for this low recovery is not known.

- ***Chromatographic analysis***

Concentration of bromide ion in the extracts was measured with a HPLC system consisting of a Spectroflow 400 pump (Separations) and a Marathon auto sampler (Spark Holland). The analysis was done with a 'Hypercil ®ODS C-18 column (Thermo Quest), operated at room temperature. The steel column (25 cm x 4.6 mm i.d) was packed with octadecyl silane; 5 µm; 10 % carbon. The mobile phase was water containing 0.005 M phosphate buffer (855 g/l KH_2PO_4, 0.715 Na_2HPO_4) and 0.004 M tetrabutyl ammonium dihydrogen phosphate. The reversed phase column has first to be uploaded with tetrabutyl ammonium dihydrogen phosphate in order to be suitable as an anion exchange column. This method gave a good separation of the bromide peak with the nitrate peak. The flow rate of the mobile phase was 1.5 ml/min and 200 µl samples were injected. Bromide ion was measured with a spectrophotometer (Spectroflow 757) at a wave length of 210 nm. Data analysis was done by the ATLAS® data processing package. Calibration solutions were prepared in 0.01 M $CaCl_2$ solutions (0.5 to 50 mg dm^3). The detection limit was 0.3 mg/l.

The extraction efficiency was measured from blank soil samples spiked at a level of 1 to 100 mg/kg and found to range between 90 to 96 %. Contents were not corrected for recovery. The limit of quantification (LOQ) was set at 0.4 mg/kg dry soil or 0.50 mg/dm^3 soil (dry bulk density of 1.5 kg/dm^3).

Concentration of bromide ion in groundwater samples were analysed with the same HPLC method after filtration of the samples over a 0.45 µm filter. The limit of quantification (LOQ) was 0.3 mg/l. Detection limit in crop samples was set at 12 mg/kg. This high limit was caused by interfering compounds in the crop extracts.

4.9. Carbofuran analysis

- ***Soil extraction***

Sub samples of 100 g moist soil were put into 250 cm^3 Schott flasks with screw caps and 100 cm^3 methanol (HPLC grade) was added. The flasks were shaken (175 min) in a horizontal position for 1 h and the supernatant was centrifuged (2,500 rpm). Part of the cleared liquid was pipetted of and stored at 5 °C until analysis. Samples with high contents of carbofuran (expected) were prepared for HPLC analysis by adding 0.3 cm^3 of the methanol extract to 0.7 cm^3 water. For lower contents, 25 cm^3 methanol extract was reduced on a water bath (40°C) under an air stream to a final volume of about 3 cm^3.

Recovery for spiked (5 – 2,000 µg/kg) blank soil samples from the 0-30 cm layer was on average nearly 100 % (98.4 %, sd = 9.4, n = 17). A lower number of blank subsoil samples (50-80 cm layer) were spiked with 10-100 µg/kg and recovery was 84.7 % (sd = 4.8, n = 5). Samples were spiked at time of analyzing the soils of the different sampling times. Measured contents were not corrected for recovery.

- ***Water extraction***

Carbofuran was extracted with the solid phase extraction technique. Columns of Waters™ were used, which were packed with 0.2 g Oasis™ HLB. Columns were activated with 2 cm^3 methanol and two washes with water, each time 2 cm^3. Subsequently, a 300 cm^3 water sample (controlled by weight) was sucked over the column, followed by 5 cm^3 pure HPLC water. After drying with air, carbofuran was eluted with two portions of 1 cm^3 methanol. The 2 cm^3 methanol extract was reduced under an air stream on a water bath (40 °C) until about 0.3 cm^3 liquid was left. The residue was filled up with HPLC-grade water (by weight) to 1.5 cm^3 and filtered 0.45 µm (Spartan 13/0.45) before HPLC analysis. At each date of analysis for groundwater samples, 2-4 blank water samples were spiked with carbofuran (0.5 to 1.0 µg/l). Recovery of carbofuran was on average 89 %, sd 19 %, n = 21 (some outliners -220, 231, 8.8 and 7.5 % recovery- were not included in the average). Measured concentrations in groundwater were not corrected for recovery.

- ***Chromatographic analysis***

Concentrations of carbofuran were measured with HPLC. The system consisted of a Waters™ 590 pump, an ISS 100 auto sampler (Perkin Elmer) and a LC 90 UV spectrophotometer (Perkin Elmer) operating at 230 or 280 nm. Separation was done at 40°C on a NovaPak C_{18} column (3.9 mm x 150 mm). A Sentry™ guard column (Waters) of 3.9 x 20 mm was mounted as a pre-column. The elution liquid (flow rate 1 cm^3/min) was a mixture of acetonitrile and water 30-70 (v/v). The detector signal was processed with the data package ATLAS®. Standard solutions for calibration were prepared in HPLC water. Depending on concentrations in the extracts, a concentration range of 0.1- 2 mg/l or 0.005-0.1 mg/l was used. Detection limit was 0.005 mg/l at a signal/noise ratio of 5. The belonging limits of quantification for the samples were: water 0.05 µg/l, soil 0.4 µg/kg (about 1 µg/l).

4.10. Degradation experiments

The transformation rate of carbofuran was measured in soil samples from the 0-30 cm and 50-70 cm layers. An overview of the performed incubation series and the specifications of each series is given in Table 7. Data on soil chemical characteristics and particle size distribution of the soil batches used for the studies are presented in Table 8. On 18 September 2000, soil for a first series of incubations (and sorption experiments) was collected from the field at the SE side of the experimental plot, which was not treated with the pesticides or bromide. Unfortunately these incubation series did not fulfil quality criteria set and the results had to be discarded.

In 2002, it was decided to start new incubation experiments with freshly collected soils, now from the area sprayed in May 2000. On 10 July 2002, 40 soil cores were randomly collected from the 0-25 cm top layer. At four spots a hole was dug to 50 cm depth and soil was collected from the 50-80 cm layer with an Edelman auger (6 cm diameter). The soil cores per layer were bulked and the moisture contents determined, which were 15.2 g/100 g and 11.5 g/100 g dry soil for the 0-25 cm and the 50-80 cm layer, respectively.

After two days, the soil batches were moistened with water until a calculated moisture content that resulted in the desired moisture content during incubation, after the pesticide was applied with a known mass of water (1 g). The moistened samples were stored for 6 days at 10 °C in plastic bags. Moist soil portions (equivalent to 100 g dry soil) were weighed into 250 ml glass jars and pre-incubated at the incubation temperatures for 5 days.

Table 7 - Characteristics of the incubation series with carbofuran in two soil layers.

Characteristic	0 - 30 cm layer			50 - 80 cm layer
	temp.			temp.
	5° C	15° C	25° C	15° C
Average mass of dry soil in flask (g)	100	100	100	100
Moisture content during incubation (kg/kg dry soil) *	0.18	0.18	0.18	0.14
Added mass of pesticide (µg)	200.5	200.5	200.5	10.0

* after addition of 1 ml solution with carbofuran.

The desired moisture contents for the soil during incubation were first determined by measuring the water content at representative pF values for the two layers. Three undisturbed soil cores (in steel rings of 7.6 cm diameter and 4.4 or 5.0 cm high) were taken from the top layer in the furrow and between 60 to 70 cm depth. The soil cores were placed on glass filter plates, which were mounted in large (loosely covered) funnels. The soil cores were water-saturated by gently flooding them (from bottom) up and left standing overnight. Subsequently the soil was stepwise brought in equilibrium with a hanging water column under the glass filter. A 125 cm water column (pF 2.1) was chosen for the top layer and a 50 cm water column (pf 1.7) for the soil from 60-70 cm depth. Details of the method are given by SC DLO Voorschrift 8. The results of the measurements are given in Table 8. From the soil water retention curves, soil moisture content can be estimated to be about 0.21 kg/kg dry soil in the 1-10 cm top layer at a bulk density of 1.20 kg/dm^3 , or 0.24 kg/kg at a bulk density of 1.05 kg/dm^3. However,

soil samples prepared with these two high water contents showed muddy and were found to be not realistic for the field situation. A moisture content of 0.18 kg/kg dry soil was therefore taken for the incubation of the topsoil samples. For the 60-70 cm layer a moisture content of 0.14 was estimated at a bulk density of 1.81 kg/dm^3, which is quite in line with the moisture content determined with the hanging water column method.

Table 8 - Soil moisture contents determined with the hanging water column method with undisturbed soil cores.

Layer	Replicate	Bulk density (kg dm^3)	Moisture content (kg/kg)
Top (1-6 cm)	I	1.3	0.188
	II	1.21	0.171
	III	1.31	0.154
	Average	1.27	0.171
60-70 cm	I	1.63	0.168
	II	1.75	0.125
	III	1.83	0.149
	Average	1.74	0.147

4.11. Sorption experiments

The sorption of carbofuran was determined at four concentration levels at 5, 15 and 25 °C with soil from the 0-25 cm layer, collected on 10-07-2002, which was also used for the degradation studies with carbofuran. Solutions of carbofuran with measured concentrations (duplicate, lowest concentration in triplicate) of 0.455, 0.0910, 0.0227 and 0.0092 µg/l were made in $CaCl_2$ (0.01 mol/l). A mass of 50 g moist soil (controlled by weight) was added to centrifuge tubes with a volume of 80 ml. The moisture content of the soil was measured by drying three soil portions of the batch at 105 °C to constant weight and was found to be 0.152 kg/kg dry soil. Then 50 ml of one of the four carbofuran solutions was added to the centrifuge tubes (triplicate for each concentration/temperature combination). Each tube contained on average 43.6 g (sd = 0.3 g, n = 26) solid phase and 56.8 g (sd = 0.3, n = 26) liquid phase. The centrifuge tubes were closed with glass stoppers and placed on a top-over rotating disk, with a rotating frequency of 0.3 s^{-1}. After rotating for 24 h in cabinets with a constant temperature of 5, 15 or 25 °C, stoppers were replaced by aluminium foil and the tubes were centrifuged for 20 min at a rotation frequency of 33 s^{-1}. This was done in a Varifuge 3.2RS centrifuge (Heraeus) that was kept at the same temperature as in the cabinets where the tubes were stored.

The concentration of carbofuran in the cleared water layer was measured by direct injection of the liquid in the HPLC after addition of 30 % acetonitrile. For the series with the lowest concentration, about 0.01 dm^3 water was extracted with the solid phase extraction technique (Oasis columns) to increase concentrations to a well measurable level. Recovery of carbofuran from water samples with 10 µg/l carbofuran was 92 % (sd = 1.1, n = 9). Concentration of carbofuran in extracts of blank soil was < 5 µg/dm^3.

4.12. Desorption of aged residues

Long-term sorption kinetics of aged carbofuran residues was tried to measure during the transformation study in soil from the 0-25 cm layer at 25 °C. After 7, 14, 28, 64 and 87 days incubation time, samples of soil pore water were collected from separately incubated flasks. Portions (about 25 g) of the total mass of the soil (about 100 g) in the incubated flasks were transported into glass centrifuge tubes that were provided with a glass filter (pore diameter 16 µm) at the bottom end and a glass compartment to collect the separated soil pore water.

The tubes were centrifuged at 2,500 rpm for 25 min and the temperature of the centrifuge was kept at 25 °C. The separated pore water was transferred into 4 cm^3, capped glass HPLC vials and stored at -20 °C until analysis with HPLC. The total mass of carbofuran in the liquid phase in an incubated flask was calculated from the measured concentration in the pore water and the total mass of water in the flask. At time of centrifugation, total remaining mass of carbofuran in the incubation flask was estimated from the average results of the parallel running transformation study.

5. MARTIGNY [EPFL]

The following provides a synthesis of the work which was undertaken at Martigny. Detailed information about the work can be found in the PhD thesis of Kirsten Meiwirth (Meiwirth, 2003).

The herbicide transport processes and the groundwater (GW) vulnerability to chemical contamination were studied in a portion of the alluvial aquifer of the Rhône River Valley located near Martigny (Southwest Switzerland). The type of soils in the vadose zone (mainly silty and sandy soils), the low clay and organic matter content, the intensive agricultural use and the low depth of the groundwater table, lead to an alleged high vulnerability of the groundwater to pesticide contamination.

The purpose of the study was to gain a better understanding of the risks of contamination of the alluvial aquifer and to study in detail the fate of some selected herbicides from the soil surface to the groundwater table in order to understand the processes involved in the transport of pesticides in the vadose zone.

The investigations were carried out at two scales:

- an in-depth study of the pesticide transport in the vadose zone at local scale field sites (4 m^2 plots);
- a systematic monitoring of the groundwater quality at the regional scale (about 400 ha).

The results of the local experiments were used to evaluate a root zone model (HYDRUS-1D) in order to clarify the dominant processes involved in pesticide transport from the soil surface to the groundwater table. Local scale and modelling results were used in the interpretation of the regional scale observations.

5.1. Material and methods

The surveyed area is situated on the left bank of the Rhône River, between the city of Martigny and the village of Charrat in the upper Rhône River Valley in the Valais canton (Southwest Switzerland, Fig. 21).

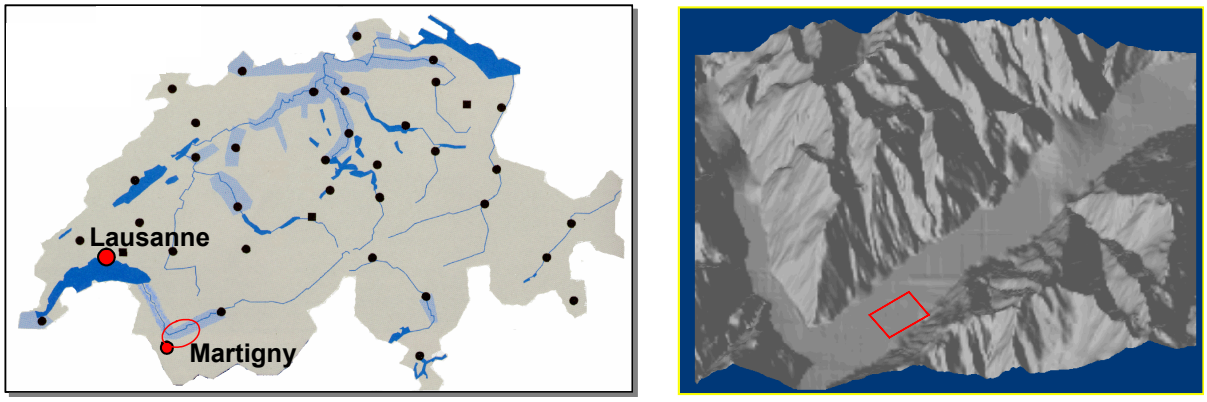


Fig. 21 - Map of Switzerland and 3D view of the Rhône River Valley (Rectangle: observation area).

The U-shaped valley is filled on an estimated height of 400-500 m with detrital deposits brought by glaciers and more recently by the Rhône River and some lateral torrents.

The aquifer is generally unconfined. The water table lies within 1 and 2 m below the soil surface. Generally, water levels are high in the summer and about 40 to 60 cm lower in the winter. The groundwater flows mainly parallel to the Rhône River in a westerly direction with an average gradient of 1 ‰. Local water flow and piezometric heights are strongly influenced by inflow from and drainage to surface waters (Rhône River, runoff from the nearby mountains, channels and agricultural drains).

The soil layers consist mainly of sand and silt near the surface, and of coarser material in the lower part of the profile. The organic matter and clay contents are generally low (<2 and <10 %, respectively). The saturated hydraulic conductivity varies between 10^{-4} and 10^{-6} m/s, the bulk density between 1.20 and 1.53 g/cm^3 and the porosity between 0.42 and 0.66 cm^3/cm^3. The volumetric soil water content varies between 20 and 40 % at field capacity (0.33 bar) and between 15 and 35 % at the wilting point (extractable water, 10 bars).

The average annual precipitation is about 750 mm at Martigny and 600 mm at Sion (Soutter, 1996). Rainfall is quite well distributed over the year but there may be strong variations from one year to another. Evapotranspiration increases from February to July, so that the water balance is negative during the summer (April to July). Towards the end of the year, evapotranspiration decreases and the water balance becomes positive.

Fruit trees, vegetables, and maize cover most of the surface within the plain, while vineyards predominate with some isolated orchards on the slopes. Most fields are equipped with a sprinkler irrigation system used primarily to protect fruit trees from frost at spring time. In especially dry summers, irrigation is practiced to overcome the lack of

water, but in 2001 and 2002, no irrigations were applied to the fields. The irrigation water is most often taken from the groundwater, sometimes also from canals or from the urban water supply.

Herbicides are applied to the fields once or twice a year. The time of application differs according to the crops: vines are generally treated in March, fruit trees from late April to early May and, if necessary, again in late July or August, maize is typically treated in late June. Farmers use different commercial herbicide products, such as simazine and diuron for vineyards, simazine, diuron, and terbuthylazine for fruit trees, and atrazine for maize. Vegetables are sometimes treated with simazine or terbuthylazine, but many other substances are also used. It is extremely difficult to quantify precisely the overall herbicide use in the study area, though farmers insist they apply the quantity indicated by the supplier of the commercial product.

5.1.1. Local scale experiments

At the local scale, four plots (termed plot 1 to 4) were installed, each of which was 2.50 m long and 1.60 m wide. The plots were instrumented at the beginning of April 2001. TDR probes and suction cups were installed at 10, 30, 50, 70 and 100 cm depth, while tensiometers were set up at 10, 20, 40, 60 and 85 cm depth (Fig. 22). Additionally, stainless steel piezometers were installed on plots 3 and 4. A rain gauge was placed between the plots.

Two herbicides (atrazine and isoproturon) and a tracer were applied in two consecutive years and the transport of these compounds through the vadose zone was studied in detail.

5.1.2. Regional observations

At the regional scale, the observation area (400 ha) was equipped with 13 piezometers and groundwater samples were collected regularly in order to determine the concentrations in six selected herbicides (atrazine, terbuthylazine, simazine, deethylatrazine, isoproturon and diuron).

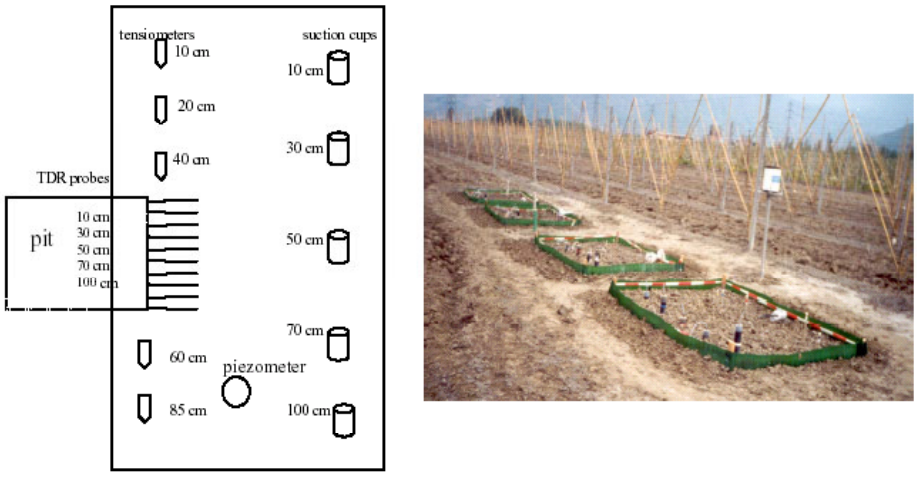


Fig. 22 - Scheme of one of the plots and view of the whole experimental site.

The piezometers were installed along four transects: two longitudinal transects in the direction of the groundwater flow (T1, T2, Fig. 23) and two transects transversal to the groundwater flow (upper and lower boundaries, T3 and T4). The piezometers consisted of 3 to 4 m long stainless steel tubes with an outer diameter of 64 mm, screened over their entire length except for the first upper metre. The tubes were placed in hand-drilled holes and the void around the tubing was sealed with bentonite mud. In order to sample the upper groundwater, the depth of the piezometers was less than 3.50 m. Consequently, the water pumped originated from the upper loamy soil layer and not from the first coarse aquifer.

Groundwater samples were taken from the beginning of May 2001 approximately every 2 weeks until mid August, and once a month during winter. The sampling frequency was adjusted in 2002 according to the findings of 2001 and weekly samples were taken in June and July 2002.

The herbicides monitored were selected in coordination with the other groups of the PEGASE project and according to previous investigations at the site.

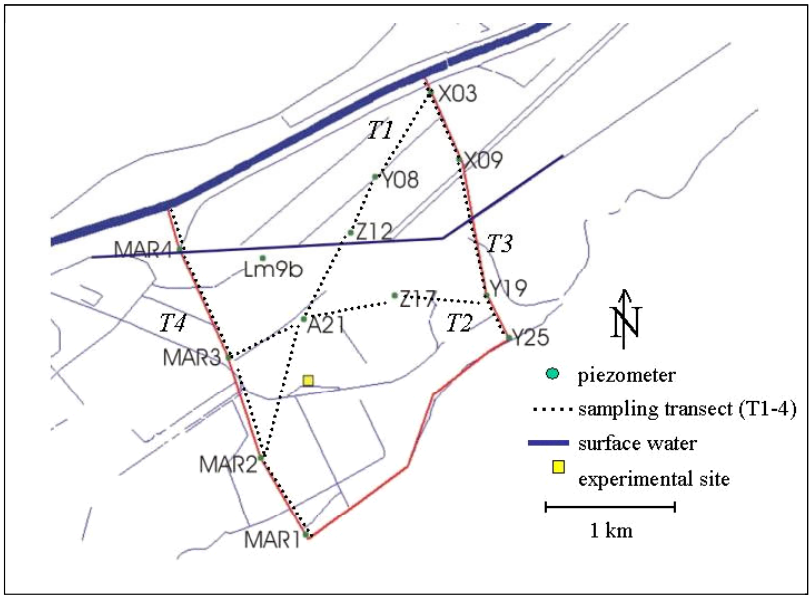


Fig. 23 - Observation area, location of the piezometers, and transects.

5.2. Results

5.2.1. Local flow experiments

- ***Water flow***

After important rainfall, the soil became extremely wet over the entire profile. Near the surface, however, the water content decreased quickly, but remained always greater than 0.28 cm^3/cm^3, indicating that water was rising from the shallow groundwater table due to capillary forces. Figure 24 shows typical water content (θ) and hydraulic head (H) profiles observed during a dry period and subsequent to a rainfall (16 mm).

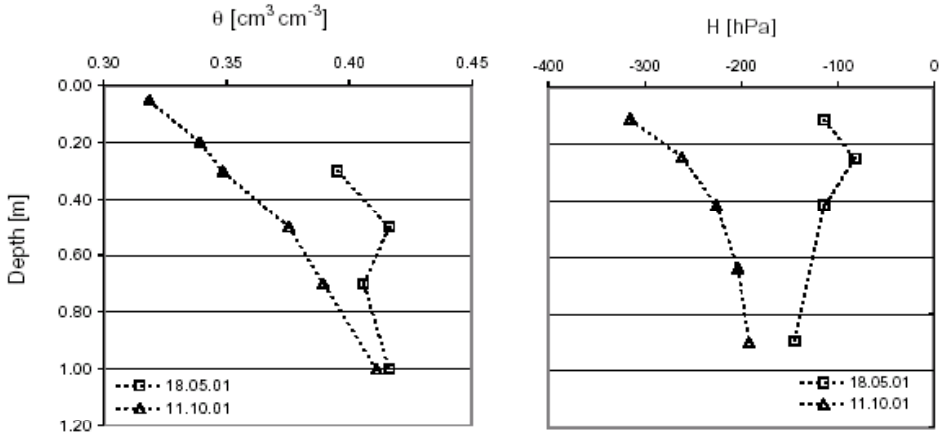


Fig. 24 - Water content and hydraulic head profiles during a dry period (11 October 2001) and after rainfall (18 May 2001).

The hydraulic head profiles strongly depended on climatic conditions. During dry periods, a water flow from the groundwater towards the soil surface was observed, while during and after rainfall events the water flow was directed towards the groundwater table (Fig. 25). Soil water pressure head and humidity measurements made every afternoon between mid May and June 2002 showed high positive hydraulic gradients during dry periods (Fig. 25) and a quick change of the flow direction in response to precipitation; water may infiltrate rapidly to considerable depth after rainfall.

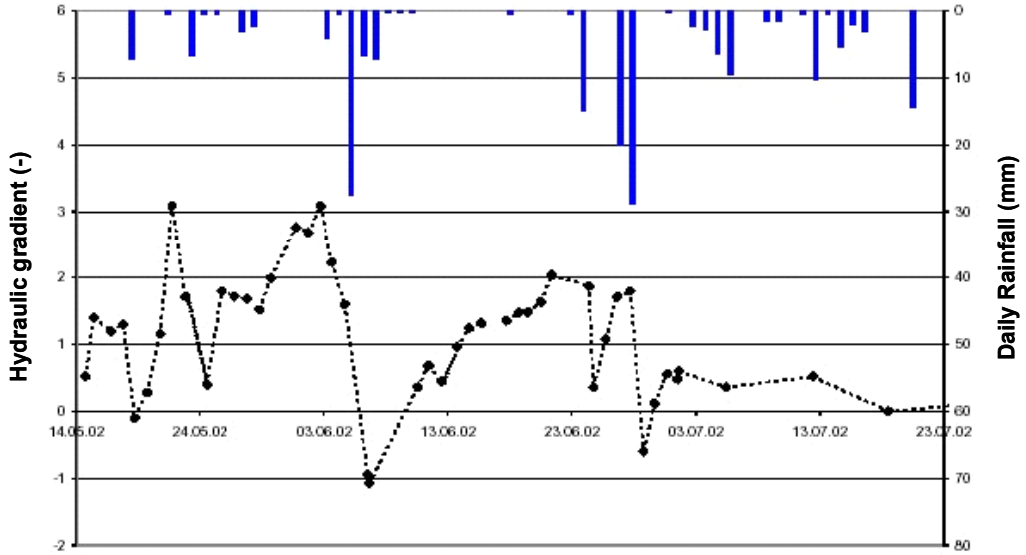


Fig. 25 - Hydraulic gradient observed at 75-cm depth during May and June 2002 and daily rainfall (secondary axis).

- ***Solute concentration***

The herbicides atrazine and isoproturon were applied to the instrumented plots in May 2001 and 2002. The transport of the pesticides through the unsaturated zone and their persistence in the groundwater were monitored during the following months, as long as the concentrations remained significant. Based on the experience gained in 2001, a more efficient sampling scheme was implemented in 2002. Accordingly, the interpretation will focus mainly on observations made in 2002.

Figures 26 and 27 show the temporal concentration changes of isoproturon and atrazine measured in the suction cups at different depths. During the two weeks without rainfall following the application, the concentrations in the unsaturated zone remained low. After the first important rainfall event (June 5), high concentrations appeared at 10, 30 and 70 cm depth. Surprisingly, the concentrations remained low at 50 cm suggesting bypassing of the suction cup. The concentrations decreased steadily during the following dry period and a second small concentration rise was measured at 10 cm after further rainfall at the end of June. From July on, the concentration remained low over the whole profile.

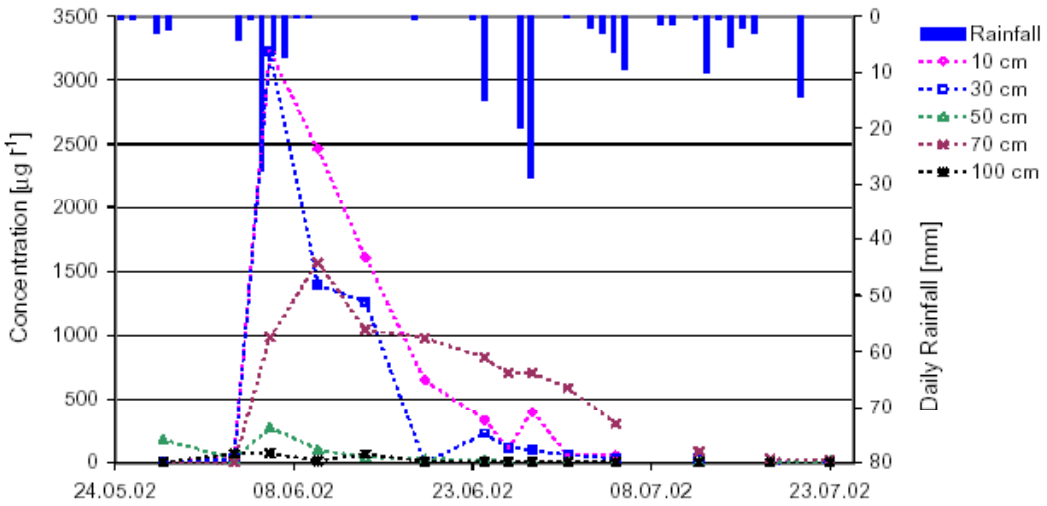


Fig. 26 - Isoproturon concentration in the suction cups at different depths on plot 4 in 2002 and daily rainfall (secondary axis).

The behaviour of the two herbicides was very similar. At 70 cm, however, atrazine was measured at a slightly larger concentration than isoproturon. A similar temporal development of concentrations was observed on the other plots.

Figure 28 presents concentrations of the two herbicides in the groundwater on plot 4 in 2002 together with the GW table depth. The temporal changes in pesticide concentrations were remarkably similar to the fluctuations of the groundwater table. The GW depth was very sensitive to climatic conditions; during dry periods the water table decreased steadily, while important rainfall events caused an almost immediate rise.

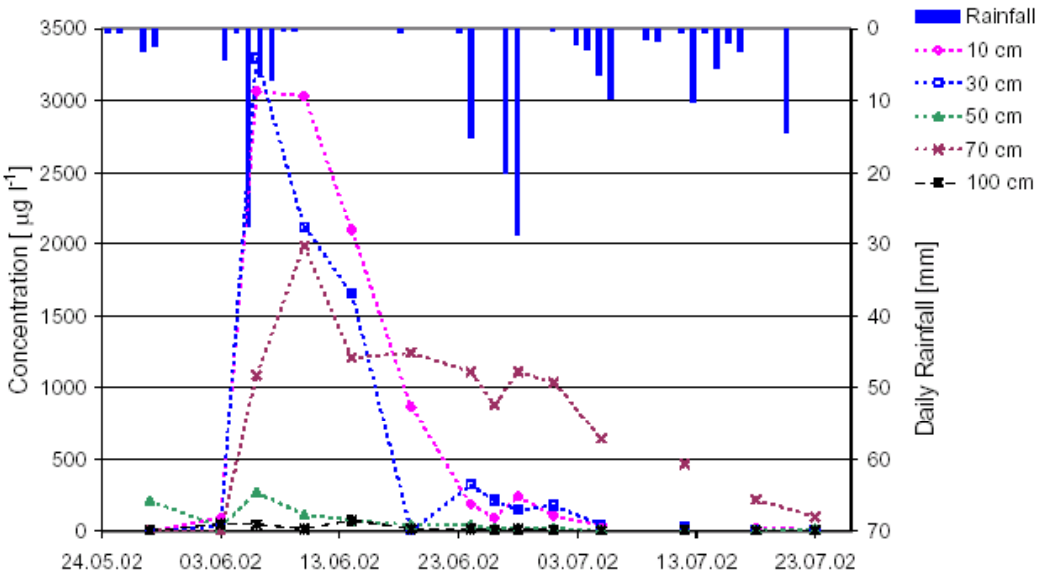


Fig. 27 - Atrazine concentration in the suction cups at different depths on plot 4 in 2002 and daily rainfall (secondary axis).

No pesticides were found in the GW during the first two weeks after application without any rainfall (Fig. 28). Like in the unsaturated zone, a sudden large pesticide peak appeared in the GW as a consequence of the precipitation on 5 June. The concentrations decreased during the following weeks and a second concentration peak appeared after the heavy rainfall at the end of June. A third attenuated concentration peak was observed in mid-July. The concentration pattern of the two herbicides was very similar, with the second concentration peak being slightly higher for atrazine than for isoproturon. On plot 3, on the other hand, atrazine concentrations in the GW were constantly larger than isoproturon concentrations (data not shown).

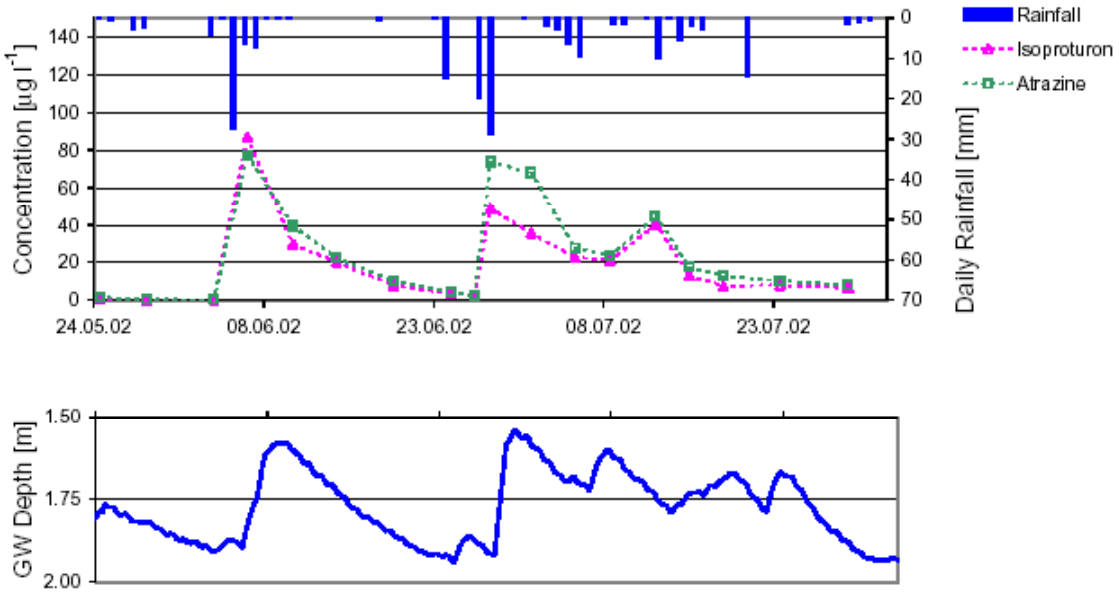


Fig. 28 - Atrazine and isoproturon concentrations in the groundwater on plot 4 in 2002 together with the GW table depth.

5.2.2. Regional observations

During the two years of the study, GW samples were collected and analysed for six herbicides (atrazine, deethylatrazine, simazine, terbuthylazine, isoproturon and diuron).

Herbicides were detected in the groundwater at 12 of the 13 piezometers. Maximum concentrations were observed during a short, critical period in 2001. Throughout the rest of the year, the concentrations remained below the drinking water limit of 0.1 µg/l. In 2002, considerably lower concentrations were detected.

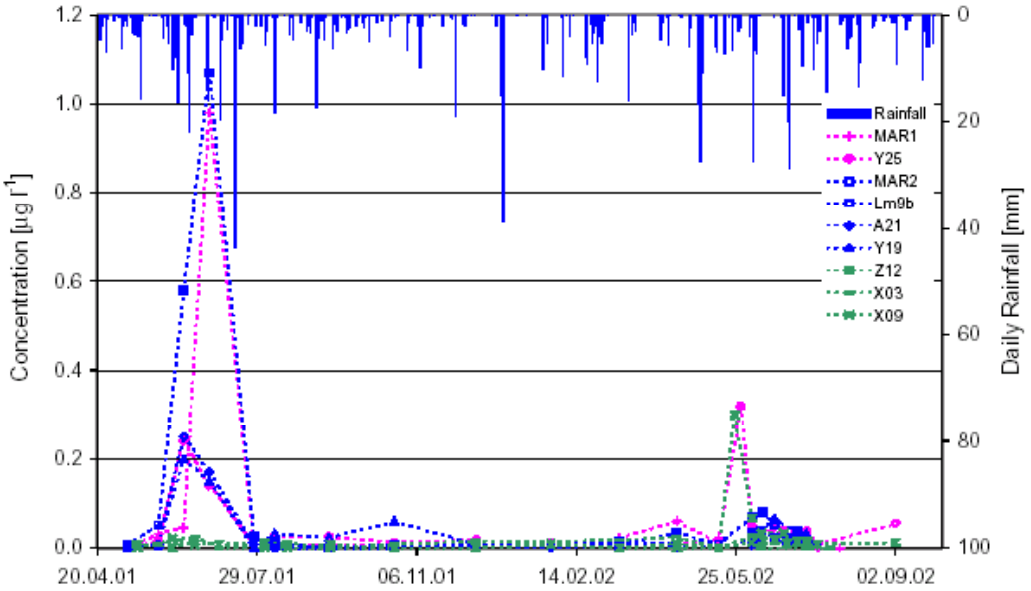


Fig. 29 - Atrazine concentration in different piezometers of the observation area.

Figure 29 shows, as an example, the atrazine concentrations in different piezometers of the observation area. High concentrations were measured in late June 2001*, i.e.* just after the first important rainfall events subsequent to the compound application. During this period, atrazine was detected in several piezometers in the plain and near the slope at concentrations varying between 0.2 and 1.1 µg/l (Y19 and MAR2, respectively). In the piezometers located near the Rhône river (X03, X09), only a very slight increase in concentration was detected.

The largest concentration was measured in the piezometer MAR2 located on a maize field to which atrazine had been applied in June 2001. In 2002, no herbicide was applied to the field and the concentrations remained low. Similarly, large concentrations were observed at the piezometer MAR1 situated on a pasture, whereas only a small atrazine peak (0.2-0.3 µg/l) was detected in both years at the piezometer Y25 also located near the hillside.

Some of the other herbicides analysed for within the framework of this study showed similar patterns. The degradation product deethylatrazine, on the other hand, was never observed at concentrations exceeding 0.04 µg/l.

The spatial distribution of the herbicide concentration was found to be closely linked to the GW characteristics. Near the Rhône river, high hydraulic head gradients quickly dilute chemicals brought from the above fields; herbicides coming from more distant fields may also be detected. The herbicide concentrations observed at the piezometers located in this zone (MAR4, X09, Y08, X03 and Z12) were relatively small. Figure 30 presents the concentrations measured in Z12 situated on a field to which terbuthylazine and diuron were applied on 14 May 2001 and on 29 April 2002.

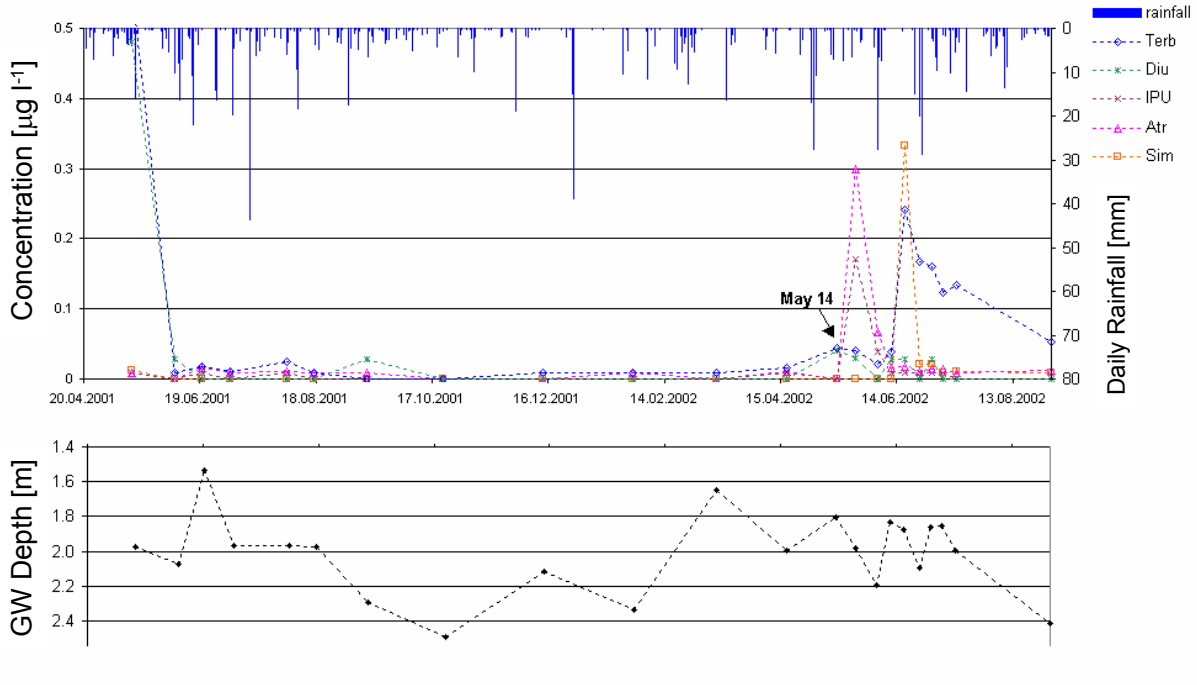


Fig. 30 - Herbicide concentration and GW depth in the piezometer Z12 in 2001 and 2002. Daily rainfall on secondary axis (Terb: terbuthylazine; Diu: diuron; IPU: isoproturon; Atr: atrazine; Sim: simazine).

The maximum concentration was observed one day after application on the above-located field (15 May 2001), indicating that the transport through the unsaturated zone was very fast. The concentration decreased quickly and two weeks later, only very low values were detected. In 2002 (herbicide application on 29 April), both substances were detected at low concentrations in the samples taken on 14 May. A larger terbuthylazine peak was observed on 18 June and the concentrations remained relatively high until mid July. In addition to the herbicides applied on the field, peaks of atrazine and isoproturon were also observed.

Close to the hillside in the south of the observation area, the GW is influenced predominantly by water infiltrating from the slope. Hydraulic gradients are lower than near the Rhône river. High herbicide concentrations were measured during the critical period in 2001 at the piezometers MAR1 and Y25 situated close to the slope. Figure 31 shows, as an example, the concentration evolution observed at Y25. The piezometer is located on a pasture where no herbicide had been applied. Notwithstanding, peaks of simazine and atrazine were detected in both years. Those substances have probably

been transported from the hillsides. The herbicide concentrations in the piezometer MAR1 showed similar behaviour.

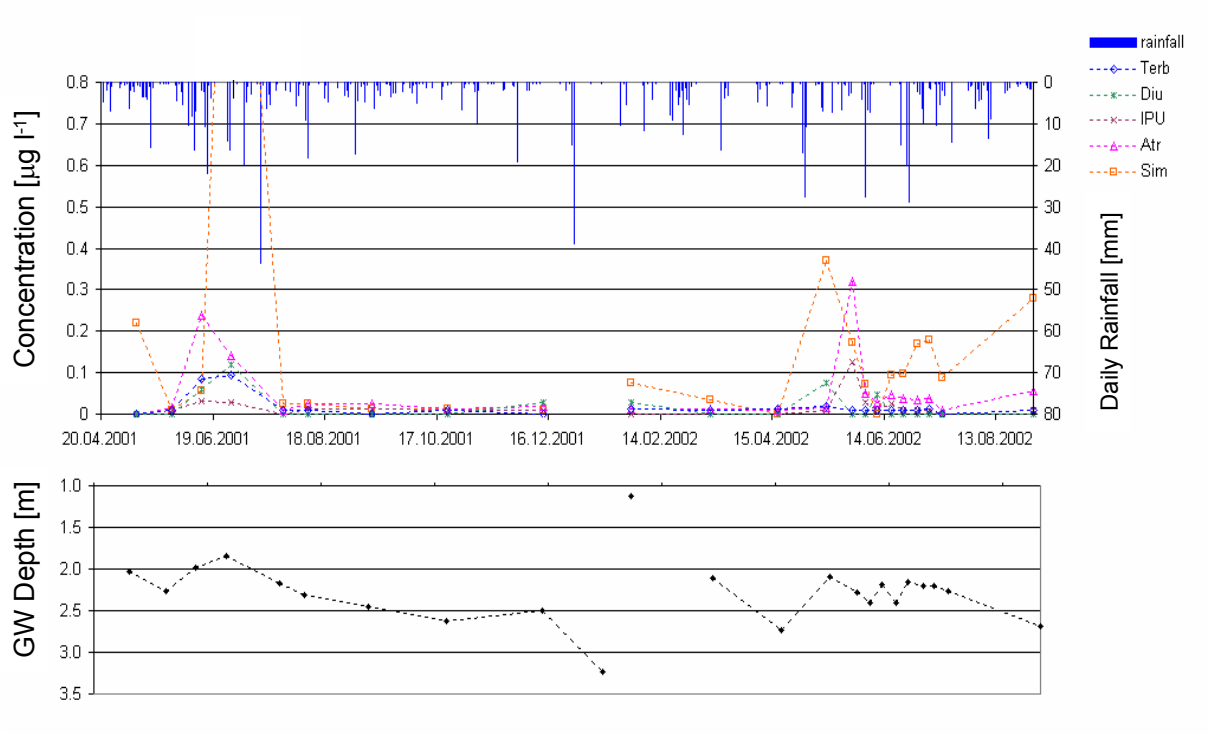


Fig. 31 - Herbicide concentration and groundwater depth in the piezometer Y25 in 2001 and 2002. Daily rainfall on secondary axis.

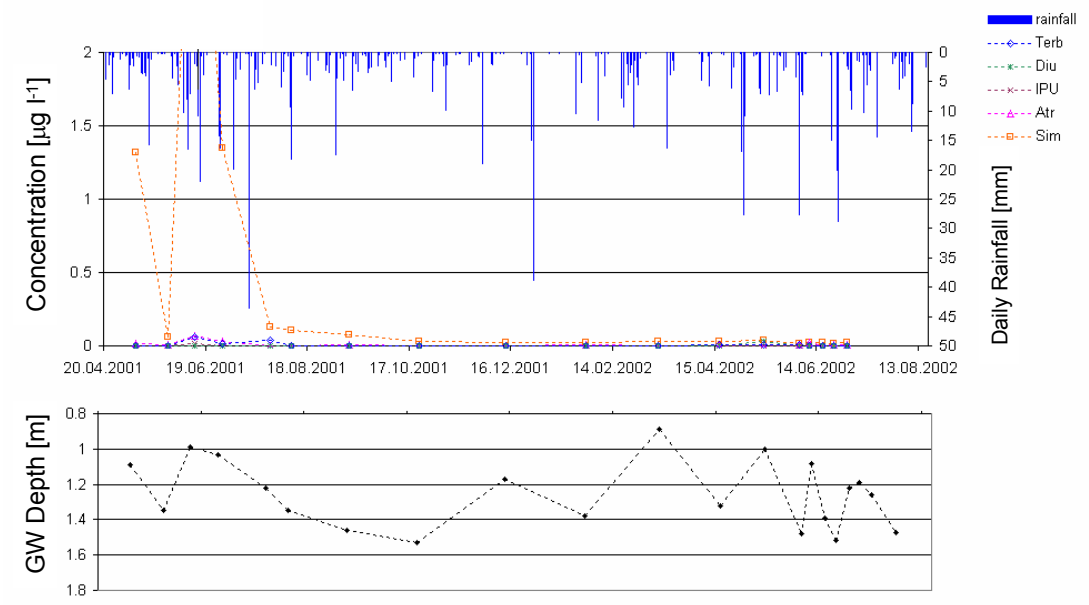


Fig. 32 - Herbicide concentration and groundwater (GW) depth in the piezometer Z17 in 2001 and 2002. Daily rainfall on secondary axis.

Within the plain, the influence of the river or the slope is far less pronounced and the average hydraulic gradient is only 0.5 - 1 ‰. Large concentrations were observed in some of the piezometers located in this zone (MAR2, MAR3, A21, Y19, Lm9b and Z17). The piezometer Z17 is situated on a pear tree field to which simazine had been applied in early May 2001. Figure 32 shows the herbicide concentrations measured during the two years.

Large concentrations were measured in the groundwater in mid May 2001 and a peak was observed in mid June. By the end of June, the concentrations had decreased considerably. In 2002 no herbicides were applied to the field and the concentrations remained low. In the other piezometers of the zone, substances not applied in the direct vicinity were also detected, but at low concentrations.

5.3. Discussion / conclusions

Intensive measurements during two years on the experimental plots have shown that the water flow and the chemical transport are closely linked to the climatic conditions. As long as no water was applied to the soil (in the form of precipitation or irrigation), isoproturon and atrazine applied recently remained near the soil surface. After the first rainfall event following the application, herbicides were quickly transported through the vadose zone into the groundwater. The rapidity of the transport and the simultaneous observation of chemicals in the upper soil layer and in the GW suggested a bypassing of part of the soil matrix. During dry periods, the concentrations decreased steadily in the soil profile and the groundwater. After further rainfall, additional concentration peaks were observed in the groundwater, while only small peaks appeared near the soil surface. Approximately 2.5 months after the application, the pesticide concentrations in water soil and in the groundwater were close to the background values.

At the regional scale, herbicides were detected in 12 of the 13 piezometers, sometimes at large concentrations, but during a short period of time (mid May to mid July). Throughout the rest of the year, the concentrations remained below the drinking water limit. The observations are in good agreement with the conclusions of the local experiments (rapid transport, important influence of the climatic conditions, quick decrease of concentration peaks). Furthermore, the groundwater characteristics play an important role on the fate of the herbicides reaching the GW. Near the Rhône river, high hydraulic gradients quickly dilute chemicals leaching from the above fields and herbicides coming from more distant fields may also be detected. Near the slope, an inflow of contaminated water from the hill side (vineyards) can contribute significantly to the groundwater contamination. Within the plain, high concentrations of herbicides applied to the above located fields can be observed temporarily. Contaminations are confined in time and space and different substances are detected from one piezometer to another. This lack of continuity in pesticide concentration suggests difficulties to predict the fate of the chemicals dissolved in the GW, and the need for a very precise knowledge of the pesticides use, both in space and time.

All the data collected during the study and the additional data on the study zone and on the aquifer properties derived by the Centre of Hydrogeology of the Neuchâtel University were brought together in a database which was made available to the groups involved in the evaluation of modelling tools (section 5 of chapter 3).

5.4. Summary

The herbicide transport processes and the GW vulnerability to chemical contamination were studied in a portion of the alluvial aquifer of the Rhône River Valley located near Martigny (Southwest Switzerland). The work was based on local transport experiments associated with a regional monitoring of the groundwater over a two-year period. At both local and regional scales, water flow and solute transport were found to be closely linked to climatic factors. After the application, the pesticides remained at the soil surface as long as precipitation did not occur. Following the first heavy rainfall, the pesticides were quickly transported through the vadose zone and compounds were found to reach the groundwater in a very short time. During subsequent dry periods, concentrations decreased steadily throughout the soil profile. New concentration peaks were observed in groundwater after further rainfall events. A few weeks after the application, pesticide concentrations in soil water and in the groundwater were again at a very low level.

6. HAVDRUP [E&R DTU]

The work performed at Havdrup in terms of monitoring and modelling has been or is in the process of being published in the refereed literature (Jørgensen *et al*., 2002, 2003, 2004a, 2004b). The reader is referred to these publications for further information. A summary of the work undertaken is presented in section 7 of chapter 3.

7. LABORATORY SORPTION AND DEGRADATION OF SELECTED PESTICIDES [E&R DTU]

Sorption and degradation are key processes affecting the fate of agrochemicals in the sediment-water environment and thorough understandings of these processes are paramount for predicting the mobility of pesticides in aquifers. The first work package of the project therefore included a dedicated study of sorption and degradation behaviour of five key pesticides. The selected pesticides were: atrazine, deethylatrazine (atrazine metabolite), isoproturon, MCPP and acetochlor (Fig. 33). The compounds are all herbicides and were selected on the basis of their present and prospective use.

Sorption and degradation of the five pesticides was investigated in four European aquifers, two aerobic [Brévilles (France) and Krauthausen (Germany)] and two anaerobic [Martigny (Switzerland) and Havdrup (Denmark)]. At the Brévilles site, sorption and degradation was also investigated in the unsaturated zone, in order to include data on degradation rates in a deep unsaturated zone of fractured limestone and to study the influence of the water content and the porosity.

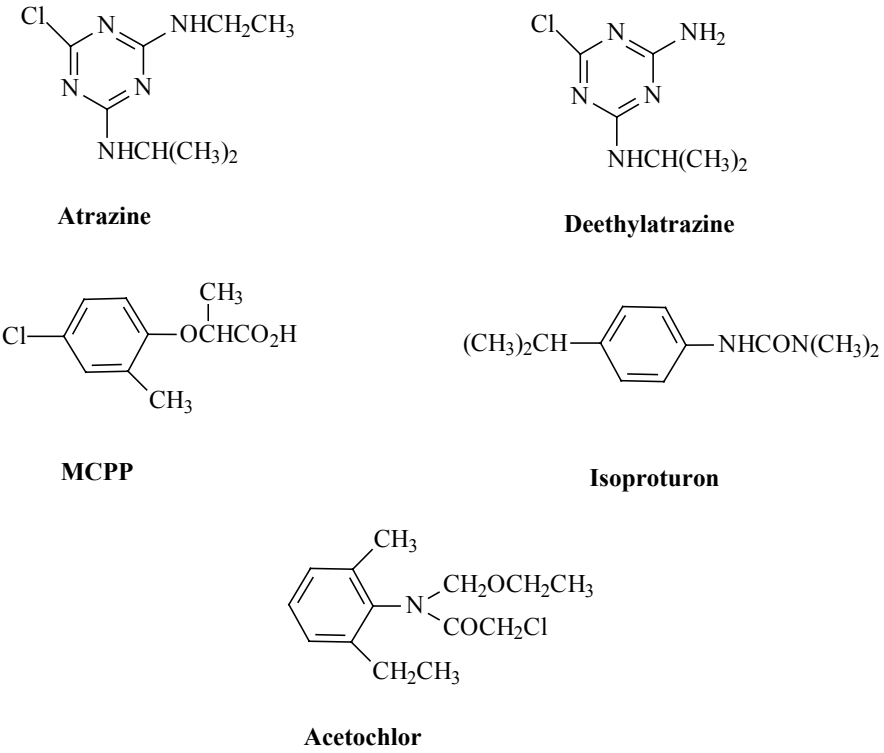


Fig. 33 - Structural formula of pesticides used in sorption and degradation studies.

7.1. Materials and methods

7.1.1. Sediment and water characterisation

- ***Unsaturated zone***

Intact sediment was sampled from the unsaturated zone at two locations at the Brévilles field site. The unsaturated zone consists mainly of fractured limestone with layers of marl. The bulk density and porosity of the sediment were calculated from measurements of the weight of the dried sample in air and the weight in mercury, and by assuming a grain density of limestone of 2.71 g/cm^3.

- ***Saturated zone***

Redox intact sediment and water were sampled from each aquifer and from the saturated zone at Brévilles field site and used for both sorption analysis and degradation experiments.

The sediments from each selected depth interval were thoroughly mixed, in order to get representative subsamples for the sorption and degradation experiments. The remaining sediment from each depth interval was freeze-dried and the grain size was characterized by sieving and particle distribution (Micrometrics Sedigraph 5,000 ET). The specific surface area was measured by Multipoint N2-BET analysis (Micromeritics, Gemini III 2375 surface area analyzer), after being outgassed (Micromeritics, FlowPrep

060 Degasser) for 24 h at room temperature. Total organic carbon content (TOC) was measured using a total elemental carbon analyzer (LECO CS-225) after removal of carbonates using 6 % sulphurous acid (HSO_3^-).

Groundwater from the aquifers at Krauthausen, Martigny and Havdrup were sampled from preinstalled wells located close to the sediment sampling points. In the experiments with sediment from Brévilles field site, sterile filtered water from the Brévilles spring were used since this spring is fed by the aquifer. The sampled water was characterised with regard to cations and anions, dissolved oxygen, pH, conductivity and dissolved organic carbon.

7.1.2. Compounds

Adsorption and degradation were investigated with a combination of [Ring-^{14}C]-pesticides (Table 9) and unlabeled pesticides, except in the degradation investigation of acetochlor, where only unlabeled pesticide was used. This was due to the labelled compound having been made available by the company at a late stage in the project.

Pesticide stock solutions (3.5 mg/l) of unlabelled compounds were prepared by dissolving technical grade pesticides (PESTANAL, Purities: atrazine, 99.4 %; deethylatrazine, 99.9 %, isoproturon, 99 %; and MCPP 99 %) in autoclaved Millipore water. Stock solutions of ^{14}C-compounds (c. 87,500 DPM/ml) were prepared from stock solutions of the compounds dissolved in methanol, acetonitrile or water. Organic solvents were evaporated by N_2-gas prior to adding Millipore water, in order to avoid adding substrate to the stock solution.

Table 9 - Purity and specific activity of the ^{14}C-labelled pesticides used in sorption and degradation investigations.

Pesticides	Label	Purity	Specific activity (mCi/mmol)	Manufacturer
MCPP	Ring-^{14}C	> 95 %	23	Izotop
Deethylatrazine	Ring-^{14}C	-	50.7	via BRGM
Atrazine	Ring-^{14}C	> 95 %	18.8	SIGMA Chemical company
Isoproturon	Ring-^{14}C	> 97 %	24.7	Amersham LIFE SCIENCE
Acetochlor	Ring-^{14}C	> 99 %	57.8	Dow AgroScience

7.1.3. Adsorption studies

The adsorption investigations were conducted by a batch equilibrium technique based on the OECD guideline 106 (1993). The adsorption was measured at an initial pesticide concentration of 50 µg/l prepared from stock solutions of ^{14}C-labeled pesticide and corresponding unlabeled pesticide. To investigate the effect of the initial concentration, additional sorption investigations were conducted at a lower concentration level of 0.5 µg/l prepared from stock solutions of ^{14}C-labeled pesticide only. The investigations were carried out in glass tubes (10 mL) with Teflon caps at 10°C in the dark. Preliminary tests excluded adsorption on those materials. In preliminary experiments the sorption was measured after 7 and 14 days. For MCPP, deethylatrazine, and acetochlor 7 days were sufficient as equilibrium time, but the sorption of atrazine and isoproturon increased slightly from 7 to 14 days, and 14 days were therefore chosen as

equilibrium time. Triplicate 5 ± 0.0005 g of sediment (0.2500 ± 0.0005 g in investigations of acetochlor) were pre-equilibrated with 4 mL sterile filtered (0.2 µm Minisart, Sartorius) groundwater for at least 20 h. After pre-equilibration 1 mL pesticide solution was added, and each test tube placed in a vertical rotator. After 168 h or 336 h the suspension was centrifuged and 1 mL of supernatant was removed for analysis. The pH of the remaining solution was measured by electrode. The removed supernatant was mixed with 10 mL OptiPhase "HiSafe" 3 (Wallac) scintillation cocktail and the amount of radioactivity determined by counting for 20 min. in a 2000 TriCarb Liquid Scintillation Analyser (United Technologies, Packard). For each sorption experiment reference samples were prepared in triplicate without sediment but otherwise handled identically to the other samples. The amount of adsorbed pesticide was calculated as the difference between the radioactivity measurements in the supernatant solution at equilibrium and the radioactivity measurements in the reference solution.

7.1.4. Degradation studies

- ***Unsaturated zone***

The sediments were gently crushed and homogenized in order to place the sediment in 100-mL airtight glass flasks. 33 g (dry weight) of the sediment were used in the incubations.

The bioassays were set-up with approximately the natural water content spiked with 0.5 mL of ^{14}C-labelled pesticide solution resulting in an initial concentration of 10 µg/kg. The pesticide solution was prepared in sterile filtered water from the Brévilles spring in order to maintain the water chemistry. Each sediment was set-up in triplicates where one of the incubations was a sterilised control (autoclaved three times, 1 hour at 100 °C at 24-hour intervals). The incubations were placed in the dark at 15 ± 2 °C.

To trap the produced amount of $^{14}CO_2$, a test tube containing aqueous sodium hydroxide (2 mL, 0.5 M NaOH) was placed in each flask. When sampling, the sodium hydroxide was replaced and the flasks were left open for 5 min. in a laminar flow bench in order to replenish oxygen. The removed sodium hydroxide was mixed with 10 mL OptiPhase HiSafe scintillation fluid and counted for 20 min in a 1414 WinSpectralTM Liquid Scintillation Counter (Wallac).

- ***Saturated zone***

The anaerobic cores from Havdrup and Martigny were cut in 22 cm long sections after removing at least 5 cm of each core end. The core sections were then transferred to an anaerobic glove box (Coy®, with an atmosphere of approximately 1 % H_2 in N_2) for further handling. Inside the anaerobic glove box approximately 1 cm of sediment was removed from each end of the core sections using a sterilized spoon. In addition, the outer 0.5 cm of the sections, which had been in contact with the inner walls of the aluminia tubes, were pared off using a paring device modified after Wilson *et al.* (1983). For each of the anaerobic samples, portions of 40 g ww (wet weight) sediment were transferred to 118 mL glass serum bottles inside the anaerobic glove box and sealed with a 1 cm thick butyl rubber stopper. Outside the anaerobic box the headspace of the bottles was replaced with 80 % N_2/20 % CO_2-gas mixture in order to remove any trace amounts of O_2. 60 mL groundwater was transferred to the decapped bottles under

constant flushing with N_2/CO_2-gas mixture. The bottles were resealed with the rubber stopper and crimp caps, and flushed again with N_2/CO_2-gas mixture with a syringe through the stopper. The pesticide stock solutions were prepared in anaerobic autoclaved Millipore water and 1 mL of both labelled (10 %) and un-labelled stock solution were added to the serum bottles through the stopper, resulting in an initial concentration in the water phase of approximately 50 µg/l of each pesticide. Three serum bottles were set up for each sample. One of these was autoclaved (20 min, 1.5 bar, 120 ºC) three times with one-day intervals, and used as a control for biological activity.

Aerobic samples from Brévilles and Krauthausen were prepared in the same way, but under aerobic conditions and without the flushing procedures. During the incubation period the serum bottles were kept in the dark at 10 °C.

For ^{14}C-activity measurements 2 mL filtered subsample was transferred to a 20 mL polyethylene scintillation vial containing a 6 mL scintillation vial with 1 mL 2.5 M KOH. The subsample was acidified by adding 0.1 mL 37 % HCl for stripping off $^{14}CO_2$, and the vial was capped and shaken gently to mix subsample with acid. The 6 mL inner-vial of this ”double-vial” system served as a CO_2 trap. The inner-vial was removed after 48 hours. Scintillation cocktail (Optiphase “HiSafe” 3, Wallac) was added (3:1 v/v of scintillation cocktail to sample) and the ^{14}C-activity of both the 20 mL vial (dissolved ^{14}C-activity fraction, excluding the inorganic ^{14}C-fraction) and the 6 mL vial (inorganic ^{14}C-fraction, i.e mineralized ^{14}C-pesticide) was quantified by counting for 20 min. in a 2000 TriCarb Liquid Scintillation Analyser (United Technologies, Packard).

7.1.5. Data analysis

- ***Sorption***

The sorption data were analysed assuming a linear sorption isotherm:

$$Kd = Cs/Ce$$

where Kd is the adsorption distribution coefficient, Cs is the equilibrium concentration of sorbate associated with the sorbent, and Ce is the equilibrium concentration of sorbate in solution. The adsorption was measured in percentage from the Liquid Scintillation Counting and the Kd-values (l/kg) were calculated as:

$$Kd = A/(100-A) \cdot (V0/M)$$

where A is the adsorption in percent, V0 is the initial volume of aqueous phase in contact with the sediment (l), and M is the mass of the dried sediment (kg). The standard deviations of Kd were calculated from the formula of propagation error (First order Taylor expansion series).

- ***Degradation***

Degradation rates were roughly quantified by applying a pseudo first-order degradation model:

$$Ct/C0 = Ce/C0 \cdot e^{-kt}$$

In the saturated sediments Ct is the measured concentration in the water phase (µg/l) at the time t (days), C0 is the initial concentration, Ce/Co (intercept) is the measured sorption expressed as the concentration in the water phase at sorption equilibrium

normalized to the initial concentration, and k is a time constant ($days^{-1}$). The time required for the pesticide to undergo degradation to half its initial concentration ("Half-life" (T½)) is then defined as:

$$T½ = ln2/k$$

The time constant (k) has been calculated by nonlinear least squares (NLLS) analysis, using the TableCurve software.

The first-order model does not account for shifts in degradation rates or lag phases. In cases of shifting degradation rates, the first-order model was applied to the initial part of the degradation curve. Lag phases have not been taken into account.

For sediments from the unsaturated zone at the Brévilles field site, the first-order degradation model was applied to the measurements of the produced amount of $^{14}CO_2$. The first order time constant is therefore a total mineralization rate, which is the time required for the pesticide to undergo complete degradation to CO_2, and mineralization rates are not comparable to the degradation rates determined in the saturated samples. The amount of $^{14}CO_2$ incorporated in the biomass is not included in the calculation and the mineralization rate is therefore a conservative estimate.

7.2. Results

7.2.1. Characterisation of the aquifer sediment and water

The major physicochemical properties of the sediments studied are presented in Table 10. The sediment from the aquifer at Brévilles field site is mainly sand with a low TOC content. However, the sediment from piezometer 1 has a high clay content (17-29 %) compared to the other samples were the clay contents are 1.5-9.6 %. The sediment was yellow/orange, which clearly indicated aerobic conditions. One exception was, however, the sediment from piezometer 4 which had a grey colour, which indicated anaerobic conditions in this part of the aquifer. Oxygen measurements made by BRGM in piezometer 4 at a later stage confirmed anaerobic conditions in the depth where the sediment cores were sampled. The core samples from Krauthausen are mainly gravel and sand and the aquifer sediment was clearly aerobic. Sediment from Martigny aquifer is characterized by a high content of silt and organic carbon compared to the other investigated aquifers. The sediment was clearly anaerobic with grey and black coloured sediment and a smell of sulphide. The sediment cores from Havdrup are mainly grey sand indicating anaerobic conditions. The clay and silt contents in the sand layer varies significantly in the aquifer, as the sediment cores from the east part of the aquifer (Ha-A and B) have a high content of clay (13-17 %) and silt (22-25 %), whereas the sediment core from the western part of the aquifer is mainly sand with only 3 % of clay and 13 % silt. The investigated sediments represent a broad range of aquifers as the investigation includes sediments with different TOC content and different clay and silt content as well as sediment sampled from different redox zones.

Table 10 - Sediment characteristics (m bgl = meters below ground level).

Sampling site/depth	Surface area (m^2/g)	TOC[b] (wt. %)	Grain size distribution[c] Gravel (wt. %)	Sand (wt. %)	Silt (wt. %)	Clay (wt. %)	Classification/ matrix color
Brévilles (F)							
18.4-18.7 m bgl (Pz 8)	2.7	0.026 ± 0.004	0.4	97.4	0.8	1.5	Sand/yellowish
18.5-18.9 m bgl (Pz 7)	10.1	0.039 ± 0.003	0.0	85.0	5.5	9.6	Loamy sand/yellowish
22.6-22.9 m bgl (Pz 4)	11.1	0.014 ± 0.007	0.5	81.5	9.6	8.4	Loamy sand/grayish
38.5-38.7 m bgl (Pz 1)	24.6	0.018 ± 0.008	2.1	68.2	0.7	29.0	Sandy clay loam/ yellowish
39.0-39.3 m bgl (Pz 1)	34.6	0.012 ± 0.005	0.0	79.6	3.4	17.0	Sandy loam/yellowish
46.8-47.1 m bgl (Pz 2)	10.6	0.007 ± 0.005	0.0	88.4	2.8	8.8	Loamy sand/yellowish
Krauthausen (D)							
1.7-1.9 m bgl (KR-A)	5.0[a]	0.042 ± 0.004	56.3	40.5	1.7	1.5	Gravel sand/yellowish
1.7-1.9 m bgl (KR-B)	5.7[a]	0.057 ± 0.05	67.7	27.9	2.2	2.2	Gravel sand/yellowish
Martigny (CH)							
2.54-3.14 (Ma-A)	1.5	0.480 ± 0.073	0.3	36.9	57.2	5.7	Silt loam/ grayish
2.54-2.96 (Ma-B)	1.5	0.546 ± 0.151	0.0	31.7	64.2	4.0	Silt loam/ grayish
Havdrup (DK)							
4.96-5.78 m bgl (Ha-A)	10.7	0.057 ± 0.008	4.2	56.9	22.1	16.9	Sandy loam/ grayish brown
4.78-5.44 m bgl (Ha-B)	4.6	0.061 ± 0.035	2.7	59.9	24.8	12.6	Sandy loam/ grayish brown
3.32-4.48 m bgl (Ha-C)	-	-	-	-	-	-	
3.28-4.60 m bgl (Ha-D)	-	0.023 ± 0.004	7.9	76.0	12.8	3.3	Loamy sand/ grayish brown

[a]determined for the sediment < 2 mm.
[b]TOC (Total Organic Carbon) is shown as the mean and standard deviation of three replicates.
[c]Grain size distribution: Gravel (> 2 mm), Sand (2.00-0.063 mm), Silt (0.063-0.002 mm), and Clay (<0.002 mm)

Table 11 - Groundwater chemistry.

	Brévilles spring	Krauthausen Pz 70	Martigny Pz 17	Havdrup Pz 25 + 26	Havdrup Pz B1,3 +D1,3
NVOC (mg/l)	2.17	1.38	8.12	4.05	4.20
O_2 (mg/l)	8.1	8.9	<0.5	0.8	0.7
pH	6.8	6.6	6.8	6.7	6.8
Temperature (°C)	-	16.9	15.8	7.1	4.5
Conductivity (µS/cm)	627	783	2,400	343	207
Cations: (mg/l)					
NH_4^+	0.22	0.08	0.18	0.95	0.68
Na^+	6.17	26.01	100.01	27.15	23.03
K^+	1.64	3.99	9.37	8.38	6.24
Mg^{2+}	7.99	25.93	207.62	27.18	19.71
Ca^{2+}	132.67	169.79	354.28	343.62	188.54
Fe^{2+}	b.d.[b]	0.27	0.74	0.46	0.33
Anions: (mg/l)					
Cl^-	24.62	80.78	220.45	121.16	19.80
NO_3^-	14.44	16.52	0.33	0.11	0.55
SO_4^{2-}	7.79	42.62	307.01	75.60	25.30
TAL (meq/l)	5.40[a]	3.20	11.10	7.57	7.98

[a] Calculated from the charge balance; [b] below detection limit.

The water from the Brévilles spring and Krauthausen is calcium-bicarbonate rich with high concentrations of oxygen and relatively high concentrations of nitrate caused by the intensive agricultural land use in these areas (Table 11). The groundwater chemistry in the aquifer at Martigny field site is strongly influenced by inflow of highly mineralised water from the slopes located north and south of the valley, and the electrical conductivity is therefore high. The water chemistry at the Havdrup field site

was anaerobic or micro aerobic, with oxygen at 1.1 mg/l or below. However, investigations of the water chemistry in the sandy layer in the western part of the aquifer, showed that during heavy rain events, aerobic rainwater leached to the aquifer, resulting in oxygen concentrations of 4-6 mg/l.

7.2.2. Linear distribution coefficients (Kd values)

In three aquifer samples (Brévilles 18.4-18.7 m bgl, Brévilles 39.0-39.3 m bgl, and Krauthausen 1.7-1.9 m bgl (Kr A)), sorption was investigated at two concentration levels (0.5 and 50 µg/l). However, the results showed no significant differences in Kd values determined at a low or high initial concentration showing approximately linear adsorption behaviour for the investigated pesticides in the investigated concentration range (0.5-50 µg/l). The sorption data were therefore analysed assuming a linear sorption isotherm (Table 12).

Table 12 - Sorption distribution coefficients (Kd values) for the selected pesticides (mean ± standard deviation calculated from triplicates).

Sampling depth and piezometer	K_d (l/kg) MCPP	Deethyl-atrazine	Atrazine	Isoproturon	Acetochlor
Brévilles unsaturated zone					
C1 0-0.25 m bgl	0.49 ± 0.17	1.79 ± 0.15	2.42 ± 0.11	5.01 ± 0.41	4.96 ± 0.28
C1 0.25-0.50 m bgl	0.32 ± 0.02	0.92 ± 0.09	1.07 ± 0.09	1.78 ± 0.10	2.02 ± 0.09
C1 3.10-3.25 m bgl	0.08 ± 0.02	0.40 ± 0.06	0.27 ± 0.04	0.28 ± 0.08	0.49 ± 0.04
C1 6.00-6.20 m bgl	0.03 ± 0.02	0.13 ± 0.05	0.03 ± 0.02	N.S.	0.02 ± 0.01
C1 9.00-9.12 m bgl	N.S.	0.12 ± 0.06	N.S.	0.14 ± 0.13	0.06 ± 0.01
C1 13.00-13.12 m bgl	0.04 ± 0.01	0.09 ± 0.05	N.S.	N.S.	N.S.
C2 0-0.25 m bgl	0.40 ± 0.14	1.61 ± 0.02	2.30 ± 0.09	3.44 ± 0.27	3.39 ± 0.25
C2 0.25-0.40 m bgl	0.19 ± 0.10	0.47 ± 0.04	0.55 ± 0.09	0.71 ± 0.10	0.84 ± 0.12
C2 1.00-1.30 m bgl	0.13 ± 0.11	0.20 ± 0.02	0.09 ± 0.04	0.13 ± 0.07	0.22 ± 0.03
C2 3.22-3.34 m bgl	0.07 ± 0.08	0.14 ± 0.07	0.05 ± 0.03	N.S.	0.06 ± 0.03
C2 8.00-8.20 m bgl	N.S.	0.07 ± 0.05	N.S.	N.S.	0.07 ± 0.05
C2 15.37-15.56 m bgl	N.S.	0.05 ± 0.02	N.S.	N.S.	N.S.
Brévilles saturated zone					
18.4-18.7 m bgl (Pz 8)	0.02 ± 0.01	0.05 ± 0.01	0.02 ± 0.01	0.06 ± 0.01	0.06 ± 0.03
18.5-18.9 m bgl (Pz-7)	N.S.	0.10 ± 0.07	0.13 ± 0.02	0.25 ± 0.04	0.18 ± 0.04
22.6-22.9 m bgl (Pz-4)	0.23 ± 0.03	0.50 ± 0.04	1.90 ± 0.14	3.06 ± 0.09	4.60 ± 0.29
38.5-38.7 m bgl (Pz 1)	N.S.	0.15 ± 0.06	0.15 ± 0.02	0.23 ± 0.01	0.15 ± 0.03
39.0-39.3 m bgl (Pz 1)	N.S.	0.11 ± 0.06	0.13 ± 0.02	0.15 ± 0.02	0.11 ± 0.09
46.8-47.1 m bgl (Pz 2)	N.S.	0.04 ± 0.02	0.07 ± 0.01	0.05 ± 0.05	0.11 ± 0.04
Krauthausen					
1.7-1.9 m bgl (Kr-A)	0.02 ± 0.02	0.14 ± 0.04	0.17 ± 0.04	0.21 ± 0.02	N.S.
1.7-1.9 m bgl (Kr-B)	0.03 ± 0.02	0.12 ± 0.04	0.22 ± 0.02	0.32 ± 0.06	0.07 ± 0.06
Martigny					
2.54-3.14 (Ma-A)	0.08 ± 0.04	0.26 ± 0.05	0.61 ± 0.20	1.55 ± 0.19	1.42 ± 0.22
2.54-2.96 (Ma-B)	N.S.	0.29 ± 0.04	0.69 ± 0.22	1.95 ± 0.26	1.07 ± 0.07
Havdrup					
4.96-5.78 m bgl (Ha-A)	0.08 ± 0.02	0.34 ± 0.04	1.63 ± 0.76	3.08 ± 1.2	2.38 ± 0.36
4.78-5.44 m bgl (Ha-B)	0.08 ± 0.02	0.25 ± 0.02	0.74 ± 0.23	1.51 ± 0.3	1.03 ± 0.18
N.S. = Not Significant, as the sorption was less than the standard deviation (approximately 3 %).					

In the unsaturated zone at the Brévilles field site, sorption decreased with depth in both profiles (Fig. 34) and the sorption of all pesticides was limited below the topsoils. In several limestone samples the sorption was even below the detection limit. This illustrates that the TOC and clay contents in the limestone were very low. Earlier work had demonstrated that the sorption of pesticides on limestone is related to small quantities of organic matter or clay located in fractures in the chalk, whereas the

limestone matrix itself is relatively inert (Johnson *et al.*, 1998; Madsen *et al.,* 2000; Clausen *et al.,* 2001).

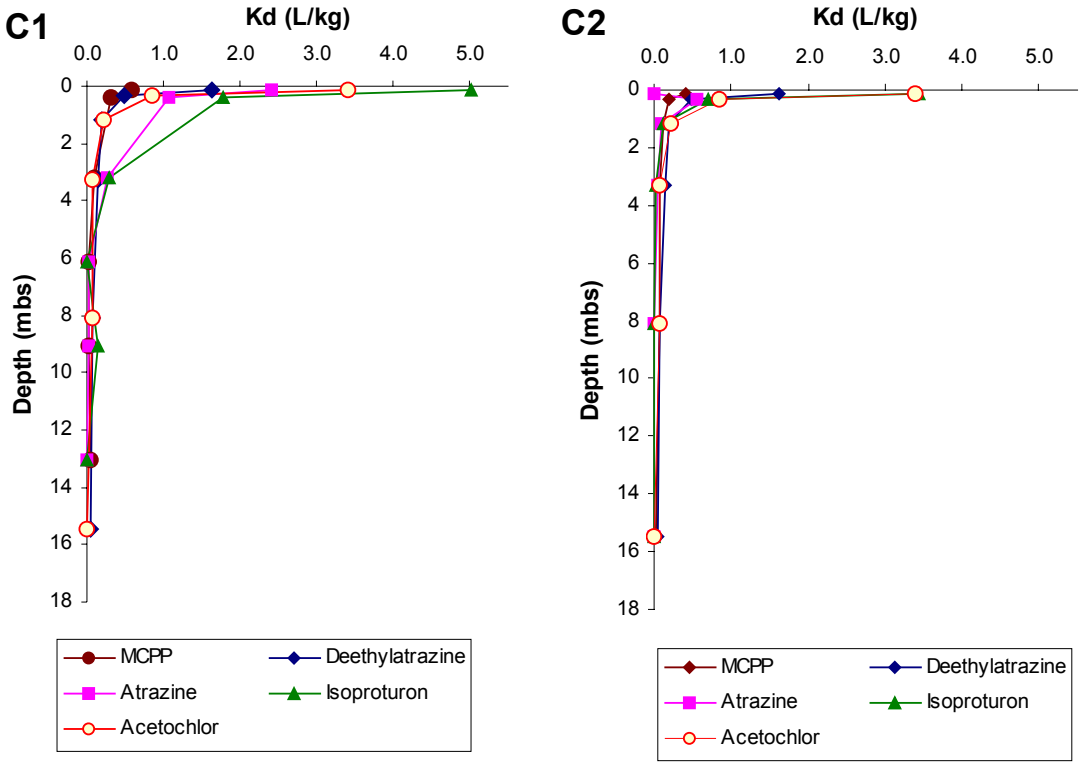


Fig. 34 - Sorption distribution coefficients (Kd values) of investigated pesticides at an initial pesticide concentration of 50 µg/l in two profiles C1 and C2 from the unsaturated zone at Brévilles field site.

In the investigated aquifer sediments, the sorption in terms of Kd values was in general decreasing in the following order: acetochlor > isoproturon > atrazine > deethylatrazine > MCPP. The Kd values corresponded to retardation factors of between 1.3 and 19.5 for isoproturon and of between 1.4 and 28.6 for acetochlor (assuming a sandy aquifer with a bulk density of 1.8 g/cm^3 and a porosity of 0.3). For atrazine the Kd values corresponded to retardation factors between 1.1 and 12.4. The metabolite deethylatrazine was less adsorbed than the parent compound with retardation factors between 1.2 and 4.0 and the sorption of MCPP was limited with a retardation factor between 1.0 and 2.4.

In general the sorption of the investigated pesticides was higher in the sediments from the anaerobic aquifers (Martigny, Havdrup and Brévilles 22.6-22.9 m bgl) than in the aerobic sediments (Fig. 35). Adsorption properties of soils and sediments are known to be strongly influenced by constituents with high specific surface area such as TOC and clay (Bailey and White, 1970). However, the measured sorption in the aquifer sediments could not be correlated to neither clay content, organic carbon content nor surface area, due to the significant high sorption observed in the sediments from the anaerobic part of the aquifers. This was especially obvious in the sediment from Brévilles piezometer 4 (22.6-22.9 m bgl) which has a lower clay and organic carbon

content than most of the other sediments (Table 10), but still the sediment from piezometer 4 contains a highly reactive surface, which may be due to the original redox conditions. The redox conditions may therefore be a key factor controlling the sorption of pesticides in aquifers, probably because the redox conditions changes the nature of functional groups on the organic carbon (Clausen *et al.,* submitted.).

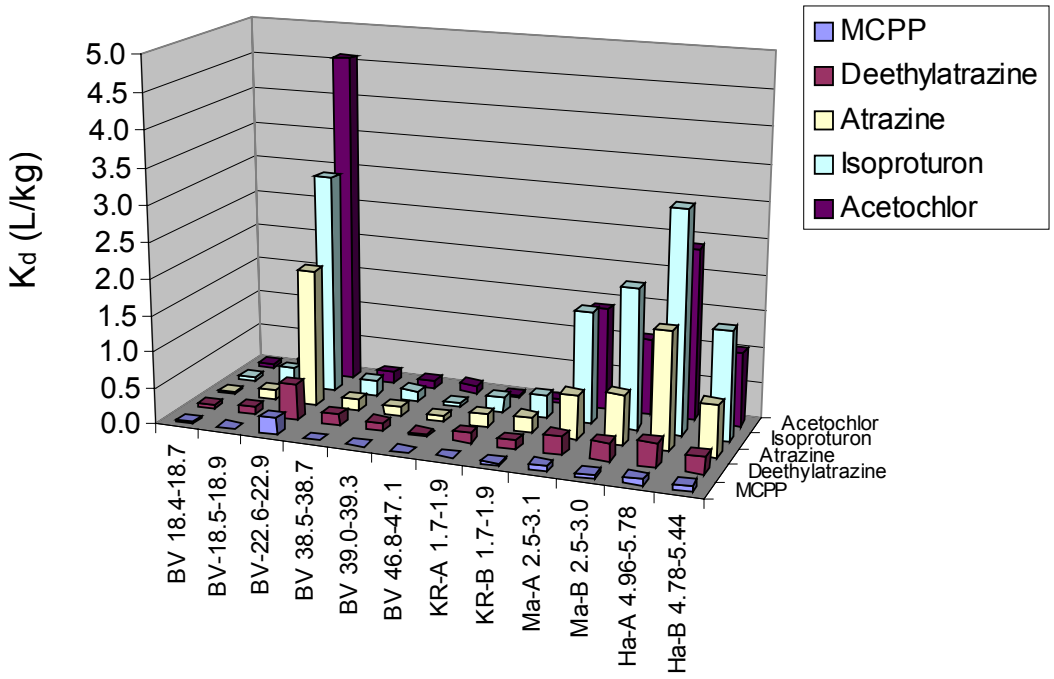


Fig. 35 - Sorption distribution coefficients (Kd values) of investigated pesticides at an initial concentration of 50 µg/l in sediments from four aquifers. BV: Brévilles (F); KR: Krauthausen (D); Ma: Martigny (CH); Ha: Havdrup (DK).

7.2.3. Degradation bioassays

- ***Unsaturated zone***

The unsaturated zone at Brévilles consists of mostly limestone until 16 m below surface. Surprisingly, samples of this material were able to mineralise MCPP, isoproturon and acetochlor (Fig. 36, Table 13). The rate decreased with depth until 3 m bgl, with a slow but significant mineralization until 16 m bgl. The degradation rate was not correlated to the water content or porosity of sediments from the unsaturated zone (Fig. 36). In contrast, atrazine and deethylatrazine were only mineralized in the topsoils (0-0.5 m bgl) (Fig. 36, Table 14).

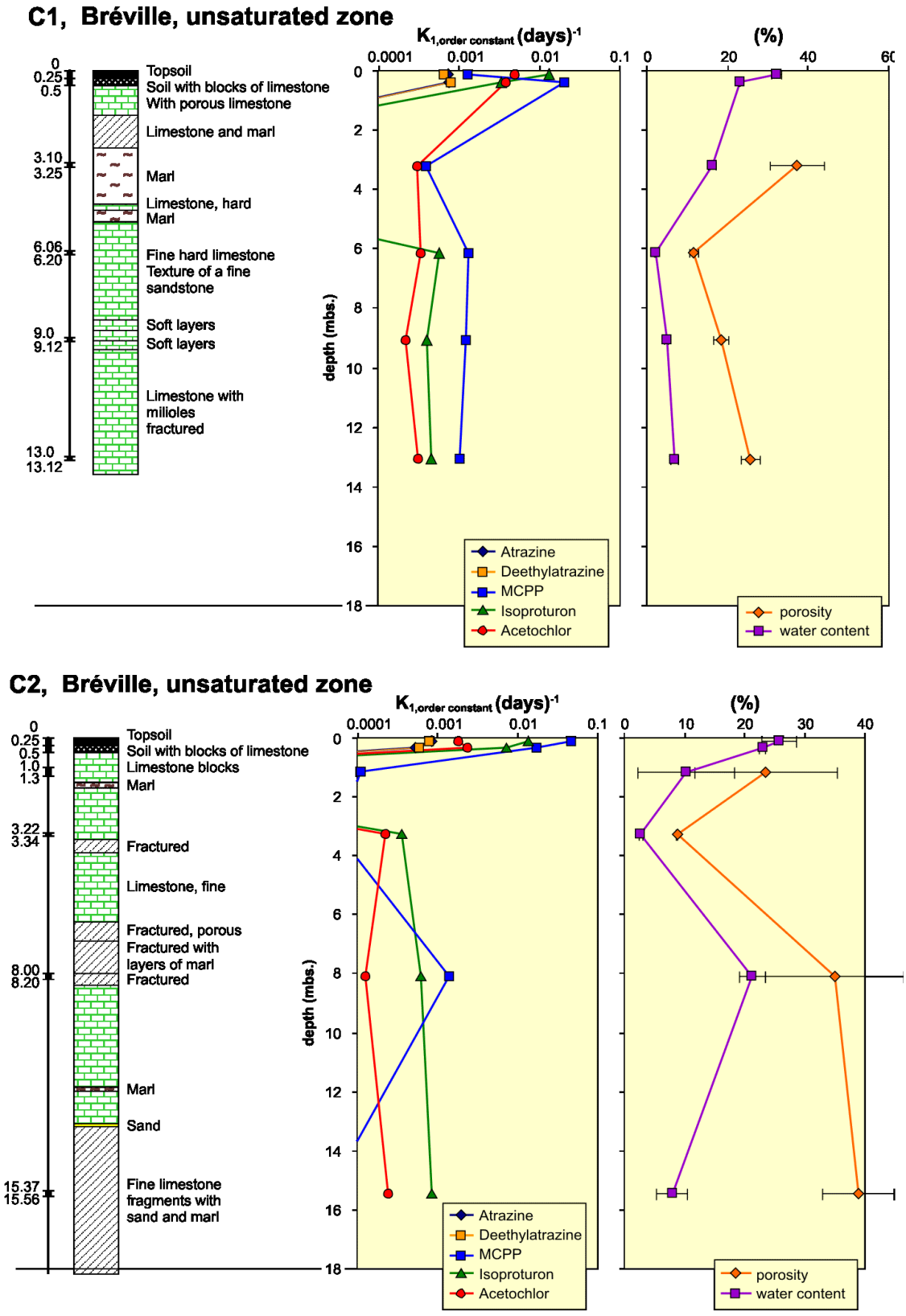


Fig. 36 - First order initial rate constant calculated from the production of $^{14}CO_2$ in incubations with sediment from the unsaturated zone at Brévilles field site, with indication of geology, water content and porosity.

Table 13 - First order degradation rates in sediment samples from the unsaturated zone at Brévilles field site. The rates are calculated from data from duplicate incubations unless there was a significant difference between these. The figures in brackets are the period where the first order model has been applied.

Sampling depth	MCPP		Isoproturon		Acetochlor	
	$T_{½}$	R^2	$T_{½}$	R^2	$T_{½}$	R^2
Brévilles, unsaturated zone C1						
C1 0-0.25 m bgl	21 (0-14)	0.51	52 (0-14)	0.99	140 (0-14)	0.96
	539 (14-182)	0.90	603 (14-182)	0.91	458 (14-182)	0.95
C1 0.25-0.50 m bgl	34 (0-14)	0.90	208 (0-45)	0.99	183 (0-59)	0.99
	428 (14-182)	0.93	549 (45-182)	0.95	403 (59-182)	0.98
C1 3.10-3.25 m bgl	1,761 (0-22)	0.79	N.S.		2,288 (0-22)	0.93
	9,881 (22-182)	0.97			16,900 (22-182)	0.68
C1 6.00-6.20 m bgl	530 (0-14)	0.50	1,198	0.95	2,060	0.93
	9,867 (14-182)	0.95				
C1 9.00-9.12 m bgl	566 (0-14)	0.69	1,732	0.97	1,850 batch 1	0.95
	10,871 (14-182)	0.86			32,029 batch 2	0.89
C1 13.00-13.12 m bgl	C.N.P.		1,506	0.99	1,406 batch 1	0.90
	13,922 (14-182)	0.65			2,239 batch 2	0.99
Brévilles, unsaturated zone C2						
C2 0-0.25 m bgl	15 (0-7	0.93	50 (0-22)	0.96	383	0.89
	867 (7-182)	0.91	619 (22-182)	0.90		
C2 0.25-0.40 m bgl	40 (0-14)	0.94	95 (0-22)	0.95	290	0.94
	463 (22-182)	0.95	400 (22-182)	0.89		
C2 1.00-1.30 m bgl	711 (0-14)	0.59	N.S.		N.S.	
	6,193 (14-182)	0.90				
C2 3.22-3.34 m bgl	C.N.P.		1,300 batch 1	0.96	3,090	0.98
	11,902 (14-182)	0.93	1,916 batch 2	0.97		
C2 8.00-8.20 m bgl	488 (0-22)	0.83	1,103 (0-45)	0.95	5,441 batch 1	0.99
	3,952 (22-182)	0.86	5,801 (45-182)	0.93	9,550 batch 2	0.99
C2 15.37-15.56 m bgl	C.N.P.	-	803 (0-45)	0.98	2,846 (0-45)	0.91
	15,835 (14-182)	0.76	1,992 (45-182)	0.89	7,670 (45-182)	0.92

N.S. = Not Significant, as the detected $^{14}CO_2$ was less than the chemical impurity (Table 9).
C.N.P. = correlation to the 1.order equation was not possible.

Table 14 - First order degradation rates for atrazine and deethylatrazine in sediment samples from the unsaturated zone at Brévilles field site.

Sampling depth	Atrazine		Deethylatrazine	
	$T_{½}$	R^2	$T_{½}$	R^2
Brévilles, unsaturated zone C1				
C1 0-0.25 m bgl	946	0.89	1062	0.99
C1 0.25-0.50 m bgl	910	0.98	871	0.99
Brévilles, unsaturated zone C2				
C2 0-0.25 m bgl	804	0.93	876	1.00
C2 0.25-0.40 m bgl	1,288	0.96	1155	0.94

- ***Saturated zone***

The degradation experiments with aquifer sediments showed no significant degradation of atrazine, deethylatrazine and acetochlor during a two-year long incubation period (Figs 37 to 39).

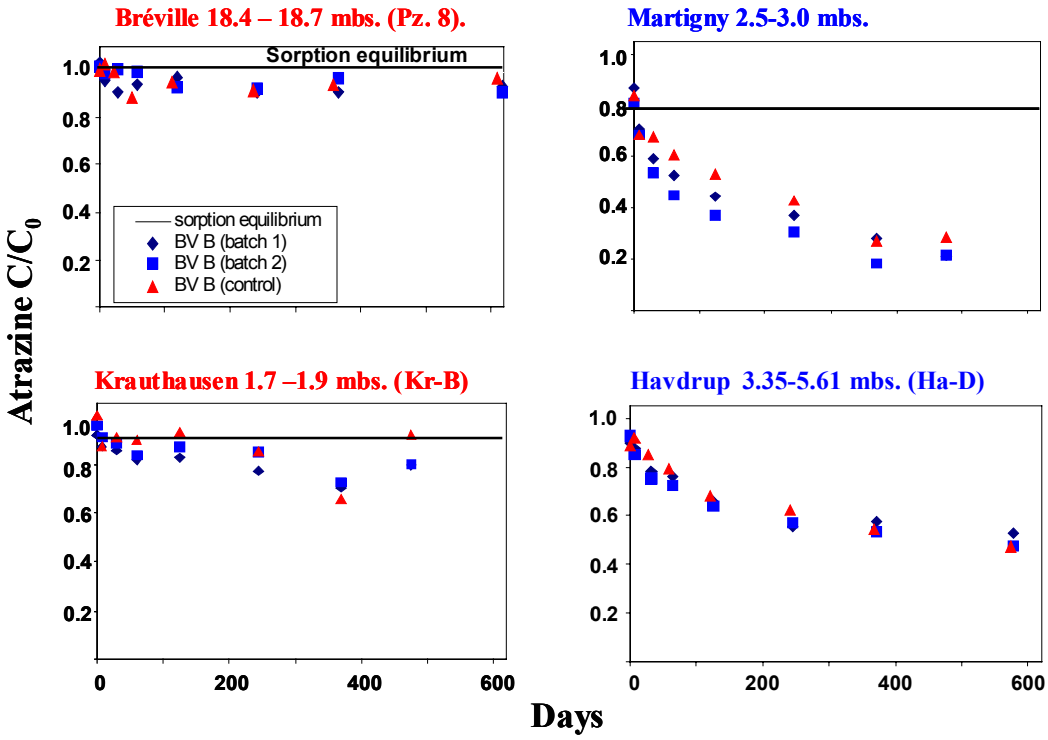


Fig. 37 - Concentration of atrazine (dissolved ^{14}C-activity) in incubations with sediment from the four aquifers. Controls: 3 x autoclaved.

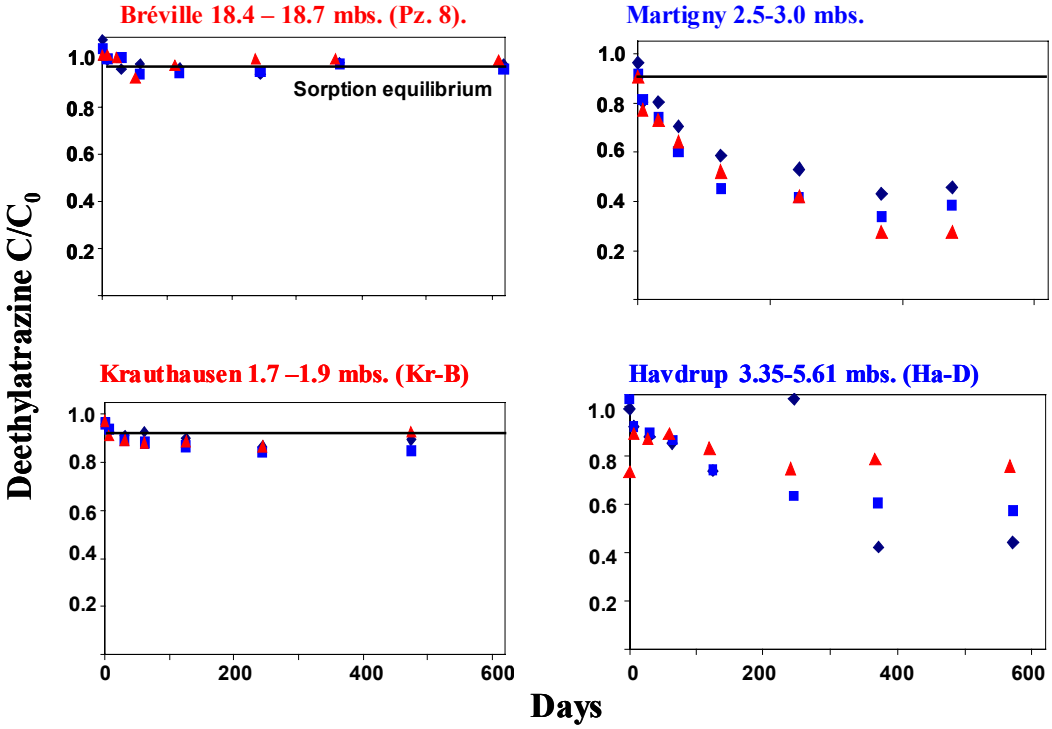


Fig. 38 - Concentration of deethylatrazine (dissolved ^{14}C-activity) in incubations with sediment from the four aquifers. Controls: 3 x autoclaved.

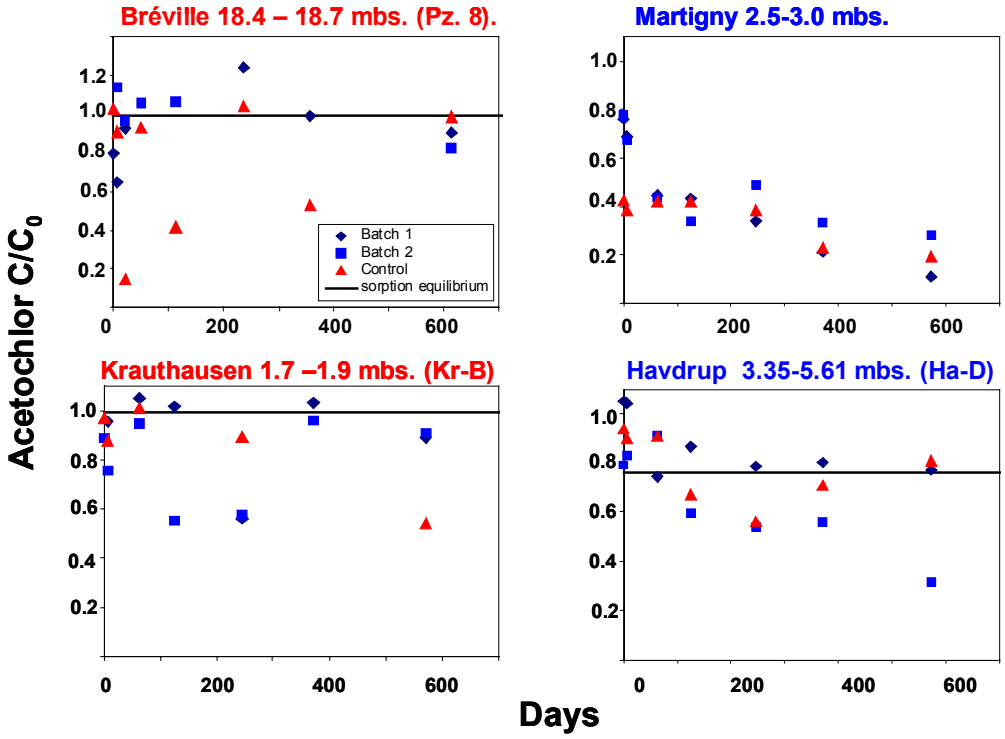


Fig. 39 - Concentration of acetochlor in incubations with sediment from the four aquifers. Controls: 3 x autoclaved.

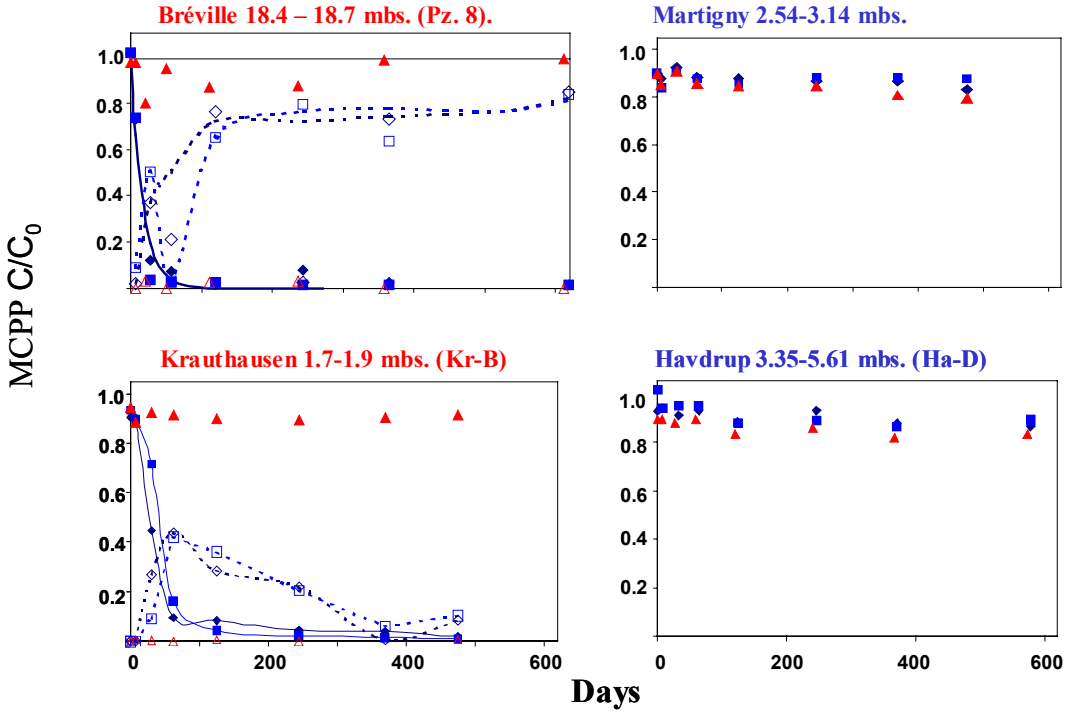


Fig. 40 - Concentration of MCPP (dissolved ^{14}C-activity) and concentration of $^{14}CO_2$ in incubations with sediment from the four aquifers. Controls: 3 x autoclaved. The lines represent the applied first order model.

In some incubations with atrazine, deethylatrazine, and acetochlor the concentration in the water phase decreased significantly during a period of more than 100 days (data not shown), and in most cases the concentration reached corresponded well to that expected from the sorption experiments. In contrast, concentrations decreased more than expected from the sorption experiments for the Martigny sediment (Figs 37 to 39). Since there was no significant difference between the autoclaved controls and the biologically active bioassays (batch 1 and 2) and no $^{14}CO_2$ was produced in experiments with atrazine and deethylatrazine, there was no direct evidence for degradation. Similar decreases in the dissolved atrazine has been observed in samples from a number of anaerobic Danish aquifers, which were attributed to a slow sorption process since no degradation products were found (Pedersen *et al.,* 2002).

In general, no degradation of MCPP was observed in the anaerobic aquifers (Martigny and Havdrup) (Fig. 40). However, MCPP was degraded in 7 of the 8 investigated aerobic core sections from Brévilles and Krauthausen, indicating a strong impact of redox conditions on the ability to degrade MCPP (Fig. 40). A significant $^{14}CO_2$ production was observed in all the experiments where the MCPP concentration in the water phase decreased, demonstrating a fast mineralization of MCPP.

- ***Spatial variability in degradation***

The degradation time for MCPP varied substantially between the different core sections from the aquifers (Table 15). Significant spatial variability was also observed in a small-scale investigation of degradation of MCPP, where incubations with sediment from Brévilles piezometer 1 (38.71-39.91 m bgl) were set-up with only 4 cm depth-interval (Fig. 41).

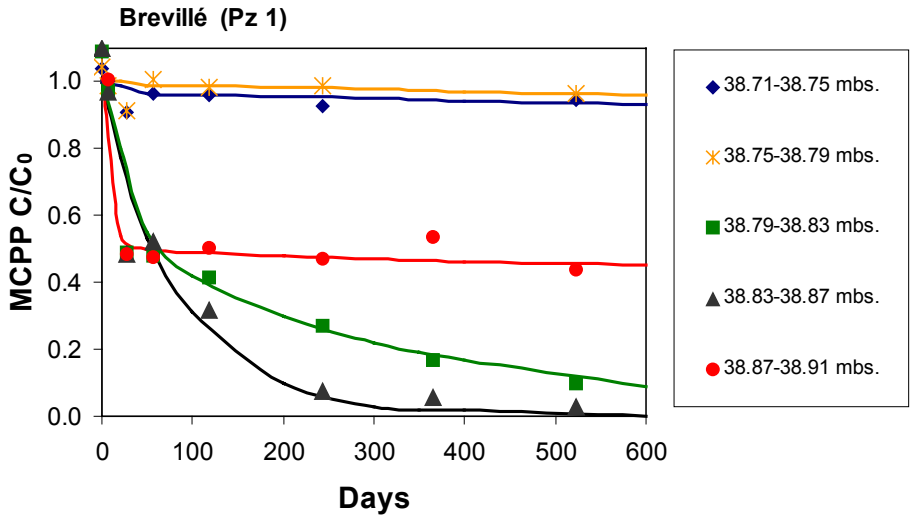


Fig. 41 - The concentration of MCPP (dissolved ^{14}C-activity) as a function of time in the small-scale investigation with sediment from Brévilles (Piezometer 1). Controls: 3 x autoclaved.

- ***Biodegradation of isoproturon***

The small-scale investigations showed a sharp limit between zones where microorganisms degraded MCPP, and zones where the degradation of MCPP was slow or even insignificant. Results showed that spatial variability is significant and that an assessment of "an overall" degradability description behaviour of MCPP in aquifers needs to involve zones with fast degradation and zones with much slower degradation.

Isoproturon was significantly biodegraded in all investigated aerobic sediments from Brévilles and Krauthausen, but not in the anaerobic aquifers (Fig. 42). In all incubations with a significant degradation $^{14}CO_2$ was produced, showing mineralization of isoproturon (Fig. 42).

The degradation rate for isoproturon varied substantially between the core sections, as was observed for MCPP. The degradation rates for the two compounds seemed to be correlated to some extent, since in sediments where MCPP was degraded fast, isoproturon was also degraded fast (Figs 40 and 42).

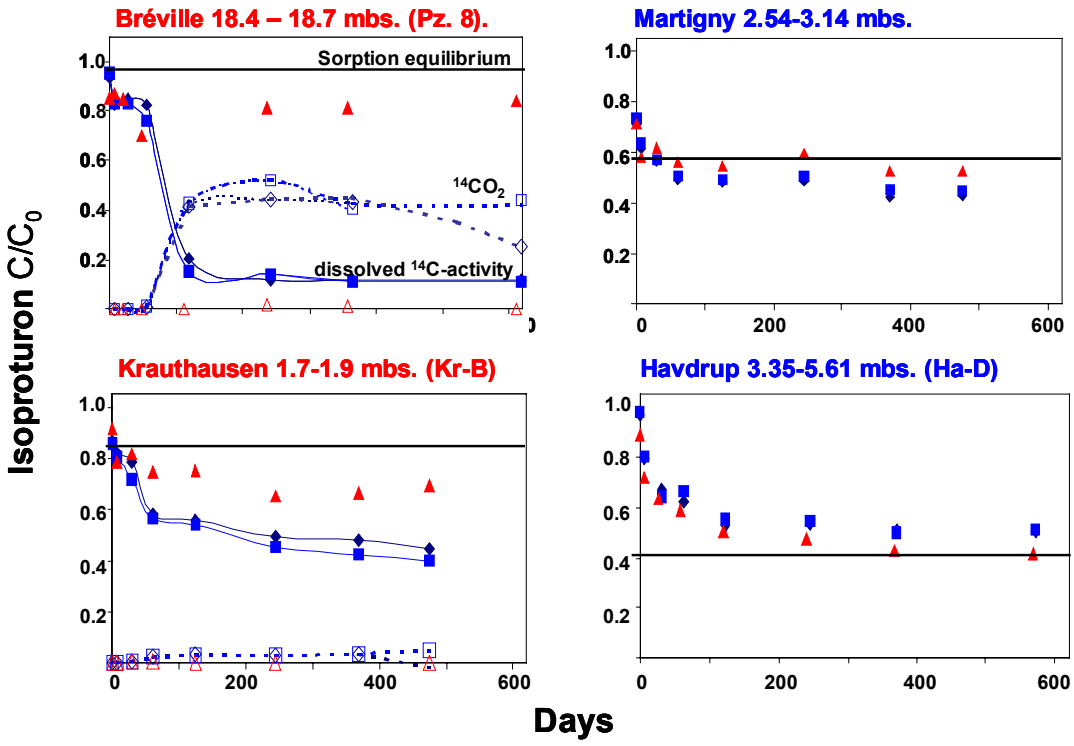


Fig. 42 - Concentration of isoproturon (dissolved ^{14}C-activity) and concentration of $^{14}CO_2$ in incubations with sediment from the four aquifers. Controls: 3 x autoclaved. The lines represent the first order model.

Only few publications in literature have showed degradation of isoproturon in aerobic chalk aquifers (Kristensen *et al.,* 2001; Johnson *et al.,* 1998, 2000), and in these studies, full mineralization of isoproturon has not been observed. Also, no studies conducted with sandy aquifer sediments have observed degradation of isoproturon

(Larsen *et al.,* 2000; Broholm *et al.,* 2001). Therefore, the result obtained in this project regarding isoproturon is somewhat surprising. The significant degradation of isoproturon observed in the sediments from Brévilles and Krauthausen may be a result of the history of exposure of isoproturon in these areas, which may have lead to communities of microorganisms to adapt.

- ***Degradation rates***

In order to quantify the observed degradation of MCPP and isoproturon in the aerobic aquifer samples from Brévilles and Krauthausen, a first order degradation model was applied to the data (Table 15).

Only in one sediment from Brévilles (18.4-18.7 m bgl) was a good fit of MCPP data to the first order model observed. In the other sediments, the degradation rate shifted after approximately 50 % MCPP degraded. For these sediments, the calculated rates described the initial part of the degradation curve. In order to describe the degradation of MCPP below 25 µg/l, a Monod expression or a much slower first order degradation rate may be applied to the data. The shift in degradation rate after approximately 50 % MCPP was degraded, could imply enantioselective degradation of MCPP, as MCPP was applied as a racemic mixture. Enantioselective degradation of MCPP in groundwater has been proposed by Heron & Christensen (1992) and Williams *et al.* (2001), but another study demonstrated an identical degradation patterns for both (R)- and (S)-enantiomers (Rügge *et al.,* 2002). Enantioselective degradation of MCPP can therefore not be rejected nor confirmed by the literature and specific measurements would be necessary to draw further conclusions on this matter.

Table 15 - First order degradation rates in sediment samples from the aquifer at Brévilles field site and Krauthausen field site. The figures in brackets are the period where the first order model has been applied.

Sampling depth	Replicates	MCPP		Isoproturon	
		$T_{½}$ (Days)	Correlation R^2	$T_{½}$ (Days)	Correlation R^2
Brévilles					
18.4-18.7 m bgl (Pz 8)	Incubation 1	11.8	0.98	33[A]	0.93[A]
	Incubation 2	10.3	0.97	28[A]	0.90[A]
18.5-18.9 m bgl (BV-7)	Incubation 1	349	0.50	339	0.92
	Incubation 2	408	0.91	354	0.75
22.6-22.9 m bgl (BV-4)	Incubation 1	71 (0-61)	0.91	630	0.88
	Incubation 2	80 (0-61)	0.86	653	0.85
38.5-38.7 m bgl (Pz 1)	Incubation 1	122 (0-119)	0.96	1,302	0.38
	Incubation 2	N.D.	-	1,234	0.60
39.0-39.3 m bgl (Pz 1)	Incubation 1	30 (0-28)	0.87	201[B]	0.70
	Incubation 2	30 (0-28)	0.85	100 [B]	0.99
46.8-47.1 m bgl (Pz 2)	Incubation 1	N.D.	-	F.N.P.	-
	Incubation 2	N.D.	-	F.N.P.	-
Krauthausen					
1.7-1.9 m bgl (Kr-A)	Incubation 1	39	0.91	335	0.50
	Incubation 2	2,110	0.86	365	0.81
1.7-1.9 m bgl (Kr-A)	Incubation 1	25	0.97	321	0.74
	Incubation 2	36	0.95	266	0.75

N.S. = Not Significant
C.N.P. = correlation to the 1.order equation was not possible.
[A]After a lag phase of 50 days
[B]After a lag phase of 100 days

Isoproturon degradation did not fit very well to a first order model. Two sediment samples (18.4-18.7 m bgl and 39.0-39.3 m bgl) had a lag-phase of 80 and 110 days, which cannot be modelled by a first order expression. For these sediments, the rates given in Table 15 were therefore calculated without considering lag-phases. Lag-phases were not observed in the other investigated sediments where the degradation was much slower, and the first order expression therefore only provide a rough description of the degradation curve. In one sediment (BV. 46.8-47.1 m bgl), application of the first order model was not meaningful due to the very slow degradation of isoproturon.

In general, the results demonstrated spatial variability in the degradation of MCPP and isoproturon within the same aquifer. These results may explain the difficulties in modelling the fate of these pesticides in aquifers since a simple first order model cannot account for the observed shifts in degradation rates for MCPP or the observed lag phases for isoproturon.

7.3. Summary

Sorption and degradation of five herbicides (atrazine, deethylatrazine, isoproturon, MCPP and acetochlor) were investigated in 14 aquifer sediment samples from four aquifers with different redox conditions: Brévilles (France), Krauthausen (Germany) – both aerobic - Martigny (Switzerland) and Havdrup (Denmark) – both anaerobic. At the Brévilles site, the unsaturated zone was also investigated in two cores.

Sorption investigations showed a significant sorption of isoproturon, atrazine, deethylatrazine, and acetochlor in the aquifer sediments investigated, whereas the sorption of MCPP was limited. The sorption varied significantly between the aquifers, but in general, sorption was largest in the anaerobic parts of the aquifers.

The unsaturated zone at Brévilles consists of limestone until 16 m below surface. Samples of this material were able to mineralize MCPP, isoproturon, and acetochlor. In contrast, the degradation of atrazine and deethylatrazine was restricted to the top-soils. Mineralization rates decreased with depth, but were not correlated to the water content or porosity of the samples.

In the aquifer samples, atrazine, deethylatrazine, and acetochlor were not degraded in any of the samples. The degradation of MCPP and isoproturon was also insignificant in the two anaerobic aquifers. However, MCPP was biodegraded in 7 of the 8 investigated sediments from the aerobic aquifers, and isoproturon was degraded in all 8 sediments. $^{14}CO_2$ was produced during degradation of both compounds, which demonstrated full mineralization.

8. DISCUSSION OF DATA MONITORING ACTIVITIES

A total of six sites were monitored for water and pesticide fluxes in the soil and the subsoil. It is believed that the data collected form very useful experimental datasets for the evaluation of pesticide fate models, as i) monitoring activities and associated experimental work were designed to support model evaluation exercises right from the start of the project; and ii) pesticide fate was studied in the soil-unsaturated zone-groundwater continuum. Some of these datasets are made freely available to pesticide fate modellers through the project web site should they wish to evaluate pesticide fate models against these datasets. The data have been structured in such a way that a scientist not familiar with PEGASE can quickly gain an understanding of the work done and utilise the data collected in his/her modelling activities.

The selection of study sites on the basis of their contrasting properties was reflected in the diversity of results for water and pesticide fluxes. For instance, The Brévilles hydrogeological catchment, despite its small alleged size, was characterised by a very slow response of the aquifer to water inputs whereas aquifer levels for Martigny showed a strong response to precipitation. The monitoring activities demonstrated that gaining an understanding of flow in the subsoil on the basis of experimental observations only remain a challenge despite the large amounts of information which were collected on the soil and the subsoil. Modelling activities proved a useful complement to monitoring activities in most of the cases studied.

A potential for a fast transport of pesticides from the soil surface to the groundwater was noted at most study sites, especially when significant rainfall events occur within a few weeks after application. This was attributed to the transport of water through preferential flow phenomena even in coarse soil and subsoil materials. For instance, isoproturon was found at the same time in the soil and in the upper groundwater two weeks after application at Martigny. Isoproturon was also found in the groundwater shortly after application at Brévilles or Les Trois Fontaines. Interestingly, concentrations of isoproturon were also found to decrease rapidly in the groundwater at all study sites which monitored concentrations of this particular compound. This fast decrease may be attributed to dilution effects, transport, pesticide degradation or a combination of all these processes. In contrast, atrazine concentrations were generally found to be relatively stable throughout the monitoring periods, even for catchments where the compound had not been applied for years. This suggests a particularly limited potential for degradation of this compound in the saturated zone (which was confirmed by the laboratory experiments which were undertaken) and the presence of a stock of atrazine extending most likely below the root zone, which would act as a slow-release source of contamination. This contrasted behaviour between the different compounds resulted in concentrations exceeding legal thresholds for drinking water (0.1 μg/l) either for a limited period (*e.g.* isoproturon) or for most of the time (*e.g*. atrazine). Large concentrations were occasionally detected (*e.g*. 12 μg/l for isoproturon in a single well at Zwischenscholle), but these were considered to originate from point source inputs.

Very significant spatial and temporal variabilities in pesticide concentrations in the various piezometers were noted at all study sites. This has important implications for the design of monitoring activities which aim at characterising groundwater contamination by pesticides. First, a network of piezometers should be installed on study areas to grasp the variability in concentrations and to allow an understanding of

the transport processes involved. Secondly, the sampling frequency should be high enough - *e.g.* twice a month - to allow an unbiased picture of the groundwater contamination to be drawn. Thirdly, detailed information on the application of pesticides at the soil surface should be collected as part of the monitoring work. Failure to collect this information at a fine enough resolution would make subsequent modelling activities difficult. Besides, the importance of the duration of the monitoring studies was clearly illustrated in the Brévilles catchment where acetochlor was first used in 1999 and the compound was analysed in samples taken from piezometers or the spring at the outlet of the catchment. The fact that the compound was not detected in the samples collected does not mean that the product would not lead to later contamination of the aquifer at a later stage given the slow response time of the Brévilles aquifer and the fact that the compound was found at 1-m depth in the soil. Monitoring activities should therefore be designed so that the duration of monitoring is compatible with the expected response time of aquifers. This would also allow the capturing of important changes in the transport of water in the aquifer such as those which were observed at Les Trois Fontaines within a 13-year period.

Laboratory experiments to determine sorption and degradation properties of samples of the unsaturated and saturated zones of the various sites yielded results of particular interest. The studies confirmed that the potential for sorption of pesticides in the subsoil is limited. However, sorption in sediments from anaerobic aquifers was found to be significantly larger than that in sediments originating from aerobic aquifers. Reasons for differences in sorption according to the redox potential of the subsoil are unclear at this stage and should be investigated further.

In contrast to literature results, a significant degradation of MCPP, isoproturon and acetochlor in sediments from the unsaturated zone was found at the Brévilles catchment down to a depth of 16 m, except for a particular geological formation. In contrast, atrazine and one of its metabolites were only degraded in the soil. These results may have important implications for pesticide fate modelling activities as modellers traditionally assume that no degradation occur in the subsoil. This suggests that the risk of contamination of groundwater resources might have been somewhat overestimated in the past (at least with regard to this particular aspect). In the saturated zone, no degradation of atrazine, deethylatrazine and acetochlor was observed over a two-year period. In contrast, MCPP and isoproturon were degraded, but only in the two aerobic aquifers. Again, the influence of redox conditions on degradation should receive more attention in the near future. Finally, a full mineralisation of isoproturon leading to the release of carbon dioxide was found for the limestone aquifer, which has never been observed before.

In conclusion, the monitoring and characterisation of water and pesticide fluxes in the six catchments have provided valuable information on the functioning of these systems. Some of these findings have a particularly high relevance for risk assessment activities for pesticides as they question hypotheses which have been made for years (*e.g*. the lack of potential for degradation of pesticides in aquifers). Results of the laboratory experiments have yielded results of particular interest with regard to the sorption and degradation properties of subsoil materials in relation to redox conditions. The datasets collected were subsequently used to evaluate modelling tools which were developed or refined within the scope of the project (chapter 3).

Chapter 2 -

Development and refinement of modelling tools

A large number of models have been developed to simulate and predict the fate of pesticides in the environment and to estimate the risk of pesticide leaching to depth. Most of these leaching models can be either categorised into: i) root zone models which focus on the first metre or few metres of soils; and ii) groundwater flow models which concentrate on the saturated zone with possible extension to the unsaturated zone. It is interesting to note that these two categories are almost exclusive and that in instances where a bridge between the soil and subsoil has been attempted, groundwater processes have been treated in a simplistic way in root zone models and conversely, processes occurring in the soil have been treated in the same way in groundwater models.

The development work undertaken within PEGASE aimed at allowing the simulation of pesticide fate in the soil-groundwater continuum, *i.e*. in the root zone, unsaturated and saturated zones. The work concentrated on: i) the adaptation and improvement of root zone models (MACRO and ANSWERS); ii) the combination of root zone models with groundwater codes (MACRO+FRAC3DVS, MACRO+MODFLOWT and ANSWERS+ MODFLOWT); iii) the integration of pesticide fate subroutines and the adaptation of groundwater to result in integrated models capable of simulating pesticide fate from the soil surface to and in the groundwater (MARTHE, TRACE+3DLEWASTE, POWER and PESTGW).

1. ADAPTATION AND IMPROVEMENT OF ROOT ZONE MODELS

1.1. Macro [SLU]

1.1.1. Context

MACRO (Jarvis, 1994) is a one-dimensional 'dual-permeability' model, operating at the scale of a soil profile or small plot. The model accounts for preferential flow and transport in soil macropores by dividing the soil pore system into two parts, one part with a high flow capacity and low storage capacity (macropores) and the remainder with a low flow capacity and a high storage capacity (micropores). The boundary between the pore regions is defined by a fixed water tension, and corresponding water content and hydraulic conductivity. Classical continuum equations are used to model flow and transport in the micropores (Richards equation and the convection-dispersion equation) while flow in the macropores is calculated using the kinematic wave equation (Germann, 1985), assuming gravity-dominated flow (*i.e.* neglecting capillarity). Transport in macropores is calculated neglecting dispersion-diffusion, but accounting for adsorption by one parameter that partitions the sorption constant between the two flow regions. Diffusive mass exchange between the two pore regions is calculated using approximate first-order equations based on an effective diffusion pathlength.

Since it was first introduced more than 10 years ago, MACRO has undoubtedly become the most widely used model of its type, probably because it is physically-based, numerically robust for all soil (hydrological) types, even for long-term simulations (decades), easy to use, and relatively parsimonious with respect to parameter requirements. Despite the widespread adoption of the model in research and for management purposes such as pesticide registration (FOCUS, 1995), a number of limitations in the model had become apparent: i) outdated explicit numerical

solutions were used for the matrix region, leading to long run times, even for relatively coarse space discretisations, ii) only 22 numerical layers were allowed, restricting applications to the soil root zone, and leading to a poor spatial resolution near the soil surface, and iii) the use of the Brooks-Corey retention function limited model flexibility in matching measured hydraulic properties.

In the PEGASE project, it was intended that MACRO should be used to simulate spatially variable pesticide leaching through the root zone at the field- and small catchment scales, and at least at one site (Brévilles), also for very deep unsaturated zones (up to 30 m of fissured limestone). Therefore, it was considered necessary to develop a new version of MACRO (v5.0) within the framework of PEGASE, upgrading the numerical routines in the model to ensure much faster simulations. Some improvements to the process descriptions in the model were also implemented at the same time (e.g. inclusion of kinetic pesticide sorption and tillage effects) but these were financed through another 5th framework EU project (APECOP) and are therefore not described here. The new version of MACRO allows for a larger number (up to 200) of much thinner layers in the profile, which enables simulation of deeper soil profiles and vadose zones. This also allows a much finer discretisation close to the soil surface, which improves the numerical accuracy of simulations. This was confirmed by comparison with analytical solutions for transport problems with well-defined initial and boundary conditions. The new version is also approximately 10-20 times faster than the previous version, which is of considerable importance for spatialized simulations.

1.1.2. Methods

The work to upgrade the MACRO model involved the following steps:

- the program was first re-compiled using a modern compiler (Digital Visual Fortran);
- implicit numerical solutions for heat flow, water flow and solute transport were introduced to replace the existing explicit solutions;
- the original description of Mualem/Brooks-Corey hydraulic parameters (Brooks & Corey, 1964) was replaced by an approach based on a modified Mualem/Van Genuchten model (Van Genuchten, 1980).

Comprehensive descriptions of these new procedures in MACRO5.0 are given in Larsbo & Jarvis (2003), and so only brief details are given here on the new methods introduced into MACRO to deal with the generation of macropore flow and the coupling between the two flow regions. The method used to solve for flow in macropores is also described.

- ***Numerical simulations***

In the new version of the model, Richards' equation for water flow in the soil micropores is solved using the implicit iterative procedure proposed by Celia *et al.* (1990), while soil water retention in the matrix is calculated using a modified form of van Genuchten's (1980) equation (Vogel *et al.,* 2001; Fig. 43):

$$S = \frac{\theta_{mi} - \theta_r}{\theta_s^* - \theta_r} = \left(1 + \left(\alpha_{vg}\psi\right)^{n_{vg}}\right)^{-m_{vg}} \quad (1)$$

where S is an effective water content, m_{vg}, n_{vg} and α_{vg} are shape parameters (where m_{vg} is fixed equal to $1-1/n_{vg}$), θ_r is the residual water content and θ_s^* is a 'fictitious' saturated water content, obtained by extrapolating the fitted water retention function to zero pressure head. It should be noted that θ_s^* does not represent the actual saturated water content in the model, as this is separately defined by the user to reflect the macroporosity. Rather, it is only used internally in the program to extend the retention curve to pressure head values larger than Ψ_b to allow for temporary over-saturation in the matrix when solving equation 1.

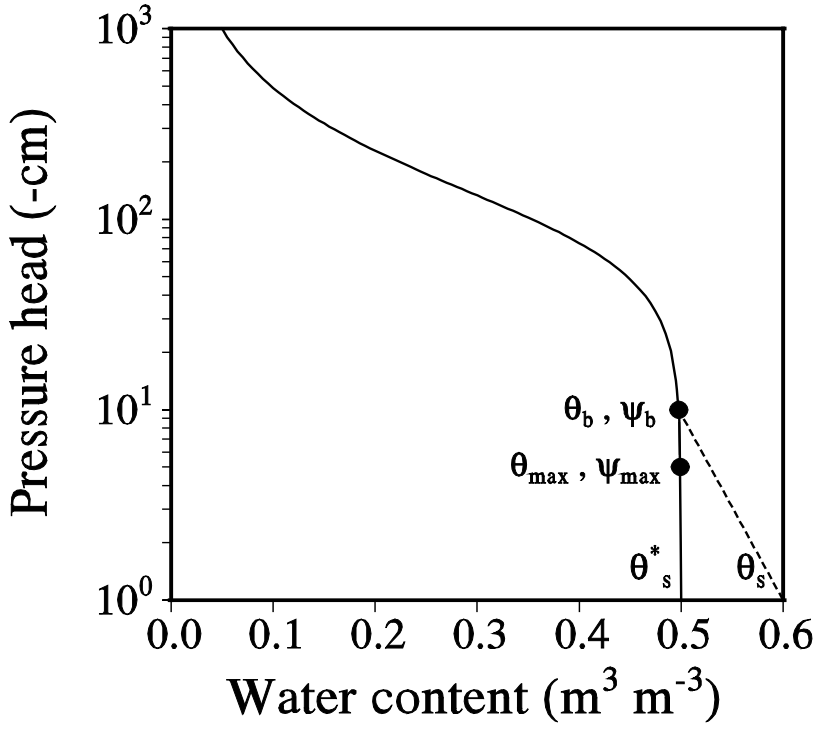


Fig. 43 - Example of the modified van Genuchten soil water retention function used in MACRO (α_{vg} = 0.01 cm^{-1}, n_{vg} = 2, θ_r = 0.0 and θ^*_s = 0.5 m^3 m^{-3}).

The surface boundary condition partitions net rainfall between infiltration into the matrix and excess water that runs off into macropores. Thus, water will flow into macropores at the soil surface if the rainfall intensity R exceeds the infiltration capacity of the matrix I_{max} calculated from Darcy's law. If $R < I_{max}$, then the surface boundary condition is defined by a known flux (Neumann condition) equal to the net rainfall. Otherwise, the surface boundary condition is given by a known tension (Dirichlet condition). Changes from a known flux to a known tension and vice versa may occur between iterations.

An implicit iterative technique (interval halving) is used to solve the local water balance in the macropores for each layer, in turn, from the soil surface downwards. If the macropore flow capacity is exceeded in any layer, then the local water balance cannot be solved (over-saturation develops in the macropores). In this case, the excess water is added to the macropore storage in the layer(s) above and the water fluxes between layers are corrected accordingly.

As shown in Figure 43, the division between flow domains is defined by a pressure head Ψ_b and the corresponding water content θ_b on a modified van Genuchten water retention curve. If the water content in the matrix exceeds θ_b, the excess water will drain into the macropores. However, the macropores only have a finite capacity to accept water, C_{ma}, equal to:

$$C_{ma} = (1 - S_m a)\ (\theta_s - \theta_b) \qquad (2)$$

where S_{ma} is the degree of saturation in the macropores and θ_s is the saturated water content. Therefore, an additional breakpoint on the water retention curve (θ_{max}, Ψ_{max}, see Fig. 43) defines the maximum amount of excess water allowed in the matrix at each timestep, corresponding to C_{ma} (*i.e.* $\theta_{max} = \theta_b + C_{ma}$). When solving Richards' equation, the pressure heads are allowed to increase above Ψ_{max} only if the macropores are also saturated. In this case, the differential water capacity is set to zero, and the matrix conductivity is fixed at the saturated value. Once Richards' equation has been solved, all water storage exceeding θ_b is instantly removed from the matrix and added to the macropores.

The heat conduction equation has also been re-programmed in MACRO and is now solved using a standard Crank-Nicholson finite difference scheme. The numerical solution to the convection-dispersion equation for solute transport has also been upgraded. It is now solved by a Crank-Nicholson finite difference scheme utilizing an iterative, fully upstream weighted procedure which minimises the 'overshoot' problems and oscillations that may sometimes be encountered in the presence of steep concentration gradients. However, upstream weighting introduces considerable numerical dispersion, which is minimized by an empirical correction:

$$Corr = abs(q)k_{corr} \qquad (3)$$

where q is the water flow rate and k_{corr} is a constant. The correction factor $Corr$ is subtracted from the effective dispersion coefficient before solving the convection-dispersion equation. The value of k_{corr} was determined from comparisons with the analytical solution for steady state water flow and a step input of non-adsorbing solutes.

- ***Parameter estimation methodology***

One important reason why macropore flow models have not been widely adopted in exposure and risk assessments for agrochemical leaching is the difficulty of parameterization. Therefore, an automatic parameter calibration routine was incorporated into the shell program for version 5.0 of MACRO. This inverse capability is supplied by the SUFI methodology described by Abbaspour *et al.* (1997). SUFI is a Bayesian global search algorithm that is considered well suited to complex simulation models such as MACRO, since it minimizes the risk of falling into local optima in the *n*-dimensional parameter space. The user first defines a prior uncertainty range or domain for each parameter to be estimated (Fig. 44). This range is divided into a number of equal-size 'strata' and the first moment of each stratum defines the parameter estimate. All combinations of parameters are then run, and the value of a user-defined objective function (*i.e.* root mean square error or model efficiency, Loague and Green, 1991) is calculated for each simulation by comparing to measured data. Based on a critical tolerance for the objective function, the parameter ranges are refined (*i.e.* narrowed) for subsequent iterations by rejecting parameter values that perform badly (Fig. 44). This kind

of optimisation technique would have been too time-consuming for routine applications with earlier versions of the model, but the enhanced speed of execution of version 5.0 makes such methods practicable.

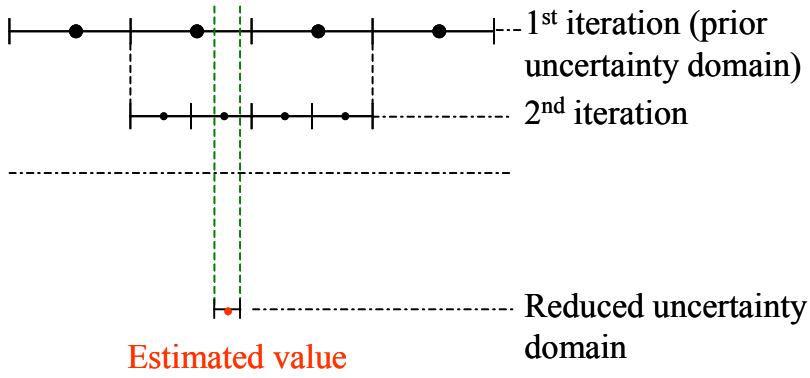


Fig. 44 - The SUFI procedure for parameter optimisation, included in MACRO5.0.

1.1.3. Summary

Mathematical modelling has been increasingly used in the last two decades to describe and predict the fate of agrochemicals in the environment, particularly the leaching of compounds to surface waters and groundwater. Preferential flow is one important process which has significant impacts on pesticide leaching, but which is difficult to model. MACRO is a widely used one-dimensional dual-permeability model which couples classical treatments of flow and transport processes in the matrix (Richards equation, convection-dispersion equation) to a macropore region where flow is assumed to be gravity-driven. A number of limitations in the model have also been identified since it was first introduced more than 10 years ago: i) explicit numerical solutions are used for the matrix region, leading to long run times, even for relatively coarse space discretisations, ii) only 22 numerical layers are allowed, restricting applications to the soil root zone, and leading to a poor spatial resolution near the soil surface, and iii) the use of the Brooks-Corey retention function limits model flexibility in matching to measured hydraulic properties.

The main limitation to a much wider adoption of dual-permeability models in both research and management is the difficulty in parameterisation, since more parameters are required compared with classical approaches, some of which cannot be directly measured. The use of inverse modelling techniques may help to resolve these difficulties with parameter estimation. However, the numerical limitations in MACRO noted above severely restrict the possibilities to make use of inverse modelling techniques.

In PEGASE, an improved version of the MACRO model (v. 5.0) was developed. The new features include: i) fully implicit numerical solutions for water, heat and solute transport in the matrix, for up to 200 computational layers; ii) use of a modified van Genuchten retention function; and iii) inverse capabilities for parameter estimation and model calibration.

1.2. ANSWERS [LTHE]

ANSWERS is a one-dimensional vertical model which can simulate water and solute fluxes in the root zone and the unsaturated zone of the soil (Bouraoui *et al.,* 1997a; Vachaud & Chen, 2002).

1.2.1. Model description

The Areal Nonpoint Source Watershed Environmental Response Simulation, ANSWERS, is originally a watershed scale, event-oriented, distributed-parameter, non point source pollution surface model for long term simulation. The first version (Huggins and Monke,1966) included only surface water hydrology. It was expanded by Bebgley *et al.* (1980) to include erosion and sediment transport. The sediment transport routine was later updated to simulate sediment detachment and transport of mixed particle sizes (Dillaha and Bebgley, 1983).

An important step was made by Bouraoui (1994) with the transformation from an event-based model to a continuous model in order to simulate runoff, erosion, transport of dissolved and sediment-bound nutrients, and transformation of nitrogen and phosphorus pools. Holtan's infiltration equation was replaced by the widely used and physically-based Green and Ampt equation. Soil water redistribution and percolation were determined on the assumption of gravity flow, and with the use of a storage routine technique (Williams *et al.,* 1985). Soil evaporation and plant transpiration were modelled separately using Ritchie's equation (Ritchie, 1972). Nutrient transformation and nutrient transport subroutines (Knisel, 1993) were also added to the model. Finally, further changes were made recently by Bouraoui *et al.* (1997a, b) to account for aquifer recharge and leaching of nitrate below the root zone of crops.

The core of the system is a one-dimensional vertical model applied to square blocks of soil for which topographic, soil and crop characteristics are uniform. A vertical discretisation (usually 3 layers: upper soil horizon (0-0.3 m), root zone, and unsaturated layer to the ground water) is considered to account for water movement through the soil profile. In its complete version, the model requires a large number of input parameters in order to simulate properly the water cycle (infiltration, runoff, evapotranspiration, drainage), the nutrient cycle (in the soil, but also in the sediments), and the crop uptake on the basis of a daily time step. Details are given in Bouraoui (1994). Since it is not in practice possible to characterise the spatial variability of all the input parameters through the watershed with the use of time consuming, difficult and costly measurements, it was decided to use Model Parameter Estimation Routines (MPER) related to easily obtainable properties, and/or to parameterise the processes with easily obtainable properties or large data bases.

In this original version, the lower boundary condition imposed in ANSWERS corresponds to a downwards drainage from the root zone, by gravity flow. All excess drainage can produce an increase in groundwater level, but the model cannot account for upwards capillary flow. In this initial stage, important processes of concern were the transport of water in the unsaturated zone of the soil-plant-atmosphere continuum, and the nutrient cycle (nitrogen). The following processes are being solved at an hourly time step, with output on a daily basis:

- in terms of the water balance: infiltration, actual evapotranspiration, runoff, change of water storage in the root zone and loss of water (drainage) below the root zone; runoff is defined as the excess of water not infiltrating in the soil at the end of the time step. In the simplest case, this excess water is routed directly to a river;
- in terms of the nitrogen cycle: mineralisation in the root zone, plant root uptake and leaching of nitrate below the root zone. Leaching is defined as the product of nitrate concentration in the root zone with the drainage of water from the root zone.

To simulate these processes, the most important MPER provide the following:

- the parameters describing the hydraulic properties of the soil; obtained with the use of statistical correlations (pedotranfer functions) from a data base of 2000 types of soils (Rawls and Brakensiek, 1989). Among others: Ks, the saturated hydraulic conductivity (cm/h); Ψ_f, the wetting front capillary pressure head (cm); n, the available porosity (cm^3/cm^3), (Green and Ampt, 1911); λ, the conductivity shape parameter (Brooks and Corey, 1964), and θ_s (cm^3/cm^3), the water content at natural saturation are determined from the knowledge of soil texture, organic matter content (OM) and cation exchange capacity (CEC);
- the parameters describing the plant behaviour in terms of water uptake and actual evapotranspiration and nutrient uptake; obtained from a data base concerning 78 different types of crop, and giving, at different phenological stages (from sowing to harvest) time course values of the Leaf Area Index and root depth (Knisel, 1980);
- the parameters describing the nitrogen cycle. The procedure is that described in GLEAMS (Knisel, 1993).

1.2.2. Model refinement

In the frame of PEGASE, developments were undertaken at two different levels within this root zone and unsaturated zone transport model:

- development of a pesticide transport routine;
- development of a simple parameterised routine to include interactions with shallow aquifer (mainly capillary rise).

The pesticide transport routine was imported from GLEAMS (Knisel, 1993). It simulates the transport by convection dispersion with a retardation factor for the following conditions: linear adsorption and first order degradation with an eventual first order production of metabolite. This routine is associated with a classical soil temperature simulation routine.

The capillary rise routine had to be developed for the application on the site of Martigny, Switzerland. In order to account for the presence of a shallow groundwater two main changes in the model calculations have been done.

1. Determination of the hydrostatic profile, i.e. the steady zero-flow profile, supposed to form an accurate estimate of the soil moisture profile when constrained by shallow water table, as observed by Salvucci & Entekhabi (1994). This profile is defined by the Brooks & Corey (1964) retention curve:

$$\frac{\theta - \theta_r}{\theta_s - \theta_r} = \left(\frac{h}{h_B} \right)^{-\lambda}$$

All parameters can be induced by pedotransfer functions.

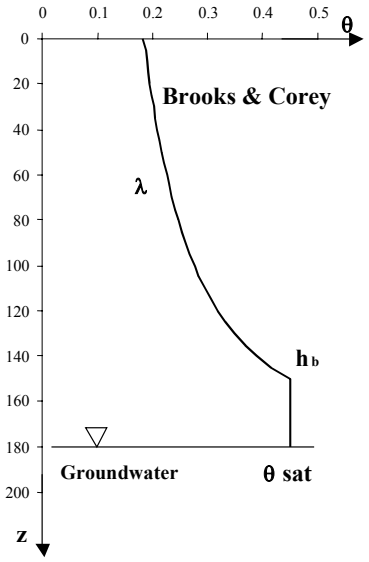


Fig. 45 - Hydrostatic profile assuming a Brooks & Corey (1964) water retention curve.

2. A routine was developed to parameterise the capillary upwards flow and the evaporation component coming from the groundwater as a function of the groundwater depth.

   The computation of the evapotranspiration now depends upon the groundwater depth ($z_{GW,}$, mbgl - meter below ground level), with 2 added parameters, L_1 and L_2.

   ET is computed as the sum of a groundwater contribution ($\alpha.ET_0$), soil evaporation (E_s) and plant transpiration (E_p). The partition coefficient α is defined by the following equation:

$$\begin{cases} \alpha = 0 & for \quad z_{GW} > L_2 \\ \alpha = \dfrac{L_2 - z_{GW}}{L_2 - L_1} & for \quad L_1 \le z_{GW} \le L_2 \\ \alpha = 1 & for \quad z_{GW} < L_1 \end{cases}$$

   E_s and E_p are calculated using the Ritchie's method. Thus, when the groundwater is above L_1, the system evaporates at the maximum level defined by the reference evapotranspiration, ET_0. When the groundwater is below L_2, the model computes evaporation as in the original version.

This new version of ANSWERS used as a single one-dimension column model has been tested on the Martigny dataset (see section 5.2. of chapter 3). Use of this version was abandoned since it requires a considerable amount of calibration on the choice of parameters L_1 and L_2 to provide satisfactory simulations.

1.2.3. Summary

The root zone model ANSWERS was adapted to simulate pesticide fate and upwards flow by capillary rise from shallow aquifers. The inclusion of the pesticide routine was successful. In contrast, the implementation of an upwards flow routine was later abandoned since the model could not be run satisfactorily without recurring to extensive calibration.

2. COMBINATION OF MODELS

2.1. Combination of TRACE and 3DLEWASTE [FZJ]

3DLEWASTE (Yeh *et al.,* 1992) is a computer code developed to compute large scale solute transport in variably saturated porous media. 3DLEWASTE allows the application of a conventional finite element formulation of the convection-dispersion equation or alternatively the use of a hybrid Lagrangian-Eulerian approach. This model was coupled with TRACE by developing several interfaces and conversion tools.

Some modifications to the Cauchy boundary condition of 3DLEWASTE were necessary to cope with the specific requirements of pesticide transport. Further modifications concerned time step handling and the numerical scheme. These modifications were evaluated using well-defined numerical cases and analytical solutions. For further evaluation the modified TRACE/3DLEWASTE was applied to calculate pesticide transport at local and regional scale.

2.1.1. Modelling approaches

- ***Main features of 3DLEWASTE***

3DLEWASTE solves the 3D convection-dispersion equation using finite elements. The conjugate gradient method is used to solve the resulting matrix equation system. Dispersion length, diffusion, first order degradation and sorption can be handled in a spatially variable manner.

The common Eulerian approach for convective-dispersive solute transport in 3D space taking local sources or sinks (e.g. wells), sorption and degradation into account can be written as:

$$\theta\frac{\partial C}{\partial t}+\rho_b\frac{\partial S}{\partial t}+V\cdot\nabla C=\nabla\cdot(\theta D_D\cdot\nabla C)-\lambda(\theta C+\rho_b S)+QC_q-$$
$$\alpha'(\theta C+\rho_b S)\frac{\partial h}{\partial t}-K_w\theta C-K_s\rho_b S-\frac{\partial\theta}{\partial t}C+\left(F\frac{\partial h}{\partial t}-Q\right)C$$

where C is the liquid phase concentration [M L^{-3}], S is the sorbed concentration of the solute [M/M], λ is the decay constant [T^{-1}], K_w is the biodegradation rate for the liquid phase [T^{-1}], K_s is the biodegradation rate for the solid phase [T^{-1}], Q is the flow rate of the source/sink [$L^3/L^3/T^1$],C_q is the concentration of the source/sink [M/L^3], θ is the volumetric soil moisture [L^3/L^3], h is the pressure head [L], ρ_b is the bulk density [M/L^3],

V is the pore water velocity [L/T], α' is the compressibility coefficient of the solid phase [L T^2/M], t is time [T] and D_D is the dispersion coefficient tensor [L^2/T]. The storage coefficient F [L^{-1}] is calculated from:

$$F = \alpha' \frac{\theta}{\varphi} + \beta' \theta + \frac{d\theta}{dh}$$

where φ is the effective porosity [L^3 L^{-3}] and β' is the compressibility coefficient of the liquid [L T^2/M]. The sorbed concentration S can be calculated with a linear, Freundlich or Langmuir isotherm. Here the Galerkin formulation combined with the upstream weighting method can be applied for the finite element solution.

For the hybrid Lagrangian-Eulerian approach the first equation is rewritten to:

$$\left(\theta + \rho_b \frac{\partial S}{\partial C}\right) \frac{D_{V*} C}{Dt} = \nabla \cdot (\theta D_D \cdot \nabla C) - \lambda(\theta C + \rho_b S) -$$
$$\alpha'(\theta C + \rho_b S) \frac{\partial h}{\partial t} - K_w \theta C - K_s \rho_b S - \frac{\partial \theta}{\partial t} C + \left(F \frac{\partial h}{\partial t} - Q\right) C$$

where the convective term on the left hand side of the first equation is changed and the Lagrangian velocity $V^* = \frac{V}{(\theta + \rho_b K_d)}$ for a linear isotherm is used, or the first equation is rewritten to:

$$\theta \frac{D_{V*} C}{Dt} + \rho_b \frac{\partial S}{\partial C} \frac{\partial C}{\partial t} = \nabla \cdot (\theta D_D \cdot \nabla C) - \lambda(\theta C + \rho_b S) -$$
$$\alpha'(\theta C + \rho_b S) \frac{\partial h}{\partial t} - K_w \theta C - K_s \rho_b S - \frac{\partial \theta}{\partial t} C + \left(F \frac{\partial h}{\partial t} - Q\right) C$$

with $V^* = \frac{V}{\theta}$ for Freundlich and Langmuir isotherm. To determine the change of concentrations in time caused by convective transport, a concentration based single step reverse particle tracking with sub-elements is applied.

- ***Coupling between TRACE and 3DLEWASTE***

The coupling of the two models is presented schematically in Figure 46.

The time and space dependent variables θ, V and h are outputs of TRACE. They are stored in ascii files which were converted to binary format in order to compress the file size. The input routines of 3DLEWASTE were modified to handle the binary format. The file containing the geometry information for TRACE can also be used to generate the geometry input for 3DLEWASTE by applying a conversion tool. Also the pesticide application can be automatically generated from the input relevant for TRACE. Here a tool was developed, which automatically generates the upper boundary conditions from the climatic input and the spatial structure of land use. The application rate is linked to a specific crop.

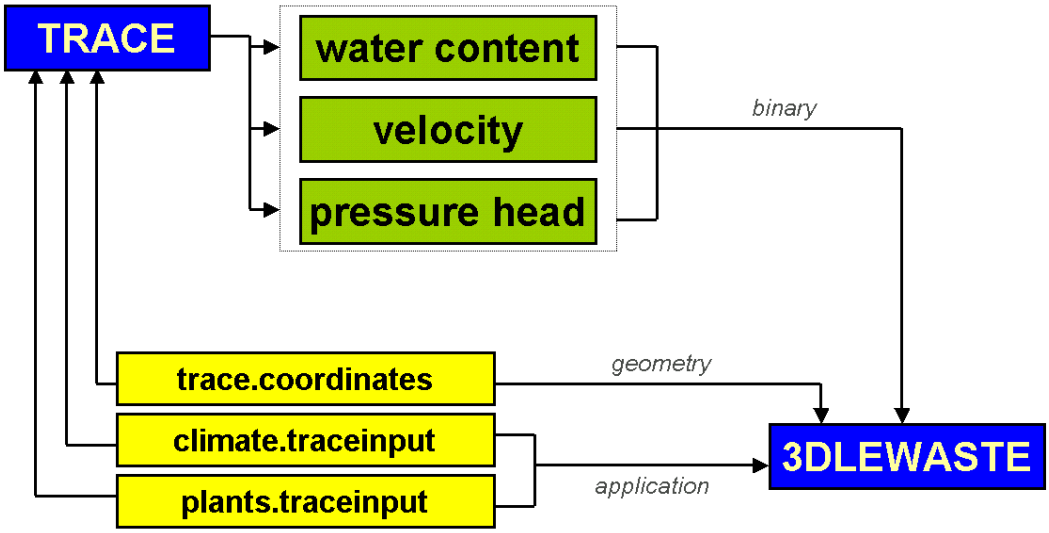


Fig. 46 - Schematic plot of the coupling between TRACE and 3DLEWASTE.

- ***Modifications to 3DLEWASTE***

For solute transport, two flux boundary conditions are relevant. The Neumann boundary condition affects the dispersive flux, while the Cauchy boundary condition affects the total (dispersive and convective) flux. The Neumann boundary is typically applied to vertical model boundaries where a zero gradient in concentration is assumed and the solute can leave or enter the flow domain as dispersive solute flux. The Cauchy boundary condition is usually applied for impermeable boundaries (like *e.g.* an aquifer base) or at the upper boundary. During the first test runs with 3DLEWASTE an inconsistency of the Cauchy boundary conditions was found, if this boundary condition was applied in combination with the hybrid Lagrangian-Eulerian approach. Here the solute left the flow domain although the flux was supposed to be zero. The inconsistency in the code was detected and the relevant routines were modified.

2.1.2. Model evaluation

After the modifications of the Cauchy boundary conditions model evaluation runs for well-defined cases were performed. The objective was to find out whether the model is able to produce physical plausible and correct results. A stationary 1D flow and transport model applying the hybrid Lagrangian-Eulerian approach was established in a vertical soil column of 100 cm length and arbitrary width. Boundary conditions for solute transport were assumed to be of Cauchy type on all sides of the domain. The vertical and the bottom boundary was assumed to be impermeable (t>0 m = 0 g cm^2/d) and at the upper boundary a pulse application (for t>1 and t<2 solute flux=1 g cm^2/d) was given. A downward Darcy flux (from z = 100 towards z = 0) of –5 cm/d was assumed in combination with a longitudinal dispersion length of 10 cm resulting in a dispersion coefficient of 125 cm^2/d as θ was set to 0.4 [cm^3/cm^3]. Figure 47 shows the concentration profiles calculated with the modified 3DLEWASTE for the first eight days. The model behaves as it is expected. The pulse moves from the right hand side of Figure 47 towards the left hand side, where the concentration increases with time as the boundary is impermeable. Then the calculated solute concentrations were

evaluated against an analytical solution of Elrick *et al.,* 1994. Here a stationary upward flux is assumed. At the bottom a zero gradient Neumann boundary condition was applied, while at the top an impermeable boundary (Cauchy with mass flux = 0) was assumed. A model set up like this is used to calculate the accumulation of solutes at the surface due to high evaporation demands. Figure 48 shows the comparison between the analytical solution and the results obtained with the modified 3DLEWASTE applying the hybrid Lagrangian-Eulerian approach for three time steps. It is visible, that the modified 3DLEWASTE is basically in agreement with the analytical solution, although 3DLEWASTE slightly overestimates the increase of the concentrations with time. Against the background of a numerical solution applied for 3DLEWASTE the analytical solutions are properly reproduced with the modified model.

After model evaluation, TRACE/3DLEWASTE was applied in the hybrid Lagrangian-Eulerian mode to the lysimeter dataset (section 4.1. in chapter 3). During this application the combined model successfully reproduced the measured pesticide concentrations. Before TRACE/3DLEWASTE was applied in the hybrid Lagrangian-Eulerian mode to the 3D test case 'Zwischenscholle' 1D models were established. The purpose of these 1D tests was to check the influence of the selected sorption and degradation parameters on the transport behaviour. Again, TRACE/3DLEWASTE showed reasonable and consistent results. So the combined model was applied to the 'Zwischenscholle' test site. A 3D model was established taking groundwater and soil water flow into account. The goal was to model the regional scale transport of isoproturon (for details see section 3.1. in chapter 3). Figure 49 shows XY-maps of the isoproturon (IPU) concentrations for two time steps. Like for the 1D models nearly all of the IPU is very close to the soil surface, due to the high sorption. The IPU was applied at simulation day 80 (start of the simulation was 1 December 1983). From time step 100 to time step 120, the centre of mass is slightly deeper in the profile. Compared to the concentrations after 100 days the concentrations after 120 days reveal a significant decrease, because of the short half-life of IPU (20 days).

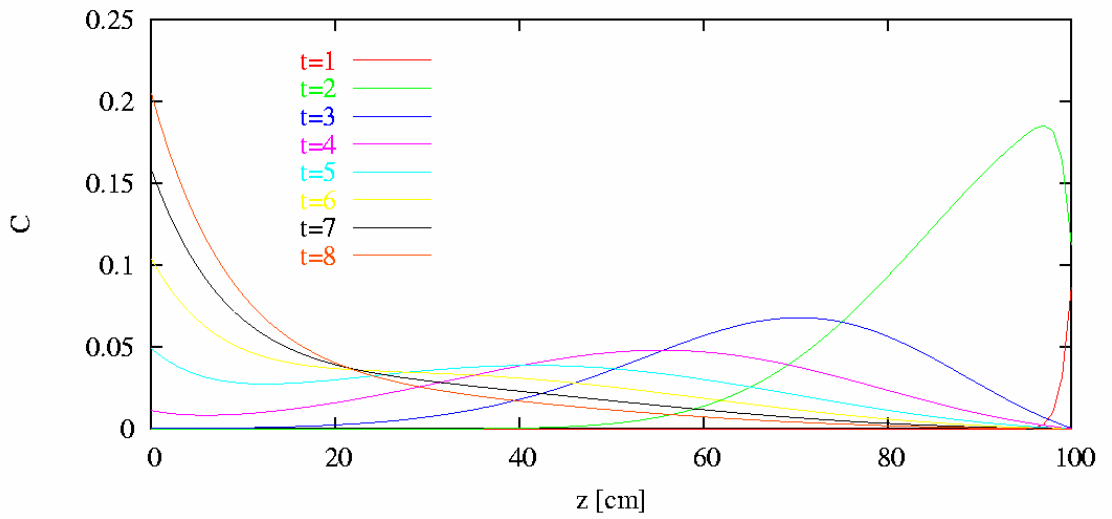


Fig. 47 - Concentration profiles for eight days of a simplified 1D model used for the functional evaluation of the boundary condition modifications.

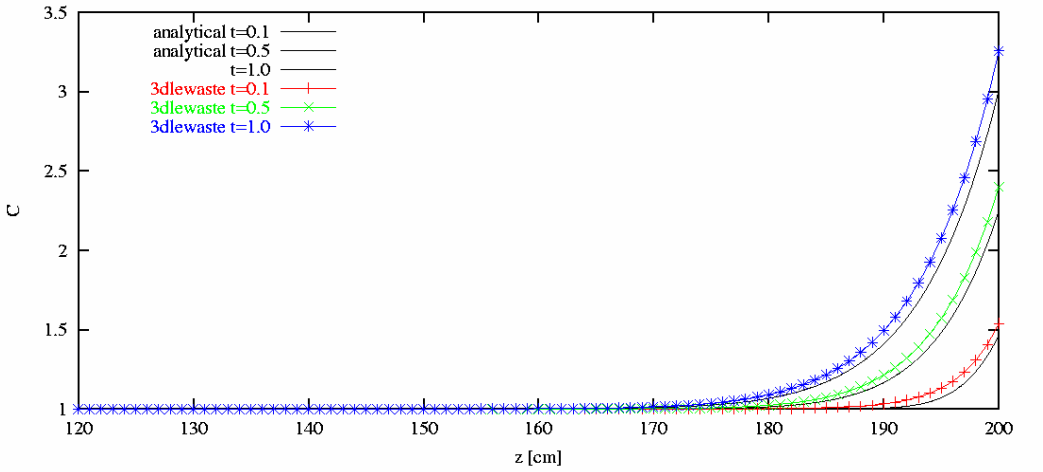


Fig. 48 - Comparison between analytical solution (Elrick* et al., *1994) and results obtained with the modified 3DLEWASTE.

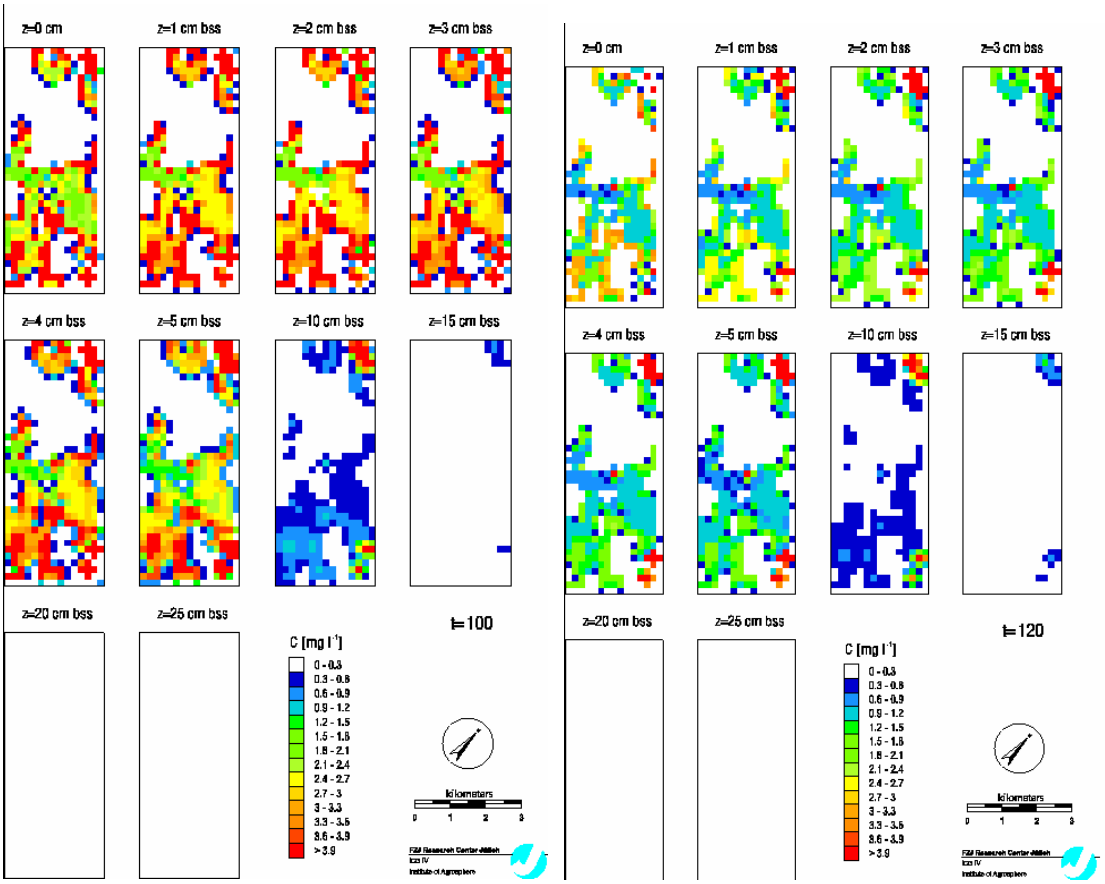


Fig. 49 - Isoproturon concentration maps close to the soil surface at the 'Zwischenscholle' test site for two dates (left: day 100; right: day 120). The application of IPU was made on day 80.

2.1.3. Discussion / implications

Several modifications to 3DLEWASTE were necessary to properly compute the local and regional scale transport of pesticides. These modifications include the input handling for the linking with TRACE, the time step discretisation and the total flux boundary condition. The modifications were checked using well-defined transport cases, before TRACE/3DLEWASTE was applied to the lysimeter dataset and the 3D modelling of pesticide transport for the 'Zwischenscholle' test site. The model runs reveal the applicability of the hybrid Lagrangian-Eulerian approach for pesticide transport. From local to regional scale TRACE/3DLEWASTE shows reasonable and consistent results after the slight modifications. By linking TRACE and 3DLEWASTE an integrated model tool for the regional scale was developed, which is able to compute the transport of pesticides by ground water flow and by the unsaturated water flow in soils under the influence of plant related processes. The linking between the integrated process model TRACE/3DLEWASTE and Geographical Information Systems offers a broad applicability to regional scale pesticide transport problems.

2.1.4. Summary

The 3DLEWASTE model is based on 3D finite elements, for which a conjugate gradient method is used to numerically solve the convection-dispersion equation. Modifications to 3DLEWASTE which were made within the scope of PEGASE included: input handling, time step discretisation and total flux boundary condition. These modifications were checked using well-defined transport cases before the combined model TRACE/3DLEWASTE was applied to the lysimeter dataset and the 1D and 3D modelling of pesticide transport for the 'Zwischenscholle' test site. Model results were reasonable and consistent. By coupling TRACE and 3DLEWASTE, an integrated model tool for the regional scale was developed, which is able to compute the transport of pesticides by the ground water flow and by the unsaturated water flow in soils under the influence of plant related processes. The linking between the integrated process model TRACE/3DLEWASTE and Geographical Information Systems offers a broad applicability to regional scale pesticide transport problems.

2.2. Combination of MACRO and FRAC3DVS [SLU, E&R DTU]

In PEGASE, a loose-link has been developed between the 1D root zone macropore flow model MACRO (section 1.1. of the present chapter) and the 3D groundwater model FRAC3DVS. Like MACRO, FRAC3DVS also deals with fissured porous formations, but instead of the dual-permeability approach, FRAC3DVS explicitly considers the locations and sizes of individual fissures. In fact, it is somewhat misleading to call FRAC3DVS a groundwater model since it can also deal with unsaturated conditions. However, the currently released version of FRAC3DVS could only accept steady-state water flow as an upper boundary condition. Since FRAC3DVS would be accepting fluxes calculated by the transient model MACRO as an upper boundary condition, FRAC3DVS was first adapted to accept transient flows as the upper boundary condition. This was thought necessary for modelling macropore flow situations such as those found at Havdrup and Brévilles. The significance of steady-state versus transient conditions at the boundary between the root zone and the

groundwater, in the presence of macropore flow, was investigated at Havdrup (section 1.4. in chapter 3).

2.2.1. Modelling

A tool to spatialise the root zone model MACRO and to link MACRO to FRAC3DVS has been developed. The link is established through an exchange of input/output files between the two models, controlled by a 'stand-alone' Visual Basic interface program. This interface program also provides tools to define the spatial distribution of soil properties or soil types as well as the spatial distribution of the necessary MACRO simulations. The tool has been designed to be compatible with the ArcView GIS program.

Figure 50 gives an overview of the coupling tool developed in PEGASE for spatial linking of the MACRO model to the 3D groundwater model FRAC3DVS. Two different approaches are available, a deterministic 'Megaplot' approach and a stochastic 'Monte Carlo' approach.

A Megaplot is defined as an area with a unique combination of model parameters (*i.e.* a single soil type with pre-defined properties and a given crop rotation). Each FRAC3DVS upper surface grid cell is allocated to one of several megaplots. An ACCESS database is used to store the spatial data and spatialized MACRO simulation results for the various pre-defined megaplots in raster format.

With the Monte Carlo approach, parameter distributions and correlations are first defined. In MACRO5.0, these distributions are then 'sampled' using the Latin hypercube method (Fig. 51), and then randomly allocated to FRAC3DVS upper surface grid cells. This has been achieved by developing a loose-link from within MACRO5.0 to the UNCSAM model sensitivity and uncertainty analysis package (Janssen *et al.,* 1992).

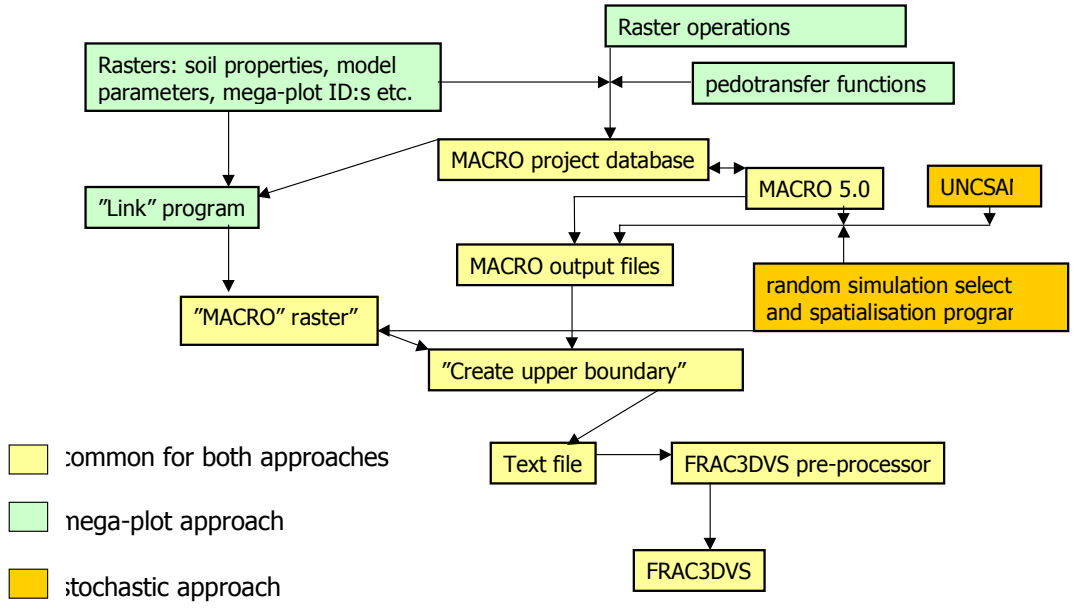


Fig. 50 - Overview of the coupling tools for spatial linking of the root zone model MACRO to the 3D groundwater model FRAC3DVS.

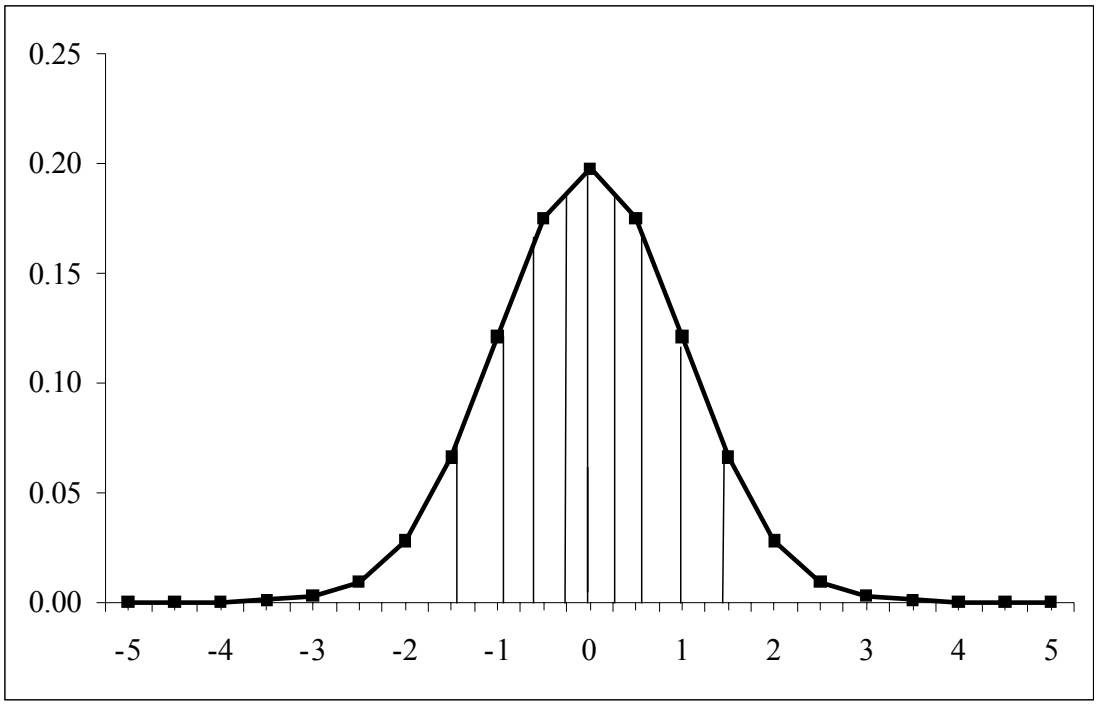


Fig. 51 - The Latin hypercube method for efficient sampling of model parameter distributions. The method involves sampling from a distribution divided up into 'equal-probability' intervals.

The file transfer between MACRO and FRAC3DVS is 'one-way', that is the water and solute fluxes simulated by MACRO constitute the upper boundary condition to FRAC3DVS, but the state variables (water potentials, concentrations) subsequently simulated by FRAC3DVS do not influence MACRO. This means that in order to maintain a perfect mass balance across the boundary, the models should be linked via fluxes and not pressures and concentrations. In addition, the approximations introduced by 'one-way' linking of the models means that the choice of depth at which to connect the two models should be quite critical. The errors introduced by linking the two models in this way should be minimised when the depth is chosen such that fluxes are almost always downwards directed, in other words well below the maximum depth of roots. The water table depth is also critical in this respect. For shallow water table situations, it is important that the soil zone within which the water table fluctuates during the year is included as part of the MACRO simulation, so that FRAC3DVS is restricted to saturated conditions. On the other hand, for a deep water table, the boundary between the two models can be set at a depth which remains unsaturated throughout the year, but which is still well below the maximum root depth.

2.2.2. Summary

Software tools were developed to (i) spatialise the one-dimensional dual-permeability model MACRO, and (ii) couple MACRO to the three-dimensional groundwater model FRAC3DVS. Both of these models account for preferential flow and transport processes. Two approaches were implemented for spatialisation of MACRO: the concept of mega-plots and Monte-Carlo simulation. The coupling between the two

models was implemented as a loose link based on a 'one-way' file transfer, such that output from MACRO is used to define the upper boundary conditions in FRAC3DVS in terms of water flow and solute transport.

2.3. Combination of MACRO and MODFLOWT [SAPROV]

The need for simulation of pesticide fate at the scale of the catchment or larger scales increased in the last few years due to the major request of detailed data for registration purposes (Vanclooster *et al.,* 2003). Regional-scale models provide users and decision-makers with maps of the potential for pesticide leaching in an entire region. Frequency distributions and percentiles of the leaching concentration can also be derived through these approaches (Tiktak *et al.,* 2002). Moreover, simulation of pesticide fate in the whole unsaturated/saturated zone is now necessary due to the more frequent monitoring of pesticide presence in some European aquifers (Leistra and Boesten, 1989). Given these requirements, a tool was developed to allow the simulation of pesticide fate in the unsaturated/saturated zone at the catchment scale. This required i) the spatialization of 1D unsaturated zone model MACRO (Jarvis, 1994) and ii) the linking of this model with the 3D saturated zone MODFLOWT (Duffield *et al.,* 2001). The final product was intended to be able to simulate the spatially variable movement of pesticides in the unsaturated zone and the fate of pesticides once they reach groundwater.

2.3.1. Material and methods

MACRO is a physically-based preferential flow model that can be used to describe water and solute transport in a variety of soil types. The total soil porosity is divided into two flow domains (macropores and micropores), each characterised by a flow rate and solute concentration.

Crop development is based on a simple model which uses dates for emergence, maximum leaf area and harvest. Pesticide degradation is modelled using first-order kinetics. Degradation half-lives need to be specified for the solid and liquid phase of the macropores and micropores, and may be adjusted for temperature and moisture effects. Sorption is assumed to be instantaneous and to be described by a Freundlich isotherm. MACRO version 4.3 (Jarvis, 2001) has been used for the work.

MODFLOWT is an enhanced version of MODFLOW, the modular three-dimensional finite-difference groundwater flow model developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988). It can simulate steady and non-steady flow in an irregularly shaped flow system in which aquifer layers can be confined, unconfined, or a combination of both. Flow from external stresses, such as flow to wells, areal recharge, evapotranspiration, flow to drains, and flow through river beds, can be simulated. Hydraulic conductivities or transmissivities for any layer may differ spatially and be anisotropic (restricted to having the principal directions aligned with the grid axes), and the storage coefficient may be heterogeneous.

MODFLOWT (Duffield *et al.,* 2001) extends the features of MODFLOW through the addition of new modules for simulating three-dimensional advective-dispersive transport of a single miscible species subject to adsorption and decay and enhances the existing modules for simulating groundwater flow. Despite the addition and

enhancement of program modules, MODFLOWT maintains complete compatibility with MODFLOW.

The ground-water flow equation is solved using the finite-difference approximation. The flow region is subdivided into blocks in which the medium properties are assumed to be uniform. In plan view, the blocks are made from a grid of mutually perpendicular lines that may be variably spaced. Model layers can have varying thickness. A flow equation is written for each block, called a cell (see Fig. 52). Cells can be active, inactive and constant head within the finite-difference mesh. Inactive cells are placed at locations within the mesh where no-flow boundaries are present in the groundwater system. Locations within the mesh where hydraulic heads are assumed fixed can be designated as constant head cells. All other cells are assumed active (variable-head cells) within the finite-difference mesh. The entry of active, inactive and constant head cells are fixed by the user when building the hydrologic model. Also for the solute transport cells can be active, inactive or at constant concentration.

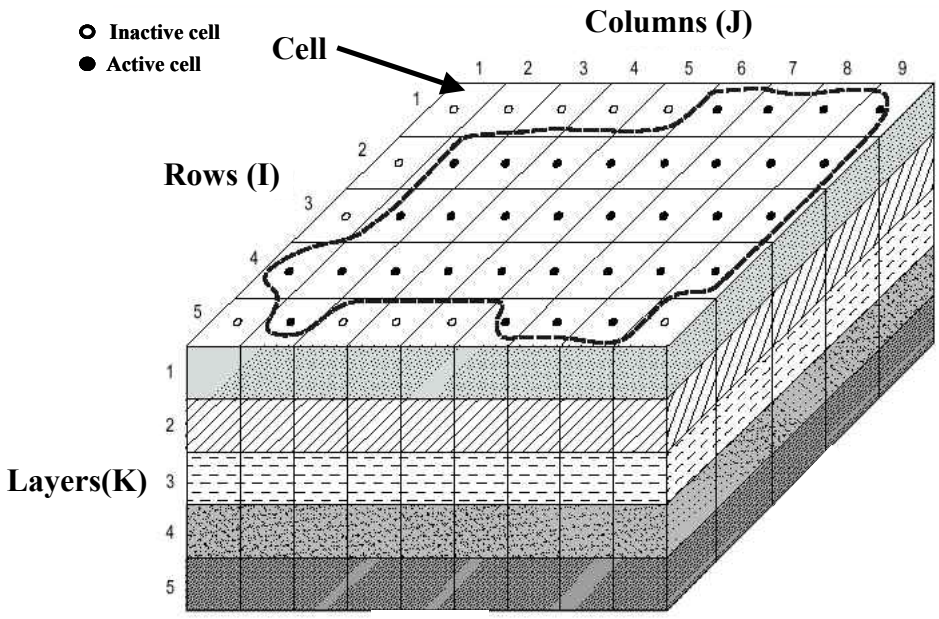


Fig. 52 - A hypothetical aquifer system for discretised modelling using MODFLOW.

In a flow and transport simulation, MODFLOWT simulates solute transport at the completion of each flow time step. The recharge flow will be given by the output of the unsaturated zone model MACRO. Water inputs (rainfall, irrigation) do not have to be accounted for except for subterraneous recharge.

Spatializing Tool - A tool has been realized using the data sheet MS Excel with the programming language Visual Basic for Application. It is structured in a series of MS Excel sheets in which the user can easily input the scenario data required by MACRO. The tool is able to divide the study area in a grid with homogeneous cells, prepare spatial distributed data required by MACRO, and prepare MACRO input data files for each cell of the grid. Successively, the tool can run multiple MACRO simulation for each cell of the grid and organize output report following the user preference as well as

generate outputs files compatible with GIS and other environmental software applications.

Coupling tool MACRO/MODFLOWT - The coupling tool MACRO/MODFLOWT is deterministic as it undertakes a single simulation for every unique soil/crop rotation combination. MACRO output data for water and pesticide percolation are used to define the upper boundary of MODFLOWT (Recharge files). The tool allows a loose coupling from MACRO to MODFLOWT only and not vice versa. The system works with a fixed layer where the groundwater depth is defined as input from MACRO simulations. The option for a daily, weekly, or monthly time step depends on MODFLOWT input management: the longer the time step, the less accurate the simulation. A 10-day time step represents the right compromise between simulation accuracy and simulation speed.

2.3.2. Results and discussion

The spatial schematization approach used is a modification of the “unique combination” technique described by Tiktak *et al.* (1996). During the first step, the simulated area is divided in a grid of homogeneous cells (raster representation). Then the scenario parameters are divided in an adequate number of classes to represent the variability of the entire area. The classes refer mainly to soil physical properties, soil profiles, land use, crop rotation. Therefore, the appropriate class number is attributed to every cell reproducing a series of map layers. Moreover, a series of map layers is produced for each year of simulation to consider crop rotation as MACRO simulates one crop at a time. In the end, a combination of class for every cell is obtained, overlapping the different map layers, and all the cells identified by the same combination are “unique combination”.

The flow diagram of the coupling tool is described in Figure 53. The spatializing tool uses a series of MS Excel sheets in which all the data for the simulations have to be stored to form a data base. The tool manages successively the class attribution, the unique-combination computation and the preparation of parameter files (*.PAR) for the model. After the input file compilation, MACRO executes all the simulations in batch mode, storing the results in a series of binary files (*.BIN). Binary files are then converted in ASCII files by a program supplied by SLU. At this point, the tool assigns the results to every cell following the schematization procedure described above and creates a plot file (MACRO Translator) (Fig. 54) which is useful to generate plot maps and/or to supply input data to MODFLOWT. Pesticide concentration (mg/l) and water flux (L/t) simulated by MACRO are supplied to MODFLOWT as recharge files with a time step chosen by user. Since the coupling tool creates only recharge files which are used by the MODFLOWT Recharges packages, all files related to other MODFLOWT packages must be prepared separately.

The coupling tool MACRO/MODFLOWT is deterministic. Each MACRO simulation is independent from the others. Boundary model specific switch is set as 3 (water table in the soil profile). The MACRO output data for water and pesticide percolation are used to define the upper boundary of MODFLOWT (Recharge files). Files *.bin generate input files for MODFLOWT (*.RCH Recharge water, *.RCT Recharge pesticide).

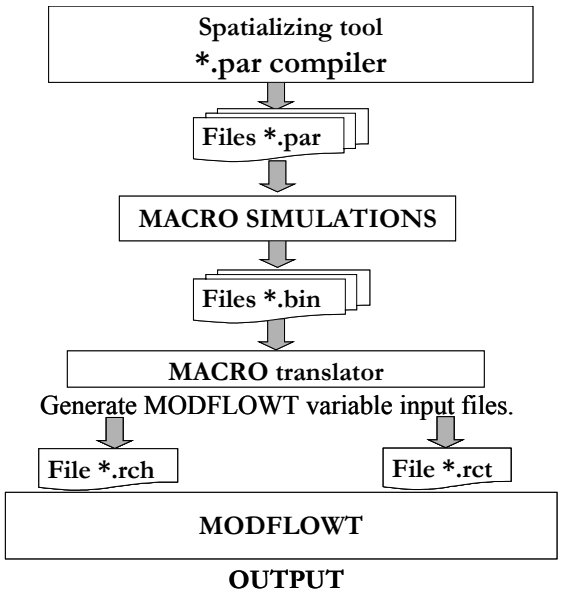


Fig. 53 - Flow diagram of coupling tool.

The user sets the MODFLOWT timestep depending on the simulation duration desired. It is considered that a 10-day time step represents the right compromise between simulation accuracy and simulation speed.

The grid of inputs works at fixed depth, independently of any groundwater fluctuation. MODFLOWT starts the simulation at the end of MACRO simulations taking cumulative water and pesticide flow every ten days from the recharge files.

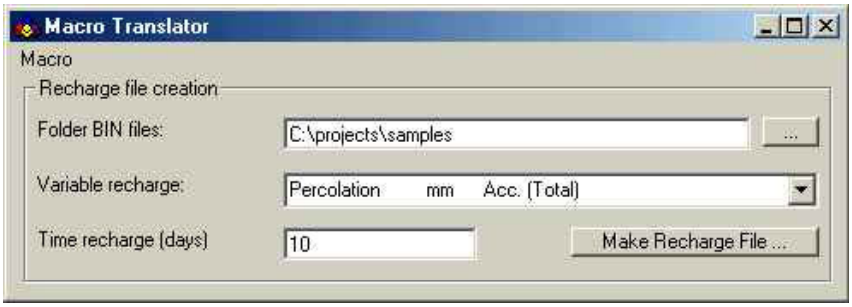


Fig. 54 - Macro translator producing input to MODFLOWT from MACRO output.

The tool has been tested to simulate the behaviour of water and isoproturon in the unsaturated/saturated zones in Zwischenscholle using 10 years of meteorological data and different crop-soil combinations (section 3.4.3. in chapter 3).

2.3.3. Summary

An information tool which allows the simulation of pesticide fate in the unsaturated/saturated zone at the catchment scale has been developed through the spatialization of the 1D unsaturated zone model MACRO and the linking of this model to the 3D saturated zone MODFLOWT model. The final product is able to simulate the

spatially variable movement of pesticides in the unsaturated zone and the evolution of pesticides once they reached groundwater. The spatialization tool divides the study area in a grid with homogeneous cells, prepares spatially distributed data required by MACRO, prepares MACRO input data files for each cell of the grid, runs multiple MACRO simulation for each cell of the grid, organises output reports following user preferences and generates outputs files compatible by GIS and other environmental software applications.

The coupling tool MACRO/MODFLOWT allows a loose coupling from MACRO to MODFLOWT only (*i.e.* there is no exchange of information from MODFLOWT to MACRO). The user needs to set the MODFLOWT timestep and this has a direct implication on the duration of the simulations. A 10-day time step is believed to represent the right compromise between simulation accuracy and simulation speed. The grid of inputs works at fixed depth, independently of groundwater fluctuations. MODFLOWT starts the simulation at the end of MACRO simulations taking cumulative water and pesticide data every ten days from the recharge files.

2.4. Combination of ANSWERS and MODFLOWT [LTHE]

A significant amount of work has been undertaken to couple a spatially distributed soil-vegetation-atmosphere model (ANSWERS) with a commercial groundwater model (MODFLOW) and a model for the transport of reactive solutes (MT3D). Difficulties in the linking of these three models were encountered at an early stage due to the requirements of each model in terms of inputs and outputs. The work involved the modification of the inner structure of ANSWERS and the establishment of a link (in space and time) between the three models.

2.4.1. Adaptation of ANSWERS to allow an automatic coupling with MODFLOW

Until this stage, ANSWERS was used on the basis of sequential simulation (Fig. 55) with the following characteristics: all blocks with similar features (soil, crop, plants) are aggregated together; for every megaplot, simulations are run from day 1 to the end of the simulation period; outputs are either cumulative values of percolation, evapotranspiration, nitrate and pesticide leaching or instantaneous daily fluxes. These are spatially redistributed with a GIS making use of the localisation of each block attribute over the catchment.

In order to insure a proper automatic coupling between transport in the unsaturated zone and transport in the groundwater, ANSWERS had to be totally rewritten to permit direct interaction between every block of the soil and land use layers with every block of the groundwater layer on a daily basis. For each individual block of the matrix, the water balance is determined on a daily basis and values of percolation, soil storage and evapotranspiration are stored in a transient buffer. Once this is done for all blocks, spatialized values of percolation from the soil are used as input in groundwater at the end of every time step. Groundwater flow is determined on a regional basis by MODFLOW. Interactions between groundwater and the above unsaturated soil zone are determined. Results are then stored in a buffer and the compilation starts again for the next day with the final boundary of the previous day used as initial boundary of the following day (Fig. 56).

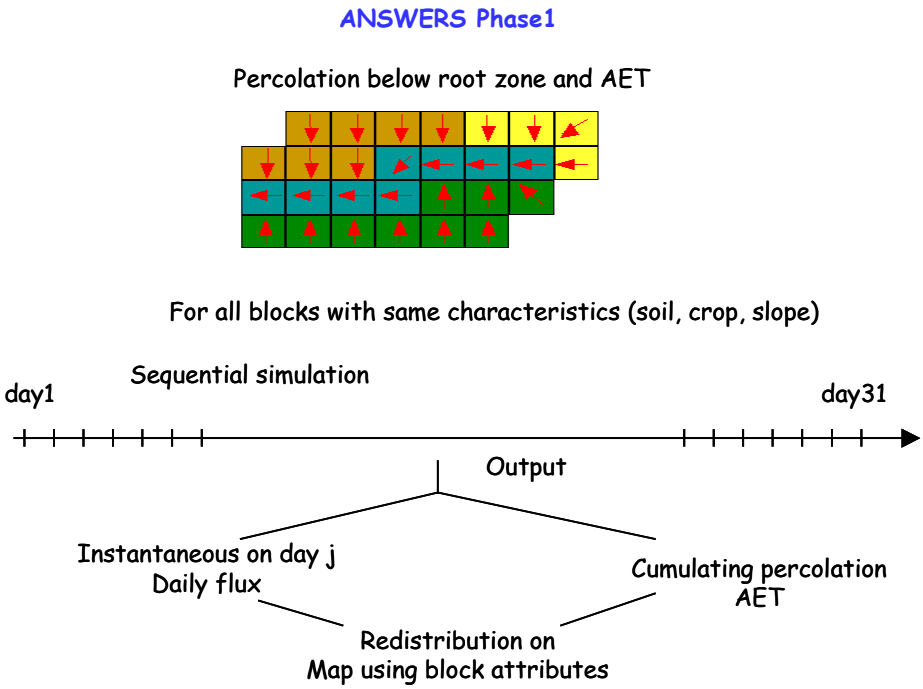


Fig. 55 - Schematic representation of the coupling between ANSWERS and a GIS in the original version.

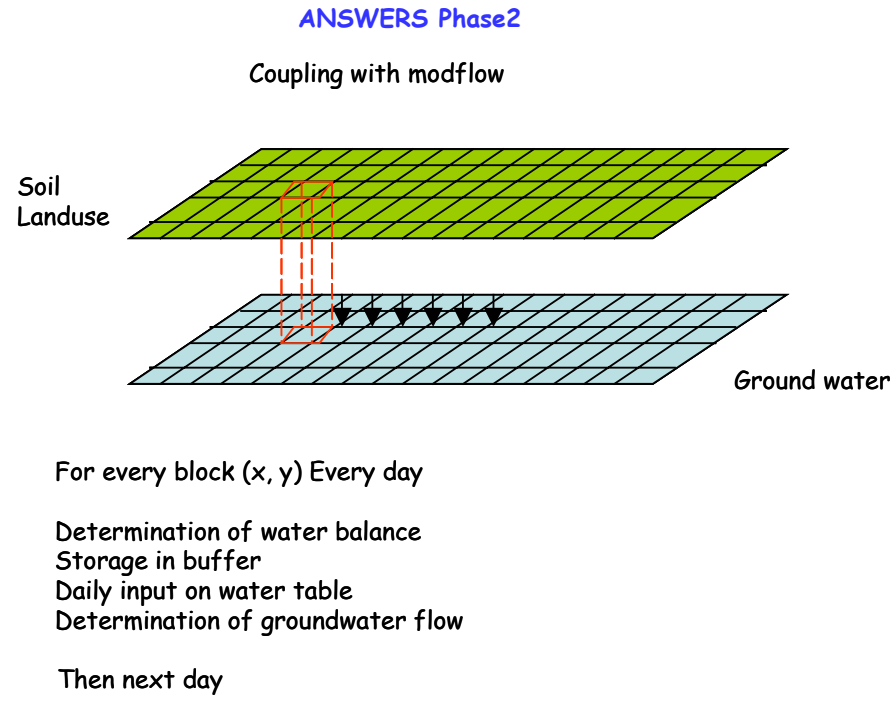


Fig. 56 - Organisation of coupling between ANSWERS and MODFLOW, new version.

2.4.2. Interconnection between models

Two independent packages have been developed (MAIN and LINKAGE) in order to permit interconnecting loops between the models. They are schematised on Figure 57.

The aims of the MAIN package are:

- control of the simulation;
- management of spatialized input (soil, land use and pesticide application);
- management of the data related to climate;
- run of the simulation on daily time steps.

The aims of the LINKAGE package are:

- initialisation of the depth of the unsaturated zone;
- determination of the proper module to determine evapotranspiration (according to depth of groundwater);
- importation of the output of ANSWERS into MODFLOW;
- exportation of the output of MODFLOW to ANSWERS.

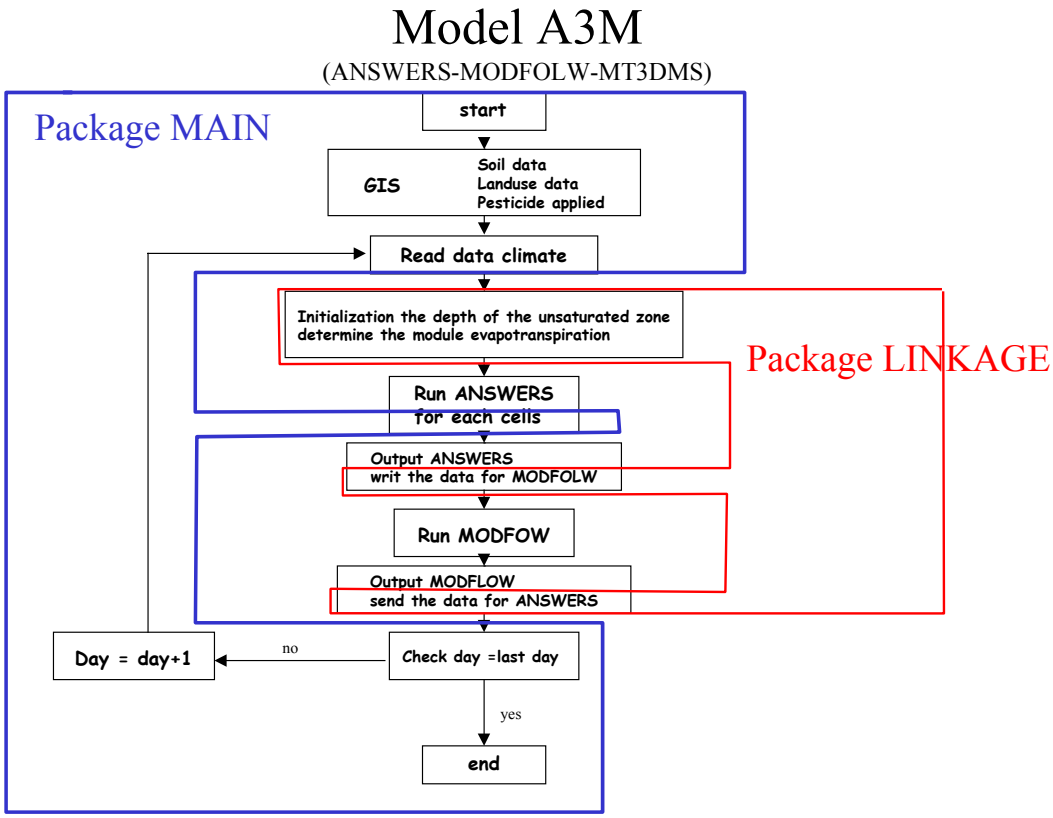


Fig. 57 - Schematical representation of the link between ANSWERS and MODFLOW.

Spatialized input data are managed using GRASS, a public domain Geographic Information System. The whole system was built to work automatically, with a routine to account from annual crop rotation. It was tested on the Zwischenscholle case study (section 3.3. in chapter 3), but could not be wholly operative in terms of groundwater coupling due to the underestimation of difficulties experienced in the algorithmic coupling between the two programmes. Another problem was also met with difficulties in simulating upwards movement of water from the aquifer to the soil (capillary rise). In consequence, the work was abandoned and efforts were concentrated on the further development of the alternative model POWER (section 3.3. in the present chapter).

2.4.3. Summary

An attempt was made to couple the soil-vegetation-atmosphere model ANSWERS with groundwater (MODFLOW) and solute transport (MT3D) models. Due to algorithmic difficulties experienced in the combination of the respective model codes, this attempt failed and subsequent efforts were concentrated on the further development of the integrated model POWER.

3. REFINEMENTS OF INTEGRATED MODELS

3.1. MARTHE [BRGM]

MARTHE (Modelling Aquifers with Rectangular cells, Transport and Hydrodynamics) is a versatile 3D groundwater model designed to enable the hydrodynamic and hydro-dispersive modelling of groundwater flow in porous media (Thiéry, 1990, 1993, 1994, 1995). MARTHE has been applied to over 200 aquifer systems since its first release 20 years ago. Fields of application have included i) the management of groundwater resources (*e.g.* water balance assessments, evaluation of potential impacts); ii) civil engineering and mining work (*e.g.* impact of underground activities); and iii) environmental assessments (both point and diffuse pollution). MARTHE integrates pre- and post-processors to facilitate the preparation, management and graphical processing of input data and modelling results. The system also allows imports/exports to be made with the GIS software MapInfo and integrates its own tool for interpolation of scattered data. Specific models describing the fate of contaminants in groundwater (*e.g.* geochemical models) can be linked to MARTHE and the aquifer system may be coupled to a river network. Hydrodynamic calculations are based on the Richards' equation which is solved using a finite volumes algorithm for which a range of solutions can be selected while advective, diffusive and dispersive transport can be simulated using three different techniques (finite differences, total variation diminishing, method of characteristics using particles) depending on the situation considered (predominance of convection or dispersion). Calculations for energy, temperature, mass and water fluxes are fully coupled within the model.

Accurate simulation of pesticide fate in soil and the unsaturated and saturated zones with MARTHE required the addition of functionalities dedicated to simulating the sorption of compounds to soil particles and their degradation. A description of degradation according to chain and parallel reaction has been introduced in MARTHE. Degradation rates can also be allowed to vary with variations in moisture and temperature. Sorption was described using the widely used Freundlich and Langmuir

equations. Crop development schemes were also introduced in the model as part of the PEGASE project to enable water fluxes between soils, plants and the atmosphere to be adequately simulated. All new functionalities were assessed against analytical solutions, existing tests or experimental datasets reported in the literature (sections 1.1., 1.2., 1.3. in chapter 3).

3.1.1. Addition of subroutines for pesticide sorption in MARTHE

The schemes selected for description of sorption for pesticides were those of Langmuir and Freundlich.

- ***Langmuir isotherm***

The classical Langmuir sorption isotherm expressing the relation between the solid phase concentration S_M and liquid phase concentration C at equilibrium is traditionally given as:

$$S_M = Q \cdot \frac{K_L \cdot C}{1 + K_L \cdot C}$$

where: S_M = Solid phase mass concentration [kg/kg]
C = Liquid phase volumetric concentration [kg/ m^3]
Q = Total sites for solid phase concentration [kg/kg]
K_L = Langmuir constant [m^3/kg]

This relation may be written using a solid phase volumetric concentration S_V (mass of product per terrain volume). $S_V = \rho_b \, . \, S_M$ where ρ_b = Dry soil density [kg/m^3] (1,600 kg/m^3 for a typical soil). S_V has the same dimension as the liquid phase concentration C and is expressed in the same unit.

With these variables, the Langmuir isotherm writes:

$$S_V = \rho_b \cdot Q \cdot \frac{K_L \cdot C}{1 + K_L \cdot C}$$

or in dimensional form, as implemented in MARTHE:

$$S_V = S_{VMAX} \cdot \frac{C / C_{REF}}{1 + C / C_{REF}}$$

where: $C_{REF} = 1/K_L$ = Reference concentration [kg/m^3]. C_{REF} is the liquid phase concentration above which the effect of the solid phase is halved;
$S_{VMAX} = \rho_b \, . \, Q$ = Maximal solid phase volumetric concentration [kg/m^3]. S_{VMAX} is the solid phase volumetric concentration, which corresponds to an infinite liquid phase concentration.

- ***Freundlich isotherm***

The classical notation for the Freundlich sorption isotherm which expresses the relation between solid phase concentration S_M and liquid phase concentration C writes:

$$S_M = K_F \, . \, C^B$$

where: B = Exponent (generally < 1),
K_F = Freundlich constant in unit $[m^3/kg]^B$.

It should be noted that the unit of K_F is generally complex because it depends on the B exponent.

Using the solid phase volumetric concentration S_V (see above), the Freundlich isotherm writes:

$$S_V = K_{FV} \cdot C^B$$

with: $K_{FV} = \rho_b \cdot K_F$ = volumetric Freundlich constant in $[kg/m^3]^{(1-B)}$.

In MARTHE, the Freundlich isotherm is described by two parameters:

- $K_{FV} = \rho_b \cdot K_F$ = volumetric Freundlich constant in [concentration unit] $^{(1-B)}$;
- A2 = B (dimensionless exponent).

When B = 1, the isotherm becomes linear and K_{FV} is identical to a volumetric Rho_kd (dimensionless). If we set $K_{FV} = (C_{REF})^{1-B}$, $S_V = C$ (which corresponds to Rho_kd = 1) when $C = C_{REF}$.

The adequate implementation of the new sorption subroutines in MARTHE were extensively tested through 1-, 2- and 3D modelling (see section 1.2. in chapter 3).

3.1.2. Addition of subroutines for pesticide degradation in MARTHE

- ***Sequential first-order decay reactions***

This functionality enables the simulation of the fate of degradation products. The degradation is considered to be sequential, in that product #1 is degraded into product #2, which in turn is degraded into product #3, etc. Each compound has its own decay factor and its own retardation coefficient or kd factor. In MARTHE, there is no restriction on the number of metabolites which can be simulated using this sequential scheme. In the current release of the model, a given compound is assumed to be degraded in no more than one "son" product (hence the name of "chain" degradation). A version of the model which allows the simulation of complex degradation schemes is scheduled to be released in the near future.

In MARTHE, the simulation of chain degradation is available when transport is computed by Finite Differences (FD) or by Total Variation Diminishing (TVD). With the transport scheme referred to as the Method of Characteristics (MOC), chain degradation can only be used if the retardation coefficients (kd factors) for all products are identical. This is due to the fact that in MARTHE, this particular transport scheme uses a single kind of particles containing all chemical components. The coupling method is sequential and iterative. A transport in steady state cannot be thus calculated directly, but should be simulated as a transient state over a long period.

The code was verified using a 1D analytical solution from Cho (1971) described and used by Van Genuchten (1984). A simulation in 2D has also been undertaken in order to verify the implementation of the code in 2D or 3D (section 1.3. in chapter 3).

- ***Effect of water content and temperature on degradation***

The decay factor (or degradation factor) usually depends on temperature and/or on water content (saturation). The simulation of the influence of these two environmental variables is also possible when the decay factor shows spatial variations. In this case, the influence of the temperature and/or of the water content appears as correction factors applying to model values.

$$\lambda(T,\theta) = \lambda(Tref , \theta ref) . F(T) . F(\theta)$$

where: λ = decay factor or degradation factor $[time]^{-1}$ = ln(2) / DT50 with DT50 is the half-life of the compound [Time];
$F(T)$ = Temperature correction;
$F(\theta)$ = Saturation correction.

It should be noted that the F(T) and $F(\theta)$ corrections as described below only apply to the decay factor λ and not to DT50. The parameters describing these corrections as for temperature and humidity have to be provided to MARTHE.

Following a review by Golaz (2001) of mathematical descriptions of these correction processes, the formulations implemented in five models (LEACHP, AGRIFLUX, MACRO, WAVE and PELMO) for the temperature effect were retained for inclusion in MARTHE while six expressions were selected for the effect of water content (AGRIFLUX offers an aerobic and anaerobic option).

- ***Effect of temperature on degradation***

For each equation presented further below, the notations used are as follows:
T = Water Temperature in °C;
T_{REF} = Reference Temperature in °C;
TK, TK_{REF} = °K equivalent of T and T_{REF};
A1 = Correction Parameter.

LEACHP and PELMO: $F(T) = A1^{(T - TREF) / 10}$
The reference values for A1 are in the order of 2 to 6 for ethoprophos and bentazone.

AGRIFLUX: $F(T) = Exp[(1/TK_{REF} - 1/TK) . A1 / 8.31]$
A1 is the activation energy (vaporization heat) in J/mol.

MACRO: If T > 5 °C => $F(T) = Exp[A1 . (T - T_{REF})]$
If 0 < T < 5 °C => $F(T) = (T/5) .Exp[A1 . (5 - T_{REF})]$
If T < 0 °C => F(T) = 0

WAVE: $F(T) = A1 . (T - T_{REF}) / 10.$
(We added: F(T) = 0 when $T < T_{REF}$)

- ***Effect of saturation on degradation***

For each equation, the notations used are as follows:
θ = Water content,
θ_R = Residual Water content,
θ_S = Water content at Saturation,

A1, A2, A3 = parameters. Each equation depends on only one single parameter except for LEACHP where three parameters are used.

LEACHP:
T_min = max (A1 , θ_R)
T_max = min (A2 , θ_S)
F_sat = A3
$F(\theta) = (\theta - \theta_R) / (T\_min - \theta_R)$ if θ < T_min
$F(\theta) = F\_sat + [(1 - F\_sat) .(\theta_S - \theta)] / (\theta_S - T\_max)$ if θ > T_max
$F(\theta) = 1$ if T_min < θ < T_max
Reference values for the F_sat parameter (which is < 1) are in the range 0.6 to 1. It should be noted that when the LEACHP option is used in MARTHE, parameters A1 and A2 (which correspond to water contents) are in the unit of water contents (*e.g.* A1 and A2 are expressed in % if water contents are expressed in %).

Aerobic AGRIFLUX:
T_cap = min(A1 , θ_S) = Field capacity.
$F(\theta) = \theta / T\_cap$ if θ < T_cap
$F(\theta) = T\_cap / \theta$ if θ > T_cap

Degradation is maximal at field capacity. It is reduced at both side of this value.

It should be noted that when the AGRIFLUX option is used in MARTHE, the parameter A1 which corresponds to water contents is expressed in the same unit as water contents.

MACRO: $F(\theta) = (\theta / \theta_S)^{A1}$
The variable θ_S refers to the porosity, excluding the possible macroporosity.

WAVE:
The WAVE expression is nearly identical to the MACRO formulation: $F(\theta) = (\theta / \theta_{REF})^{A1}$. Assuming $\theta_{REF} = \theta_S$, we obtain $F(\theta) = (\theta / \theta_S)^{A1}$ as in MACRO.

PELMO:
The PELMO expression is identical to that of WAVE.

Anaerobic AGRIFLUX:
T_cap = min(A1 , θ_S) = Field capacity
$F(\theta) = 0$ if θ < T_cap
$F(\theta) = (\theta - T\_cap) / (\theta_S - T\_cap)$ if θ > T_cap
Microbial activity is assumed to take place only when the water content is close to saturation (i.e. above T_cap). Again, the A1 parameter is expressed in the same unit as water contents.

The various schemes for correction of degradation as a function of temperature and humidity were tested through a range of evaluation exercises (section 1.3. in chapter 3).

3.1.3. Addition of subroutines for cropping in MARTHE

Interaction between the atmosphere and the uppermost soil layers depends on vegetation cover, also referred to as 'crop cover'. Vegetation influences water and pesticide fluxes in two main ways:

- plant transpiration, which depends on the condition of the vegetation;
- and, the uptake of water and solutes.

In former releases, the MARTHE code (Thiéry, 1993, 1994, 1995) used basic data on potential evapotranspiration (PET) and water and solute uptakes were only applied to the top surface layer. This prevented satisfactory calculations in the unsaturated zone with detailed soil representation and a surface layer of only a few centimetres. Applying water and solute uptake via evapotranspiration, *i.e.* extracting a large volume from a thin layer, resulted in major desaturation of this layer, in turn generating low hydraulic conductivities and large suction heads. Values for section heads could occasionally exceed the maximal suction head, thereby restricting the uptake of water.

In order to better account for the effects of vegetation, the following functionalities were added to the MARTHE code as part of the PEGASE project:

- breakdown of evapotranspiration into i) surface evaporation and ii) transpiration by vegetation. This breakdown depends on the development of those parts of the vegetation in contact with the air (essentially leaves);
- water uptake by vegetation over a variable depth that depends on the condition of root development and vertical root distribution;
- restriction of uptake according to the state of hydric stress experienced by vegetation.

With regard to the mass transfer of solutes (*e.g.* fertilisers, plant-protection products), the following functionalities were added to the model:

- no mass uptake through evaporation at the surface;
- mass uptake through transpiration of the roots, depending on the product considered.

The implementation of these new crop subroutines is detailed below.

- ***Horizontal spatialisation***

Each cell of the area simulated is associated with three zone indices:

- a meteorological zone index: at a given date, all cells within the same meteorological zone index are assumed to have equal amounts of precipitation and PET and the same air temperatures;
- a crop zone index: at a given date, the same crop type occupies all cells with the same crop zone index;
- a soil zone index: all cells with the same soil zone index are assumed to have the same "hydrological" parameters. These parameters mainly describe snow melt (degree, day, etc.) and the partitioning between recharge and runoff (equivalent depth of runoff, etc.).

- ***Crop definition***

Each crop is described by a number of parameters, including:

- a pre-maturity duration, which is equal to the period of time between germination and maturation;
- a pre-harvesting duration, which is equal to the period of time between germination and harvesting.

- ***Determination of (potential) vegetation transpiration and surface evaporation***

Three schemes have been implemented in the MARTHE code for simulating vegetation transpiration: LEACHP, MACRO 3.2 and AGRIFLUX.

The potential transpiration flux of the vegetation depends on crop foliation development, which may be characterised by:

- a foliation index (Crop Cover) in LEACHP;
- a foliation index (Leaf Area Index) in MACRO;
- a total need for the entire season in AGRIFLUX.

This transpiration flux is termed “potential” as it could be reduced should the plants be subjected to hydric stress.

- ***Transpiration according to LEACHP***

In LEACHP (Hutson, 2000), a crop cover index (CC, dimensionless) ranging from 0 to CCmax is calculated. The CCmax parameter depends on crop type. The CC index is calculated as follows:

- prior to germination: CC = 0;
- between maturity and harvesting: CC = CCmax;
- after harvesting: CC = 0;
- between germination and maturity, CC varies from 0 to CCmax according to a sigmoid function, as outlined in Figure 58.

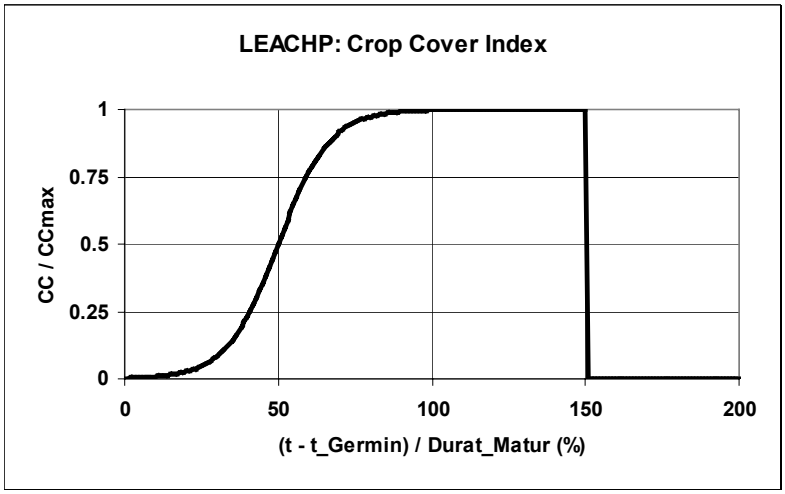


Fig. 58 - LEACHP scheme: evolution with time of the CC index.

Once the CC value has been calculated, the potential transpiration flux (Potent_Transpi) is given by:

- potent_Transpi = PET_Corr . CC;
- evaporation = PET_Corr . (1 – CC).

- ***Transpiration according to MACRO 3.2***

According to the MACRO scheme (Jarvis, 1994, 2002), a dimensionless foliation index, the Leaf Area Index (or LAI), is used. LAI typically varies from 0 to ca. 5 (Fig. 59). The parameters needed to calculate LAI depend on crop type and are defined in the crop file. These parameters are: LAImin before germination, LAImax at the date of maturity, LAIharv at the date of harvest, and two exponents describing the curvature of the curves before and after maturity.

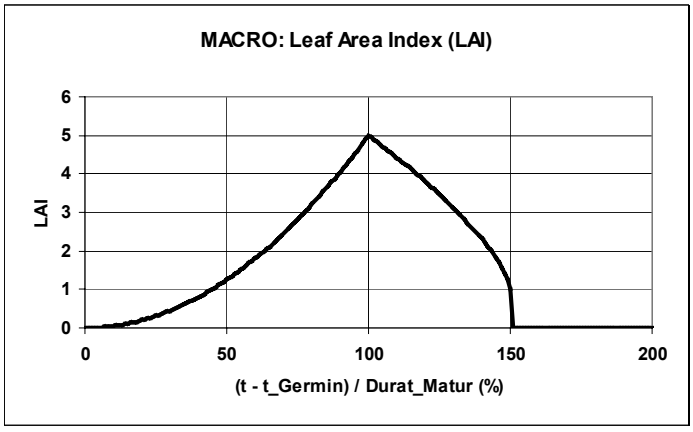


Fig. 59 - MACRO scheme: evolution with time of the LAI index.

Once the LAI index has been calculated, the potential transpiration flux (Potent_Transpi) is given by (Fig. 60):

- potent_Transpi = PET_Corr . [1 – exp(-0.6 . LAI)];
- evaporation = PET_Corr . exp(-0.6 . LAI).

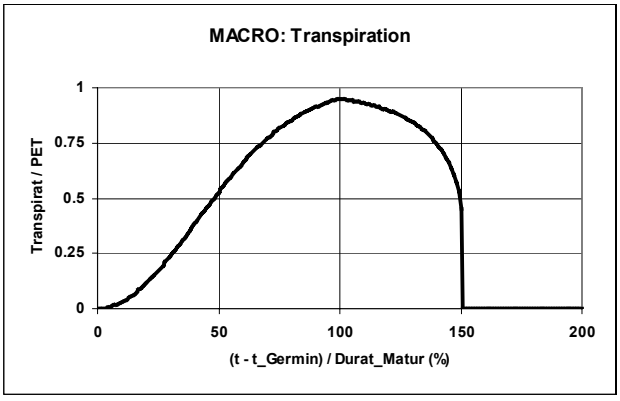


Fig. 60 - MACRO scheme: evolution with time of the ratio between potential transpiration and potential evapotranspiration.

- ***Transpiration according to AGRIFLUX***

The AGRIFLUX scheme (Banton *et al.,* 1997) requires the specification of a total need of water (Transpir_Tot; *e.g.* in mm) for the crop entire development period. Distribution with time of the transpiration flux follows a Normal probability law, centred on the middle of the growth period (from germination to maturity). The period of maturation is assumed to equal six standard deviations (Fig. 61).

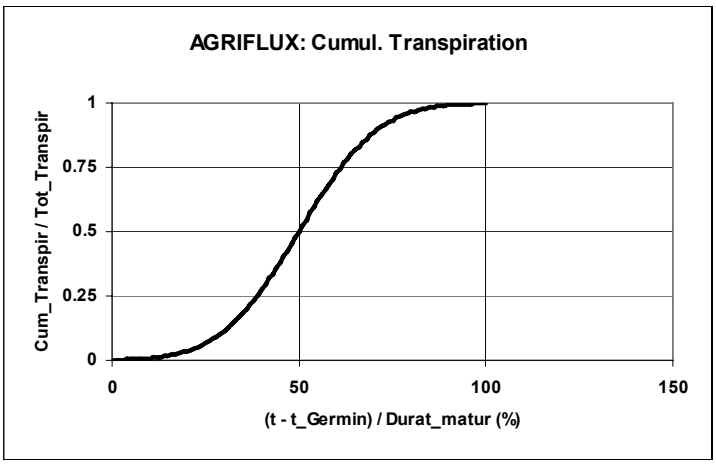


Fig. 61 - AGRIFLUX scheme: evolution with time of cumulated transpiration.

The approach is fairly different from those of LEACHP and MACRO 3.2. In contrast to these two models, transpiration in AGRIFLUX is not calculated from climate characteristics for each time step (temperature, sunshine, radiation) and is therefore independent of the climate.

Once the transpiration flux has been calculated, the evaporation flux is deduced as:

$$\text{Evaporation} = \max(\text{PET\_Corr} - \text{Transpir}, 0).$$

- ***Root development***

The development of roots can be described according to two geometric characteristics, the root depth (*i.e.* the maximum depth reached by roots at any given time) and the root distribution along this vertical depth, expressed as root density.

- ***Root depth***

Amongst the schemes available for root depth, those of MACRO (Jarvis, 1994, 2002) and AGRIFLUX (Banton *et al.,* 1997) were retained. They both assume linear growth from germination through to maturity. Root depth thus remains constant until harvesting, at which point it abruptly becomes zero. The non-linear expression scheme implemented in LEACHP (Hutson, 2000) was not retained as it involves empirical laws established on maize only. In all cases, root depth is calculated at each model step for the entire duration of the model time step, independently of any possible calculation sub-steps.

- ***Root density***

Four expressions of root density were retained for inclusion in MARTHE. All schemes depend on root depth only. The root pattern which is specific to each crop type is selected from the crop file. The four schemes retained are:

- constant density (also called "cylindrical");
- conical density (AGRIFLUX);
- "hemispherical" or "cono-spherical" density (AGRIFLUX);
- exponentially decreasing density (MACRO).

The first three schemes involve root depth alone while the exponentially decreasing density also includes a dimensionless shape factor that determines the decrease in density with depth.

Figure 60 presents three schemes of root density (with a shape factor = 3.67 for the exponential scheme). The conical density and the exponentially decreasing density are fairly similar despite the fact that the former is based on a simpler expression.

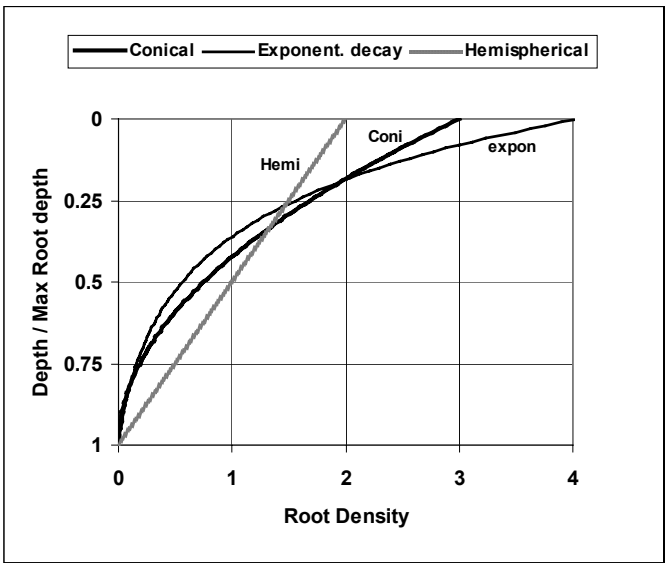


Fig. 62 - Root density according to three different schemes (exponentially decreasing density is calculated with a shape factor of 3.67).

- ***Hydric stress***

As described earlier, potential transpiration is calculated in MARTHE using a scheme of vegetation cover development ("Crop Cover" or "Leaf Area Index") and either the total need of the crop in terms of water (AGRIFLUX) or potential evapotranspiration (LEACHP and MACRO). Vegetation transpiration, however, also depends on the hydric conditions surrounding the roots. The possibility of having hydric stress conditions which restrict (potential) transpiration (*e.g*. when the soil is too dry or too wet) was introduced in the model using the schemes used in MACRO and SWAP. The two schemes involve three parameters for suction head, but MACRO also requires a stress

threshold. These stress conditions contribute to the reduction in evapotranspiration, from a potential to an actual value.

The parameters which are common to both MACRO and SWAP are:

- the wilting suction head ("wilting point"): suction_wp;
- the maximum suction head: suction_max;
- the minimum suction head: suction_min.

MACRO
The model calculates a weighted average stress factors in the vertical direction and the average is compared to the threshold value (Fig. 63):

- where mean_stress > stress_thresh: uptake is unrestricted;
- where mean_stress < stress_thresh: uptake is restricted in all cells within the ratio mean_stress / stress_thresh.

SWAP
The SWAP scheme retained (Feddes *et al.,* 1978; Van Dam *et al*., 1997) does not consider either stress averages or stress thresholds:

$$Uptake_z = Transpir \; . \; stress\_fact\_z.$$

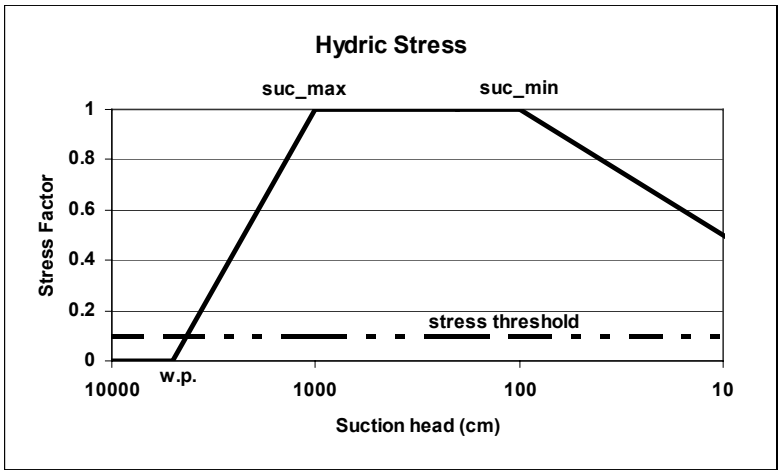


Fig. 63 - Definition of stress factor. In this example: suction_wp = 5,000 cm, suction_max = 1,000 cm, suction_min = 100 cm. Stress threshold = 0.10.

- ***Solute uptake by vegetation***

For a perfect tracer, the solute uptake by vegetation is:

$$Q\_solute = Uptake \; . \; Conc$$

where: Q_solute = solute uptake,
Conc = concentration at the end of the time step.

For an interacting compound, mass uptake is restricted:

Q_solute = fc . Uptake . Conc

where fc is a coefficient varying between 0 and 1.

For pesticides, the fc coefficient is generally of the order of 0.5-0.6. An fc coefficient <1 leads to an over-concentration of the solute in the soil due to the uptake of a greater amount of water.

As for sorption and degradation subroutines, refinements made to the model in terms of crop were tested against data obtained in the field (section 1.1. in chapter 3).

3.1.4. Summary

Accurate simulation of pesticide fate in the soil and the unsaturated and saturated zones required the addition to MARTHE of functionalities dedicated to simulating and the development of crop covers, the sorption of compounds to soil particles and their degradation. Degradation schemes based on chain and parallel reactions have been introduced in MARTHE. The degradation schemes account for the influence of temperature and humidity on degradation rates. Sorption was described using the widely used Freundlich and Langmuir equations. The development of vegetation both above- and below-ground, the uptake of water and pesticides by plants and the impact of hydric stress conditions can now be simulated using MARTHE. All new functionalities have been assessed against analytical solutions, existing tests or experimental datasets reported in the literature.

3.2. TRACE [FZJ]

TRACE (Vereecken *et al.,* 1994) is a large parallel computer code developed to solve water flow in large scale soil-groundwater systems. It is based on the 3DFEMWATER code (Yeh, 1987). The model has mainly been used to generate stochastic flow fields in order to test stochastic theories of solute transport (Neuendorf, 1996; Döring, 1997; Schwarze *et al.,* 2001; Englert, 2003). In the framework of the PEGASE project, the model was applied to agricultural soils with groundwater influence. Therefore changes to the numerical solution, the upper boundary conditions and handling of soil hydraulic properties were necessary to properly compute the unsaturated-saturated flow of water in cropped soils. To calculate plant growth the plant module SUCROS (Spitters *et al.,* 1988) was integrated in the TRACE model. This model allows the calculation of leaf area indices and rooting depth of agricultural crops, which are needed for the calculation of the actual evapotranspiration. The core of TRACE is the following modified version of the Richards` equation:

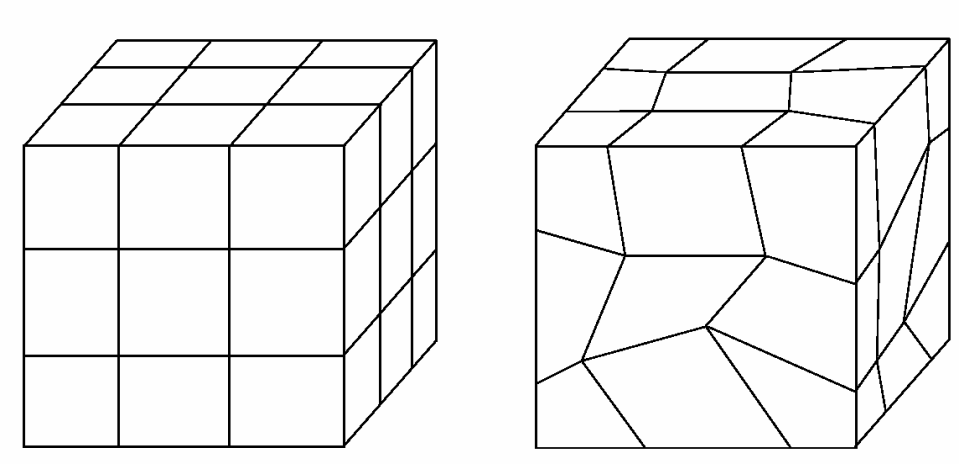
$$F_h \cdot \frac{\partial h(\vec{s})}{\partial t} = \frac{\partial}{\partial \vec{s}}(\vec{\vec{K}}(\vec{s},h) \cdot \frac{\partial (h(\vec{s}) + z)}{\partial \vec{s}}) + S(\vec{s},t) \qquad \text{with} \qquad F_h = \frac{\partial \theta}{\partial h} + S_h$$

where $\vec{\vec{K}}$ is the hydraulic conductivity tensor [LT^{-1}], $\vec{s}$ is the position vector in a three dimensional space, z is the vertical coordinate [L], h is the pressure head [L], S is the source/sink term [T^{-1}], θ is the moisture content [L^3L^{-3}], t is time [T], S_h is the specific storage coefficient [L^{-1}] and F_h is the specific water capacity [L^{-1}].

3.2.1. Modelling approach

- ***Geometry***

The equation given above is solved using Galerkin-type finite elements. The flow domain is represented by isoparameteric hexahedrons. Every element consists of eight corner nodes and six sides. The element can be distorted (see Fig. 64 right hand side) but the nodes of every side have to be located on the same plane. In order to comply with specific requirements of GIS (*e.g.* regular grid) and to provide rapid access to node indices the number of nodes in one direction of space is kept constant, *e.g.* nx and ny elements in x and y-direction respectively.



The left side shows a regular 3D flow domain, the right hand side shows an irregular 3D flow domain.

Fig. 64 - Two examples of flow domain geometry in TRACE.

- ***Numerical solution***

In order to improve the numerical solution for unsaturated conditions, several modifications were carried out. TRACE calculates the 3D unsaturated/saturated water flow in porous media with a modified Picard-iteration scheme (Celia *et al.,* 1990) which is applied in combination with a preconditioned conjugate gradient method in order to solve the modified version of the Richards' equation numerically. It was necessary to improve the mass balance in the unsaturated zone. Thus the approach of Celia *et al.* was implemented in combination with a mass lumping approach and a modified convergence criterion according to Huang *et al*. (1996). Furthermore a convergence dependent dynamic relaxation time factor was introduced to improve numerical stability and computation speed.

- ***Boundary conditions***

A special type of boundary condition relevant for the regional scale application is the 'global Dirichlet boundary condition'. This boundary condition can only be applied to the vertical sides of the flow domain. For every vertical node column of the vertical sides the groundwater level G_L [L] must be given. For this vertical column of nodes all unsaturated nodes are set at a no-flow boundary (Cauchy, with qc = 0, see Table 16). For the saturated nodes hydrostatic equilibrium is assumed and pressure head h is

calculated from G_L-z, where z is the local z-coordinate. Total head H [L] is equal to h+z. Another special type of boundary condition was implemented for the atmospheric boundary. This boundary condition is described by a variable type boundary. Depending on atmospheric conditions either a Dirichlet or Cauchy boundary conditions is prevailing. The change between both types is based on two pre-set pressure heads h_{min} [L] and h_{con} [L] which need to be given. The former is set when soil becomes too dry to sustain the potential evaporation and the latter one is used to describe the process of ponding. During infiltration a flow boundary condition (Cauchy) is applied until h_{con} is reached. Then TRACE switches to a Dirichlet boundary condition and the pressure head at the soil surface is set to h_{con} (*e.g.* 1 cm). The infiltration excess is removed at the next time step. A similar concept is applied for the reduction of evaporation. A flux boundary is applied until h_{min} is reached (*e.g.* -10^{-4} cm). At this point TRACE switches to a fixed head boundary condition set to h_{min}.

Table 16 - Available boundary conditions in TRACE.

Boundary condition	Corresponding equation
Total flux (Cauchy)	$q_c = -K \cdot \nabla H$
Flux (Neumann)	$q_n = -K \cdot \nabla h$
Head (Dirichlet)	given h
Seepage face (lysimeter)	$q = 0$ for $h < 0$ or Dirichlet with h=0

- ***Soil hydraulic properties***

Two approaches were implemented, which describe the soil water retention and the unsaturated hydraulic conductivity. The first one is the very commonly used approach of Mualem/Van Genuchten (Van Genuchten, 1980):

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left(1 + \left(\alpha|h|\right)^n\right)^m}$$

$$K(h) = K_s \frac{\left(1 - \left(\alpha|h|\right)^{mn}\right)^2}{\left(1 + \left(\alpha|h|\right)^n\right)^{2.5m}}$$

where θ denotes the water content [L^3 L^{-3})], h is the pressure head [L], θ_r is the residual water content [L^3 L^{-3}], θ_s is the water content at saturation [L^3 L^{-3}], α is the inverse of the bubbling pressure [L^{-1}], K_s [L T^{-1}] is the saturated hydraulic conductivity and m and n are dimensionless shape parameters. The following equation yields $\partial\theta / \partial h$, which is necessary to calculate the specific water capacity:

$$C(h) = \frac{(\theta_s - \theta_r) mn \alpha^n h^{n-1}}{\left(1 + \left(\alpha|h|\right)^n\right)^{m+1}}$$

For the second approach, the parameter m of the retention function of Van Genuchten is set equal to 1. Thus the closed analytical expression of the Mualem/van Genuchten approach for the K(h) function is lost. Instead the unsaturated hydraulic conductivity function of Gardner (1958) was applied:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{1 + (\alpha|h|)^n}$$

$$K(h) = \frac{K_s}{1 + (b|h|)^c}$$

Here two new parameters b (cm^{-1}) and c (-) are introduced. The derivative of θ against h is given by:

$$C(h) = \frac{(\theta_s - \theta_r) n \alpha^n h^{n-1}}{\left(1 + (\alpha|h|)^n\right)^2}$$

- ***The plant module SUCROS***

In order to take plant related processes into account the SUCROS module (Spitters, 1988), implemented in WAVE was adapted to TRACE. During the implementation several modifications and extensions were necessary to link SUCROS and TRACE, mainly because TRACE is a 3D model applicable to regional scale problems while WAVE was designed for local scale 1D problems. In the following the basic concepts of SUCROS are explained in connection to the modifications during the implementation in TRACE.

In contrast to most of the plant modules in soil water models, SUCROS calculates the leaf area index (LAI). In SUCROS the green leaf area index (LAI_{green}) is calculated from the biomass development, which is a function of the plant specific CO_2 assimilation and photosynthetic active radiation. Details on the basic principles of crop growth simulation can be found in the SUCROS manual (Spitters *et al.,* 1988).

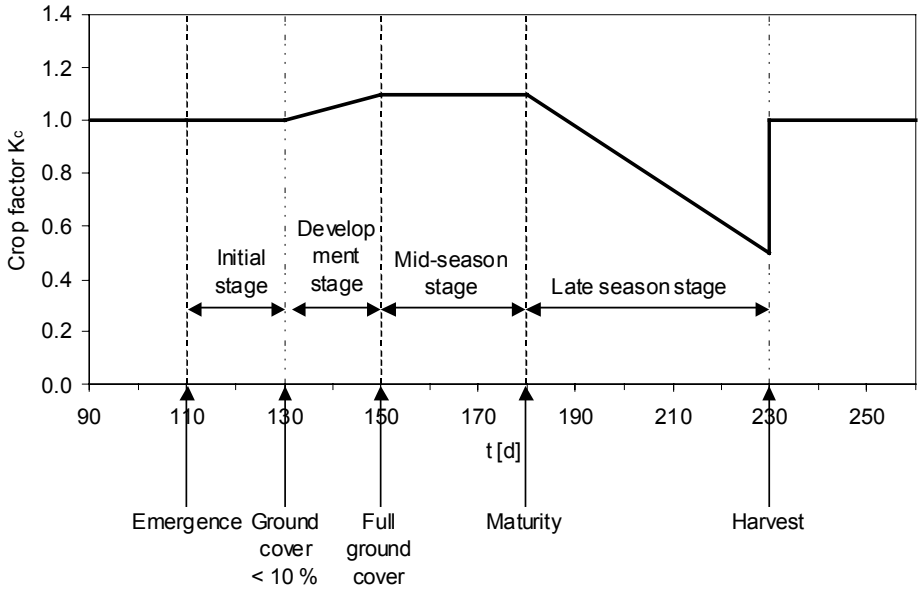


Fig. 65 - Time course of the crop K_C factor for TRACE in combination with Doorenbos & Pruitt (1977) approach.

The main purpose of a plant module is to describe root extraction of water from the soil by plants, the process of interception loss at the canopy and to estimate the amount of potential evaporation from the soil surface. The first step is to calculate the potential evapotranspiration for the reference grass cover ET_{pot} [L T^{-1}], *e.g.* with the approach of Penman/Monteith. In order to describe the seasonal deviation of the potential evapotranspiration of crops to the one of the grass reference the approach of Doorenbos and Pruitt (1977, see Figure 65) is applied:

$$ET_{crop} = ET_{pot} K_C$$

where Et_{crop} [L T^{-1}] is the plant specific potential evapotranspiration and K_c [-] is the crop conversion factor. The leaf area index LAI [L^2 L^{-2}] is used to separate potential evaporation and transpiration. The basic assumption is that the amount of potential transpiration T_p [L T^{-1}] increases with increasing soil cover by leafs and the potential evaporation E_p[L T^{-1}] is reduced accordingly:

$$E_p = ET_{crop} e^{-0.6LAI}$$

$$T_P = ET_{crop} - E_p - E_i$$

where E_i is the amount evaporation from the interception storage. For the estimation of the actual evapotranspiration T_a [L T^{-1}] the actual pressure head h [L] averaged for the volume under consideration is taken into account. The dimensionless reduction factor α [-] of Feddes (1978) is used:

$$T_a = T_P \alpha(h)$$

In order to describe the relation between h and α the four threshold pressure heads h_1, h_{2l}, h_{2h} and h_3 [L] need to be given. First the threshold value h_2 [L] depending on the transpiration demand is computed:

$$h_2 = \begin{cases} h_{2l} & T_P < 0.1 \\ h_{2h} + \dfrac{0.5 - T_P}{0.4}\left(h_{2l} - h_{2h}\right) & \text{for } 0.1 \le T_P < 0.5 \\ h_{2h} & T_P \ge 0.5 \end{cases}$$

where the threshold values of T_p are given in mm d^{-1}. Then the reduction factor is calculated according to:

$$\alpha(h) = \begin{cases} \dfrac{h_0 - h}{h_0 - h_1} & h_0 \le h \le h_1 \\ 1 & \text{for } h_1 \le h \le h_2 \\ 10^{\frac{h_2 - h}{h_3}} & h_2 \le h \le h_3 \end{cases}$$

Root extraction in the element e S_e [T^{-1}] is calculated from the actual transpiration T_a [L T^{-1}], the corresponding surface area A_T [L^2], the normalized root density ω_e [-] and the volume of the element V_e [L^3].

$$S_e = \frac{T_a A_T \omega_e}{V_e} \quad \text{with} \quad \sum_{i=1}^{n} \omega_{e,i} = 1$$

where n is the number of elements with roots below the corresponding surface. To calculate the normalized root density, the root density [-] for relative depths [-] must be specified as input. The relative rooting depth ranges between the soil surface (= 0) and the actual rooting depth (= 1). After averaging the z-coordinates of the element and with the given root depth the root density g_e [-] can be interpolated. Knowing the root density of the n corresponding elements allows to calculate the normalized root density of the element:

$$\omega_e = \frac{g_e}{\sum_{i=1}^{n} g_{e,i}}$$

The estimation of the interception loss is based on the concept of an overflowing bucket (Rutter *et al.*, 1971). The basic assumption is that the Precipitation N_0 [L T^{-1}] is separated into a fraction stored on the leaves N_i [L T^{-1}] and the fraction reaching the soil surface N_p [L T^{-1}]:

$$N_0 = N_p + N_i$$

The overflowing bucket is filled with precipitation until the maximum is reached and the fraction above the maximum is taken as the fraction reaching the soil surface. This maximum is calculated from the LAI [-]:

$$S_i = 0{,}2LAI$$

where S_i is the interception capacity [L], equivalent to the maximum volume of interception. Water is taken out of the interception storage by evaporation:

$$E_i = (ET_{crop} - E_p)\frac{C_i}{S_i}$$

where E_i [L] is the amount of evaporation from intercept for the particular time step, and C_i [L] is the interception storage for that time step. Then the amount of interception can be estimated from:

$$N_i = \begin{cases} 0 & N_0 = 0 \\ S_i - C_i \quad \text{for} & S_i - C_i < N_0 \\ N_0 & S_i - C_i > N_0 \end{cases}$$

Alternatively the empirical approach of Hoyningen-Huene (1983) for interception can be applied to time steps equal to or larger than one day:

$$N_i = -0.42 + 0.245N_0 + 0.2LAI + 0.0271N_0LAI - 0.0111{N_0}^2 - 0.0109LAI^2$$

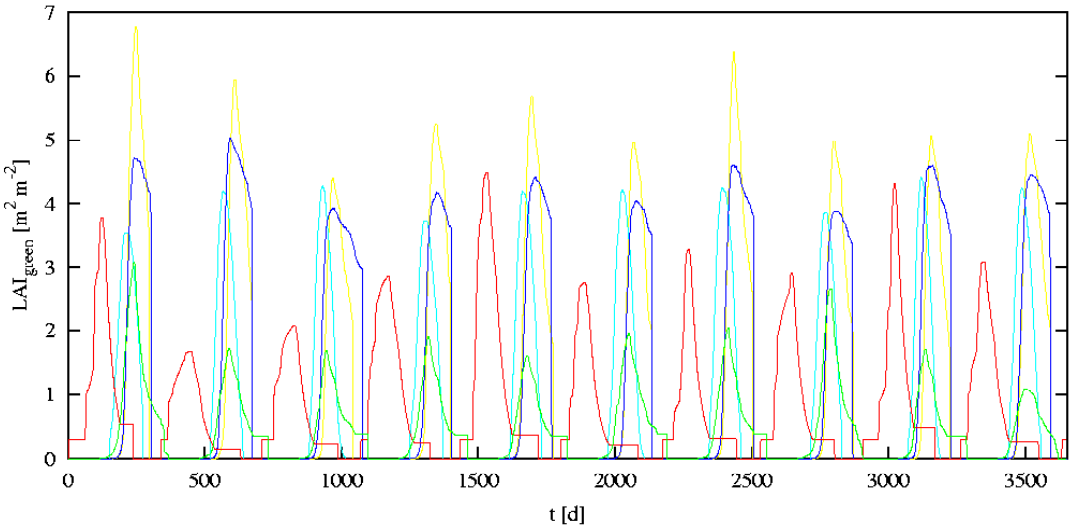
In order to account for water stress on dry matter growth rate per unit area R_m [M L^{-2} T^{-1}], the dry matter growth rate per unit area R_m [M L^{-2} T^{-1}] calculated from the radiation conditions is scaled with the ratio between actual and potential transpiration:

$$R_m = R_g \frac{T_a}{T_p}$$

A special module for perennial vegetation like forest was developed. Here the basic assumption is that the same seasonal behaviour of the plant appears every year. The key parameters LAI, rooting depth and the K_c value must be given as a function of the day of the year. A linear interpolation is applied for times between the given parameter values.

3.2.2. Modelling results

Figure 66 shows the temporal variability of the green leaf area index LAI_{green} [L^2/L^2] calculated with TRACE for grass, potato, maize, sugar beet and winter wheat. It clearly shows how the LAI_{green} differs between the years due to the influence of the meteorological conditions and their effect on plant growth. The highest LAI_{green} were calculated for maize. For winter wheat the intermediate periods without growth during the winter can be detected. These simulations were carried out in a one-dimensional mode for the meteorological data described in section 3 of chapter 1 with the representative soil profile 'agr2' in order to check the implementation of SUCROS to TRACE and the linking to the water flow modules. The plant database of Van Heemst (1988) was used.



Green=pasture, cyan=potato, yellow=maize, blue=sugar beet, red= winter wheat.

Fig. 66 - The development of the green leaf area index of the crops relevant for the test site 'Zwischenscholle' for the 10 years model period 1983-1993.

Figure 67 shows the results of this one-dimensional simulation run concerning the pressure head distribution in the soil profile. The years 1984 and 1988 can be summarized as rather wet years, with high precipitation and only little evapotranspiration. Furthermore differences in root water extraction between plants are clearly visible.

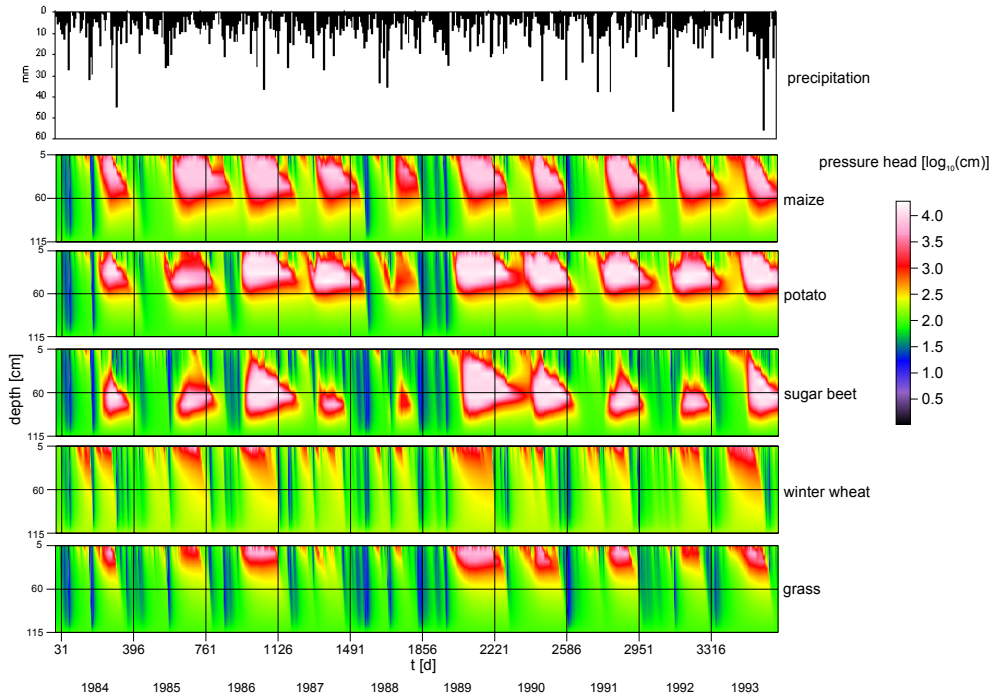


Fig. 67 - The influence of the crop on the pressure head (1D simulations with TRACE were carried out with the same soil hydraulic properties and atmospheric boundary conditions).

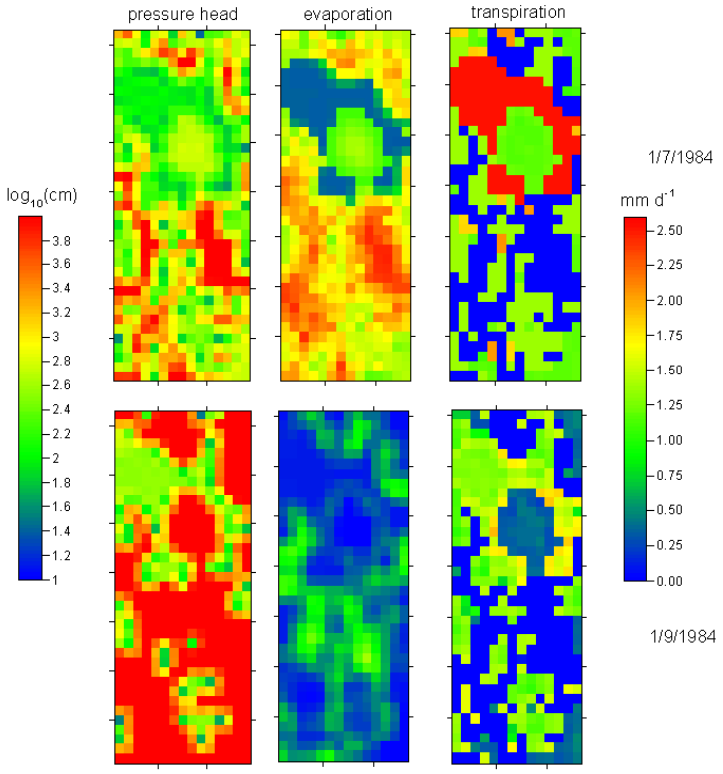


Fig. 68 - Spatial distribution of pressure head [cm] at soil surface, evaporation [mm d^{-1}] and transpiration [mm d^{-1}] for two dates (Herbst et al., 2003).

Figure 68 shows an example of XY-maps depicting the pressure head at the soil surface, and evaporation and transpiration for two dates of the modelling period. Here a full 3D model was built, and the data described in section 3 of chapter 1 were used to check the performance of the plant module linking. The biggest differences at the first date 1/7/1984 occur between the forest and the crops. The forest has high transpiration rates and low evaporation rates, resulting in a rather wet soil at the surface. Basically, the same is true for the second date two months later, but as it is late summer the soil at the surface is much dryer than at the first date. At the beginning of September, the winter wheat is close to harvest, thus the pattern with transpiration close to zero follows the spatial distribution of winter wheat.

3.2.3. Summary

TRACE is a large parallel computer code which was developed to solve large scale groundwater problems and to test stochastic theories. Modifications were made to the model to allow the computation of the saturated/unsaturated water flow at the regional scale. These included an improved numerical approach to solve variably saturated water flow, revised upper boundary conditions, adaptations to handle soil properties and the inclusion of the plant module SUCROS. An evaluation exercise demonstrated that the revised version of TRACE is able to compute variably saturated water flow from local to regional scales taking plant related processes into account.

3.3. POWER [LTHE]

POWER (Planner Oriented Watershed modelling system for Environmental Responses) is a software package developed within the Department of Hydrology at LTHE (Haverkamp *et al.*, 2003a) aimed at simulating integrated flow systems of stream and overland flow, soil water and solute movement (*i.e.,* fertilizers and pesticides) in the unsaturated and saturated aquifer zones combined with plant root uptake. The POWER modelling system is conceived as a combination of three flux-based methods which are complementary. Starting with the theoretical modelling platform presented by Reggiani *et al.* (1998, 2000), the method is coupled with the flux-based equation solver newly developed by Ross (2002, 2003), using the scale invariance approach of Haverkamp *et al.* (1998a) to describe the hydraulic soil properties.

3.3.1. Spatial discretisation strategy

The spatial and temporal discretisation technique developed for the POWER modelling system is based on the assumption that the integrated flow system at a watershed scale can be represented by five primary components of the hydrological cycle, *i.e*. (1) open channel (river) flow, (2) infiltration and/or saturation excess surface runoff, (3) vertical unsaturated subsurface flow, (4) lateral unsaturated subsurface flow and (5) groundwater flow, where each of the five flow processes is characterized by its own specific space and time scale.

The spatial discretisation geometry is based on a hierarchy of three levels, *i.e.* two in the horizontal and one in the vertical, where the second and third discretisation geometries are fully nested within their respective parent structures. The aggregation

etween the two horizontal levels is obtained through the use of an averaging approach similar to that presented by Reggiani *et al.* (1998, 1999).

- ***The REW resolution: the first level of horizontal discretisation***

Firstly, the watershed is subdivided into a series of representative elementary sub-watersheds (REWs) by the use of a digital terrain model (DTM). The topographical boundaries of the watershed and the underlying bedrock are chosen as the boundaries of the watershed where the bedrock may be either impermeable or fractured. The REWs are extracted from the digital terrain model (DTM) by the use of the threshold area method of Tarboton (1997) imposing a first, second or larger Strahler (1957, 1964) order as criterion for the identification of the given number of REWs. The REWs constitute well defined, spatial entities with irregular prismatic volumes. The REW surface is considered coincident with the soil surface with a contour line which follows the natural REW boundaries such as ridges and divides. Each REW communicates with neighbouring REWs through a vertical mantle surface which is defined by the shape of the surface contour line. As the REW volume is supposed to consist of an ensemble of smaller prismatic entities (RECs) defined through the second level of spatial discretisation, the REW contour line is made up of a series of contour segments which are REC defined. Consequently, the vertical exchange surface between two neighbouring REWs is not necessarily a plane surface. Figure 69 gives a schematic illustration of a REW entity.

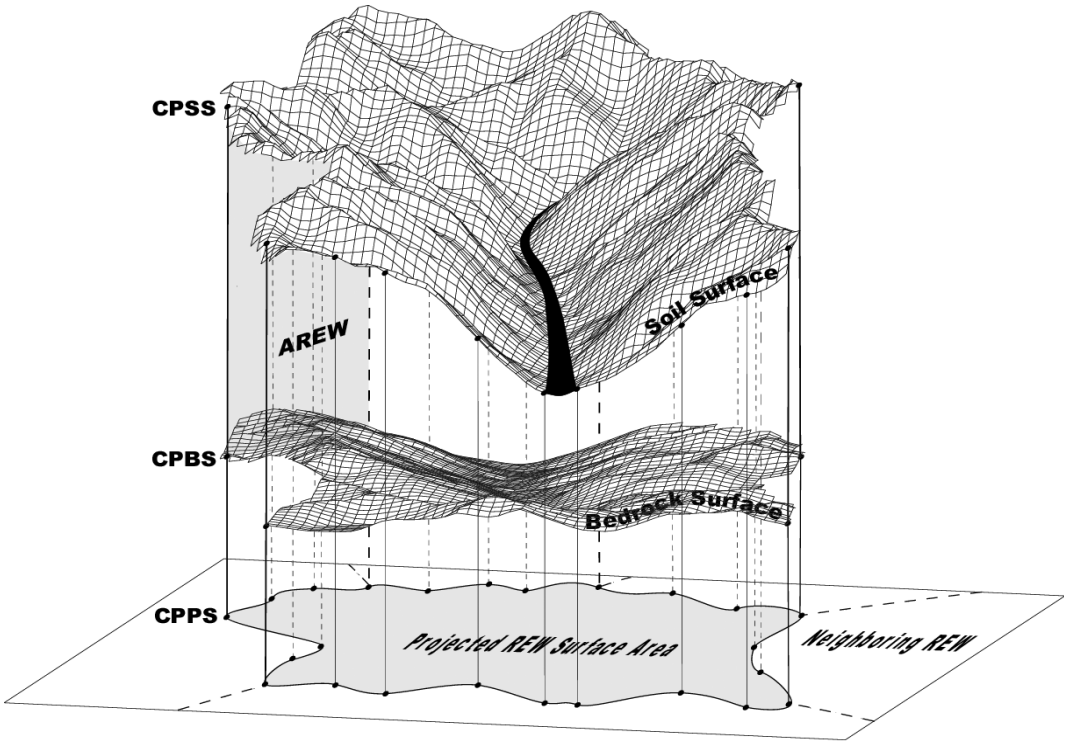


Fig. 69 - Schematic illustration of a REW entity, where the dots CPPS on the contour line of the projected REW surface area correspond with the REC defined corner points; CPBS are the corner points defining the REW entity at the bedrock surface; CPSS are the corner points defining the REW entity at the soil surface; and AREW is the vertical exchange surface in common with a neighbouring REW.

Each REW is considered to host the five water flow processes mentioned above. The REWs are considered as independent sub-basins for overland flow and lateral unsaturated subsurface flow. Hence, it is assumed that no lateral mass exchange between neighbouring REWs occurs in the vadose zone. It also means that, in a simulation, runoff and lateral subsurface flow can reach the river system only within a REW. However, the REWs communicate with each other through the river (channel) flow and the saturated aquifer flow together with their associated solute transport processes. The nodal network covering the saturated sub-region of the watershed corresponds to a full 2D network (referred to hereafter as the saturated REW network), while that covering the river flow sub-region is rather matched by a 1D tree-type branching structure (referred to hereafter as the river REW tree).

Figure 70 gives a schematic illustration of both the saturated REW network (2a) and the river REW tree (2b). Unfortunately, the use of the nodal networks has two major complications*, i.e.* i) the position of the network points is unknown *a-priori* and ii) changes in both space and time. Hence, an appropriate method for the calculation of the points has been developed for the POWER modelling system.

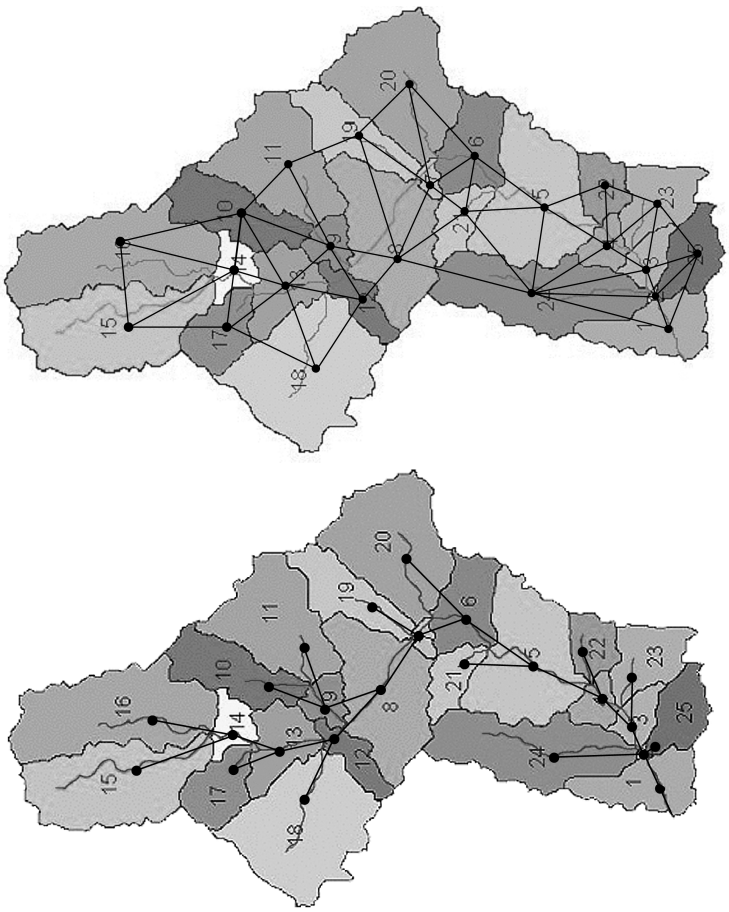


Fig. 70 - A schematic illustration of the saturated REW network (2a) and the river REW tree (2b).

- ***The REC resolution: the second level of horizontal discretisation***

The second level consists of a disaggregation of each REW into a series of vertical columns called *Representative Elementary Columns* (RECs), which involve both the unsaturated zone (vadose zone) and saturated zone (underlying regional water table) all the way down to the bedrock taken as the bottom boundary condition. The determination of the RECs is based on a series of superimposed GIS layers such as maps of soil texture, land-use, river network and infrastructure (*e.g.*, rasters of country and town planning with urbanized areas). The use of a supplementary raster defined as a function of specific end-user requirements can be included, if necessary. The combination of these GIS layers permits the identification of irregular prismatic REC entities which are characterized by their specific textural and structural soil properties, land-use patterns and management practices. An example of three superimposed GIS layers is schematised in Figure 71.

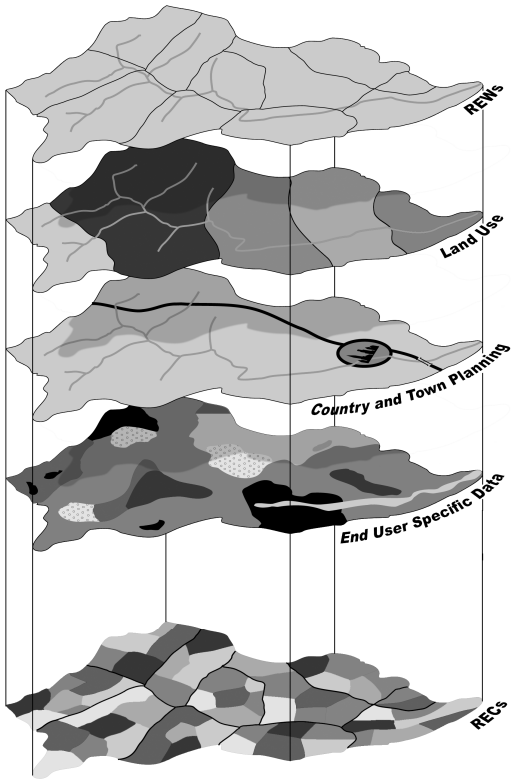


Fig. 71 - A schematic example of three superimposed GIS layers used for the disaggregation of the REWs into RECs.

Each REC is supposed to contain four sub-regions associated with one of the primary components of the hydrological cycle, *i.e.,* surface overland flow, vertical unsaturated subsurface flow, lateral unsaturated subsurface flow and water flow in the saturated zone of the aquifer. At the scale of a REW, all RECs are considered to communicate through the different sub-regions. Hence, it is assumed that lateral mass exchange and solute transport occurs between neighbouring RECs in both the vadose zone and the underlying saturated groundwater zone. It also means that, in a simulation, surface runoff is carried to the river system following a flow path which may run over various

RECs. Consequently, all surface runoff water generated at some location within a REW (and not re-infiltrated along the routing path) can only leave this REW through the river. The surface area occupied by the river section within a REW is attributed to a series of RECs identified through the GIS river network which controls the net discharge to the river generated by the overland flow and/or the unsaturated/saturated vadose zone. Similarly, specific RECs are attributed to the surface areas occupied by lakes, roads and other urbanized planning areas.

The line referred to hereafter as the REC axle, is determined by the average height of the REC entity calculated from the DTM grid overlaying the projected surface area of the irregular prismatic REC entity. The average slope of the REC soil surface (at the top of the REC axle) is calculated as well from topographic DTM information (pre-processing). However, the position of the point at which the lower end of the REC axle hits the projected reference surface is unknown a-priori. As this point is geometrically defined (*i.e.,* time independent), a special pre-processing routine is developed for its estimation from DTM information.

Subsequently, the REC axle is used for the construction of the third step in the hierarchy of spatial discretisation

- ***The Cell resolution: the level of vertical discretisation***

The vertical discretisation consists of the subdivision of each REC column (and hence, each REC axle) into a given number of cells. While the thickness of the cells remains free to choose, the total number of cells is the same for all REC columns. Hence, the number of REC cells per REC column is the same for all REWs. Figure 72 gives a schematic illustration of a vertical 2D cross-section through an ensemble of three RECs. Note that the layers are not necessarily horizontal.

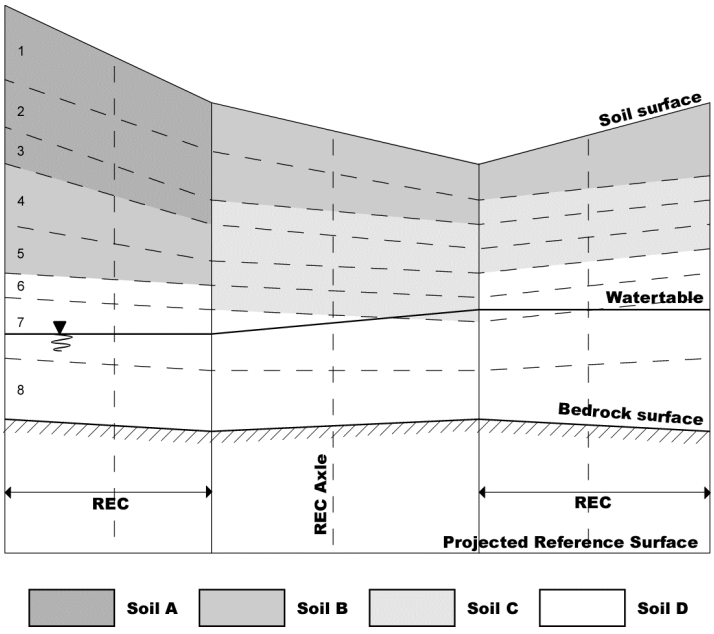


Fig. 72 - Schematic illustration of a 2D cross-section through an ensemble of three REC columns. The combination of 4 different soil types imposes an ensemble of at least 8 REC cells for each REC column.

As the REC geometry is defined by the use of a GIS analysis, the REC columns are obviously the smallest spatial entity for the GIS variables. Therefore, the REC cells of the same REC column are assumed to have the same plant characteristics, land-use patterns and management practices. As to the hydraulic soil properties, the reality shows that most natural watersheds are often poorly defined in input data, especially regarding the information on soil structural properties and subsurface soil conditions. Hence, when no specific data are available, the REC cells of the same REC column are considered to have identical textural soil properties, while the structural soil properties are changed with depth. However, when input data are available concerning soil horizons and their specific properties such as occurs in field soils where hydraulic soil properties vary with depth down the soil profile (either abruptly or gradually), then special soil characteristics are assigned to the different soil layers. For such cases, the heights of the REC cells are chosen as a function of the depth of soil horizon. This latter detail is clearly illustrated by Figure 72 where a combination of 4 different soil horizons is used for the construction of the ensemble of associated REC cells. Consequently, the POWER modelling system is conceptually able to deal with many different watershed geometries.

3.3.2. Time resolution and flow processes

Depending on the end-user requirements, the POWER modelling system may be used for the simulation of:

- either long term dynamics (*e.g.*, seasonal crop development) involving variation in climate and crops over many years;
- or short term dynamics (*e.g.,* rainfall and overland flow) involving real storm intensities with a time resolution down to 1-minute.

The calculation of the different flow processes is carried out following the bottom-up procedure, *i.e.*, for each time step in a simulation, the water flow and solute transport is calculated firstly for the resolution of the RECs followed by that of the REWs and finally for the whole watershed. The procedure follows the schematic routing diagram given in Figure 73. Starting with the ensemble of REC-columns of a given REW, the vertical unsaturated/saturated water flow and solute transport is calculated by a numerical solution of the Richards' (1931) equation combined with a standard convection/ dispersion equation with a linear equilibrium adsorption isotherm.

A highly accurate and very efficient flux-based equation solver recently developed by Ross (2002, 2003) is used. It calculates the main vertical components of the hydrological cycle within the REW subject to the different flux or head boundary conditions at the soil surface, *i.e.,* infiltration, soil evaporation, water ponding, vertical soil water redistribution, deep drainage and capillary rise. As temperature effects are of main importance for the estimation of solute transport, an additional routine is used for the calculation of the soil temperature. For the sake of simplicity, the temperature effects on the water flow are ignored. A simple root extraction model based on a study presented by Li *et al.* (2001) calculates the actual plant water uptake and transpiration as a function of root length density changing with depth and time. Even though the model architecture of the POWER code is already prepared to receive a more sophisticated plant growth model at a later stage, this first version Evolution 1.0 is

conceived as the bottom-line approach operational for a minimum number of input data. This explains the use of the simple root extraction model chosen for POWER-1.

The coupling of a nitrogen transport and transformation within the POWER system is achieved by using the model of Birkinshaw & Ewen (2000). The authors proposed a dynamic physically based system of equations for modelling the nitrogen balance in the saturated/unsaturated zone. Two significant reasons prompted the choice of this model: firstly, the approach is currently the state of the art in nitrogen models; secondly, and as opposed to the purely parametric model of GLEAMS (Knissel, 1993) used previously for the ANSWER/ITHE modelling system, the deterministic approach of Birkinshaw & Ewen can easily be coupled to the water transport equations currently used in POWER.

The pesticide transformation (adsorption and degradation) is calculated in an analogous way using the assumption of first order kinetics and instantaneous equilibrium. The amounts of residual pesticide are transported by the water cycle using a similar convection-dispersion equation as used previously for the transport of nitrate.

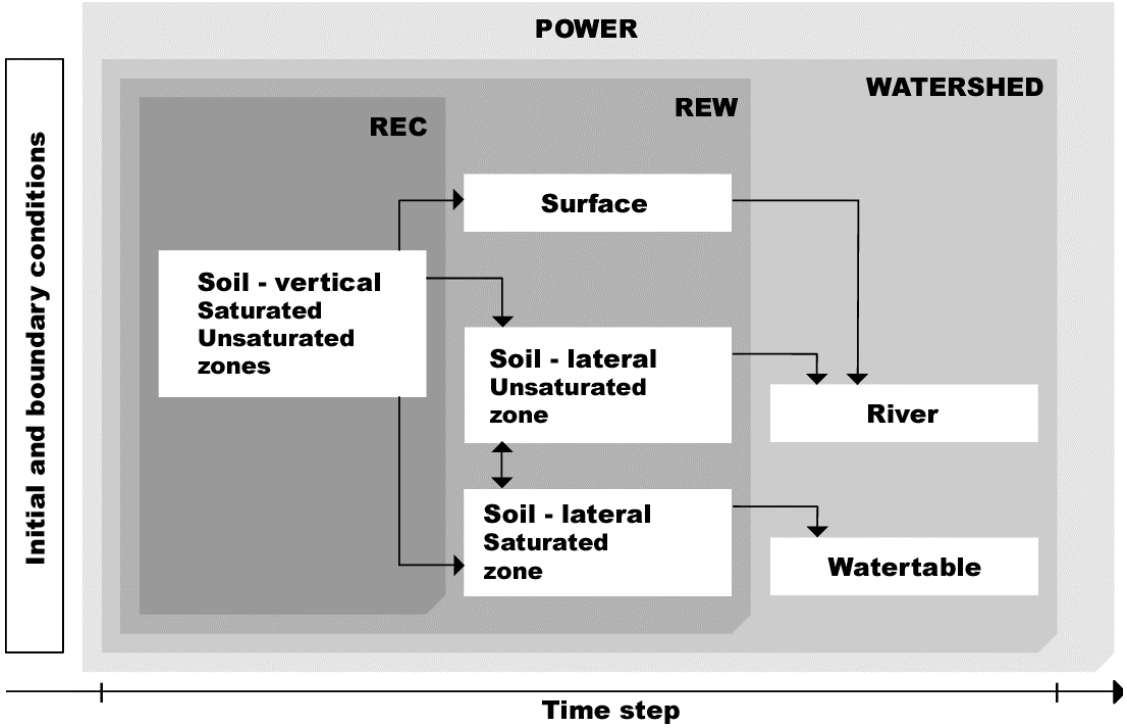


Fig. 73 - Diagram illustrating the routing procedure used for the coupling of the different flow processes through the respective levels of discretisation.

Next the lateral water movement between the unsaturated cells of the ensemble of RECs is solved. Considering the lateral nodal network of the different cell-layers (addressed in the foregoing section), the same implicit equation solver of Ross (2002, 2003) as used for the vertical flow is applied. Note at this stage that the time step chosen for the calculation of the lateral flow component within the REW is not necessarily the same as that used for the calculation of the vertical fluxes.

Finally, and still at the REW scale, possible surface run-off at the soil surface is estimated by the use of a flow-discharge equation newly developed for the case of shallow water based on a modified Manning (1891) equation. Secondary components of the hydrological cycle such as surface erosion, surface sealing or macro-pores and bypass flow which are more difficult to describe in a fully rigorous way, will be modelled (still under construction) through the use of empirical *ad-hoc* equations which are activated optionally in order to save computing time.

In this way, the evolution of the different descriptive variables such as volumetric soil water content (θ), soil water pressure (h) and solute concentration in both the saturated/unsaturated zone are calculated as a function of space and time for the ensemble of RECs within each REW. Next, and still within the same time step, this information is aggregated to the parent level of spatial discretisation by calculating the water flow and solute transport between the different REWs. Only then the transfer processes are expressed at the watershed scale.

Next, and still for the same time step in a simulation, the lateral transfer is calculated, operating hence as the second alternative direction sweep. However, before doing so, the exact position of the water table is calculated for every single REC. The saturated sub-region of each REC column is then chosen as an entity for the calculation of the lateral water movement in the saturated zones of a given REW. The saturated REC sub-region is represented by a single point situated on the REC axle. The vertical exchange terms being known, the only unknowns are the lateral exchange terms between the saturated sub-regions of the ensemble of RECs which can easily be calculated by the use of a time saving Runge-Kutta solver. The lateral transport of dissolved nitrate and pesticides is calculated by a depth averaged diffusion/convection equation with constant transverse and longitudinal dispersivities and linear equilibrium adsorption isotherm.

The REWs are supposed to communicate through two zones, *i.e.,* the saturated aquifer sub-region and the zone occupied by the channel flow. Starting with the saturated REW sub-regions, the exact position of the REW-raster nodes which represent the saturated REW sub-regions have to be determined firstly. As these points are time dependent, their position may change every time step. To do so, the centre of mass of the water phase within the saturated REW sub-region is determined from the mass distribution given by the vertical water exchange terms across the water table surface calculated at the REC resolution. This procedure, applied for each time step in a simulation, fixes the position of the computational nodes of the saturated REW network in both space and time allowing the calculation of the lateral exchange terms between the ensembles of REWs at the watershed scale using the same Runge Kutta solver as applied previously for the lateral mass exchange at the lower order REC resolution.

Hence, within the same time step, the water flow and solute transport processes are calculated at three subsequent levels which are operational at increasingly coarse space scales.

3.3.3. Data provision

Even though distributed physically-based models do not in principle require lengthy hydro-meteorological records for their calibration, they do require considerably more input parameters than the simpler lumped models. It is therefore necessary to reduce

the number of direct measurements and to employ more indirect evaluations readily available from field studies. As the parameter values should be characteristic for the spatial resolution used in the model, the sampling and evaluating of the parameters represents a supplementary difficulty.

Against the above assessment on some of the major difficulties associated with data provision, it is clear that the architecture of the modelling system is directly conditioned by the way in which the problem of data provision is handled. Precise guidelines should therefore be specified right at the beginning of the coding effort, rather than in the process of development. As the reality shows that most natural watersheds are often poorly defined in data, three different options are chosen for the data provision strategy of the POWER code:

- ***The numbers of system parameters***

During the development of the POWER code, considerable effort has been directed towards the choice of independent parameters. As the description of most of the hydrological flow processes is based on physical principles, the choice of the right combination of system parameters is obviously easier than would be the case for empirically derived flow equations. Using the scaling approach presented by Haverkamp *et al.* (1998a), all hydrological flow processes in the vadose zone (*e.g.,* infiltration, soil water redistribution, deep percolation or capillary rise) can be expressed in a scale invariant way by only three parameters, *i.e.,* one related to soil texture referred to as the texture indicator (Haverkamp *et al.,* 2003a and 2003b), and two soil structure dependent parameters. Compared to the classical approach, this new scaling concept does not only reduce considerably the number of system parameters but it also shows that the traditionally used soil characteristic parameters are not fully independent. The two soil structure parameters can finally be collapsed into one soil structure indicator (Leij *et al.,* 2003) by the use of parameterised relations based on the compilation of the two soil databases UNSODA (Leij *et al.,* 1996) and GRIZZLY (Haverkamp *et al*., 1998b). As the soil textural properties are easily accessible at large scales, the problem is reduced to the evaluation of the soil structure indicator on a spatially distributed basis.

- ***Flexibility of model architecture***

The second data provision criterion concerns the structural flexibility of the POWER code. The model should be able to match the sophistication of the solution with the specific project requirements and/or the availability of data. In this regard, two categories of input data should be considered, *i.e.,* those data which are absolutely necessary to drive the POWER modelling system, and those data which are useful in the sense that their knowledge improves the precision of simulation. The first category of data is assigned to the so-called bottom-line configuration of the POWER code.

Moreover, the flexibility of the model architecture should be able to accommodate different parameter evaluation techniques. As the parameter values are estimated from either direct or indirect measurements, the POWER code should be capable of running the specific configuration out of a wide class without any need for work at the level of the software.

- ***Pre-processing***

The last point of importance for a sound data provision strategy concerns the pre-processing of the rough field data. The pre-processor of the POWER code should include tools which are capable of aggregation, disaggregation and/or interpolation (in space and time) of various hydrological and hydro-meteorological input data. When kriging techniques are used, the specifications of the variogram parameters and the choice of the specific variogram model should be defined as a function of the project requirements (*e.g.*, the variograms used for the interpolation of rainfall data change as a function of the geographical project location). As it is often observed that lack of data does not prevent planning or development decisions from being made, supplementary statistical routines should be included able to accommodate the partial lack of input data (*e.g.*, incomplete time series of rain data). If the missing data are significant, the simulation results are obviously based on serious misunderstanding, and the consequences for a particular project could be severe. Nevertheless, the value of POWER in such a case resides in the fact that it is, in principle, capable of quantifying those consequences.

The requirement list of input data necessary to drive the POWER code is resumed hereafter. As mentioned before, the list is split up into two categories, *i.e.,* those data which are necessary for the bottom-line approach and those data which are useful as a supplement. Obviously, some of the input data listed below depend on the specific project requirements which can be ignored when not applicable.

Topological data

- Digital Terrain Model (DTM) overlapping the watershed area (vector/raster ascii format).

Hydrological and geological data

- position of the underlying bedrock (raster ascii format);
- information on network of artificial (man-made) channels and drains (vector/raster ascii format);
- information on infrastructure network of lakes, roads, villages and other urbanized areas (vector/ raster ascii format).

Soil data

- soil map (raster ascii format).

Land-use and crop data

- land use map (raster ascii format).

Management data

- information on irrigation network and irrigation practices, pumping wells and pumping practices (vector/raster ascii format).

Climate data

- rainfall, potential evapotranspiration data as a function of time.

Solute data

- organic matter or organic carbon content, calcium carbonate, soil pH;
- type of fertilization, *e.g.,* animal waste or commercial fertilizer;
- name of commercial fertilizer and pesticide characteristics;
- date of fertilizer and pesticide application, application depth.

Initial condition

- initial guess of spatial distributed soil water content profiles and groundwater table depth.

3.3.4. Conclusions

Even though the POWER code is planned as an evolutive simulation system which may be interfaced with other models such as large-scale atmospheric simulation models, plant growth models and/or economic models, the architecture of this first version is conceived as to satisfy the basic end-users requirement list necessary to provide implementers and policy makers with appropriate decision support when dealing with watershed studies. The basic features of POWER-1.0 include the ability to deal with the following hydrological flow phenomena:

- stream flow in the river network;
- vertical infiltration due to rainfall and/or overland flow;
- evaporation from the bare soil surface and transpiration from the plant cover;
- rainfall interception by plant cover;
- plant and root growth and crop rotation;
- heat flow in the unsaturated zone;
- water ponding at the soil surface due to excessive rainfall events;
- vertical soil water movement in the unsaturated soil;
- lateral soil water movement in the unsaturated soil;
- recharge to the groundwater table and capillary rise from the groundwater table;
- transport in the groundwater table;
- nitrogen transformation, transport of nitrates, transport, degradation and adsorption of pesticides in the unsaturated zone due to point source and/or diffuse pollution;
- reactive transport of nitrates and pesticides in the groundwater taking into account convection and dispersion.

3.3.5. Summary

Compared to the ANSWERS model, the POWER modelling system has a broader scope and is meant as a tool for integrated hydrological studies, suitable for coupling with planner oriented models allowing for impact studies of alternative management practices (BMP) in agriculture and land management. The modelling system is

evolutive and designed in such a way that it may be coupled to atmospheric models, plant growth models and/or economical models at a later stage.

3.4. PESTGW [WRc]

PESTGW is a simple 1D model which predicts pesticide concentrations in the groundwater and concentration profiles within the unsaturated zone. The model is pseudo-transient as the only input parameters that are allowed to vary are hydraulically effective recharge (HER) and pesticide application rate. As the data requirements for PESTGW are far less than for 3D contaminant transport models, it was deemed that PESTGW be developed and delivered as a screening tool for PEGASE.

PESTGW was produced from an existing model called PESTAQ which was initially designed as a tool for determining the effects of pesticide applications on a catchment scale. As catchment scale data were unlikely to be available at a daily resolution, HER and pesticide application rate inputs were only considered to have a monthly time step. Further, PESTAQ was originally produced for pesticide prediction within UK aquifers and it was deemed that monthly variability was sufficient to model pesticide impacts on a catchment scale. It was also not necessary to determine unsaturated zone profiles of pesticide concentration within the porewater, as the impact on the receptor (the aquifer) was of prime importance.

The only output from the unsaturated zone within PESTAQ was an average porewater concentration for the whole zone. As the Screening Tool was to be calibrated within PEGASE to unsaturated zone profiles of concentration within the porewater, the model had to be modified to provide the required profiles. This modification was implemented by the partitioning of the unsaturated zone into layers, and from each layer a determination of the concentration of pesticide within the porewater was provided by the model. It is these outputs that are used for the calibration of PESTGW.

PESTGW also varies from the PESTAQ by having the flexibility of the following parameter inputs:

- Half life of pesticide in chalk (λ_{chalk}), as this was previously fixed at being 10 % of the half life in soil parameter (λ_{soil});
- Unsaturated zone porosity (n_{unsat}), as this was previously fixed at being 75 % of the saturated zone porosity (n_{sat});
- Unsaturated zone dry density and fraction of organic carbon (ρ_d and foc, respectively), as this was not previously required by PESTAQ as it assumed that unsaturated zone adsorption was negligible.

On-site data were used to calibrate PESTGW and where possible verify the predictions that were made regarding pesticide impact on the aquifer.

3.4.1. PESTGW methodology

A diagram showing how PESTGW predicts pesticide concentrations within the groundwater and unsaturated zone is shown in Figure 74.

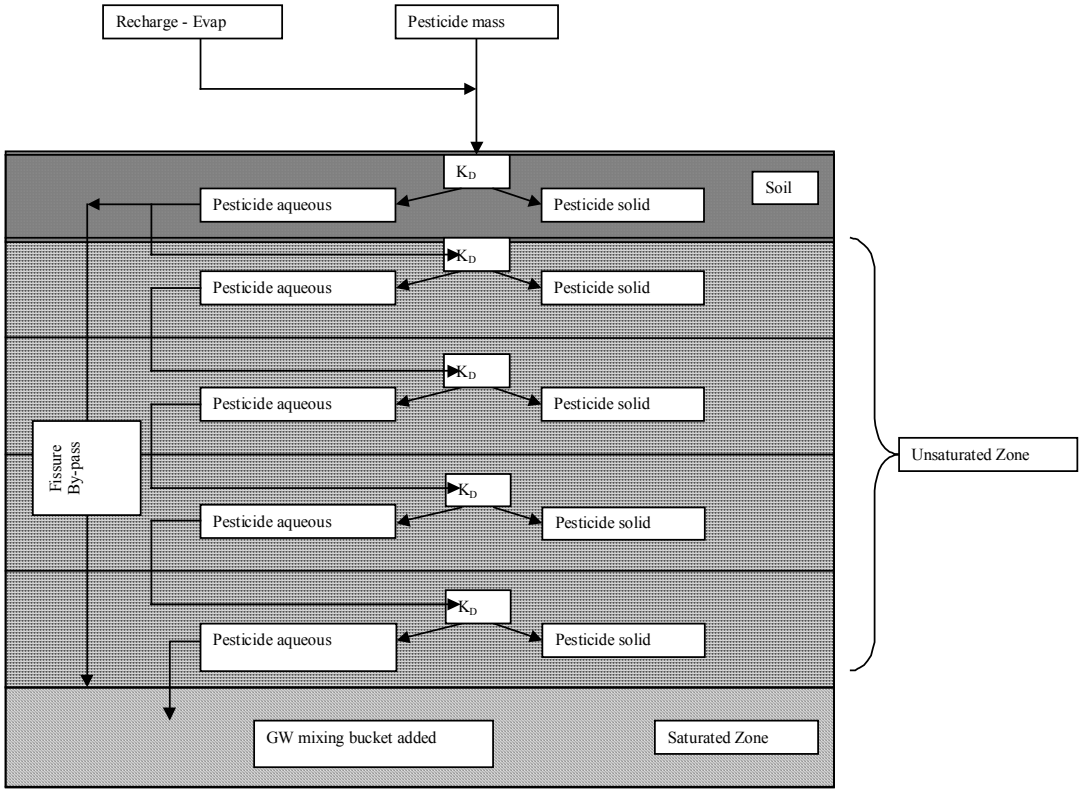


Fig. 74 - Diagram presenting the principles of PESTGW.

The input file for PESTGW is a space separated MS-Dos data file (.dat) and can be initially created/edited within Excel (Fig. 75).

11						Duration of model run (years)									
118.49	58.4	11.6	0	0	0	0	0	13.531	17.5	94.17	92.84	Infiltration (HER) mm/month			
34.73	49.6	11.8	0	0	0	0	0	0	0	39.444	14.68				
11.39	57.1	0	0	0	0	0	0	0	0	42.142	52.01				
77.8	0	16.52	65.7	0	0	0	0	0	93.663	59.18	68.1				
108.57	15.04	0	1.228	0	0	0	0	47.182	41.8	41.7	109.3				
82.13	101.3	0	0	0	0	0	0	0	0	0	20.574				
84.46	21.89	16.9	2.1	0	0	0	0	0	0	3.032	9.36				
14.85	15.7	9.1	2.8	0	0	0	0	61.956	43.4	125.2	54.82				
77.1	0	0	10.434	0	0	0	0	0	75.62	28.08	90.6				
74.52	54.2	1.5	0	0	0	0	0	0	16.628	53.55	77.35				
118.49	58.4	11.6	0	0	0	0	0	13.531	17.5	94.17	92.84				
0	0	0	0	0	0	0	0	0	0	0	0	Pesticide application rate (kg/km^2/month)			
0	0	0	0	0	0	0	0	0	0	0	0				
0	0	0	0	0	0	0	0	0	0	0	0				
0	0	0	0	0	0	0	0	0	0	0	0				
0	0	0	0	0	0	0	0	0	0	0	0				
0	0	0	0	11.22	0	0	0	0	0	0	0				
0	0	0	0	11.22	0	0	0	0	0	0	0				
0	0	0	0	5.61	0	0	0	0	0	0	0				
0	0	0	0	5.61	0	0	0	0	0	0	0				
0	0	0	0	5.61	0	0	0	0	0	0	0				
0	0	0	0	0	0	0	0	0	0	0	0				
106	750	7500						Koc (litres/kg)	λ soil (days)	λ unsat (days)					
1								No. of soils per km^2							
1								Fract. Of soil in 1km^2 grid							
0.94	1							BFI	No. of soil layers						
0	100	1.8	1.5	47.8				top depth (cm)	base depth (cm)	foc (%)	Pb (Mg/m^3)	porosity-n (%)			
1	7.7	20	1	1.5	1E-07	10	20	% fissure	unsat base (m below soil base)	n (%)	foc (%)	Pb (Mg/m^3)	Dispersivity (m^2/d)	Aquifer mixing thickness (m)	Aquifer porosity (%)

Fig. 75 - Example of PESTGW input file showing format and parameter identities.

PESTGW produces two output files. One output file provides unsaturated zone profiles and can include profiles from numerous time steps (Fig. 76), while the other provides predicted groundwater concentrations (Fig. 77).

The PESTGW model was evaluated against field data through calibration against data from Compton (UK) and Martigny (section 5.4. in chapter 3).

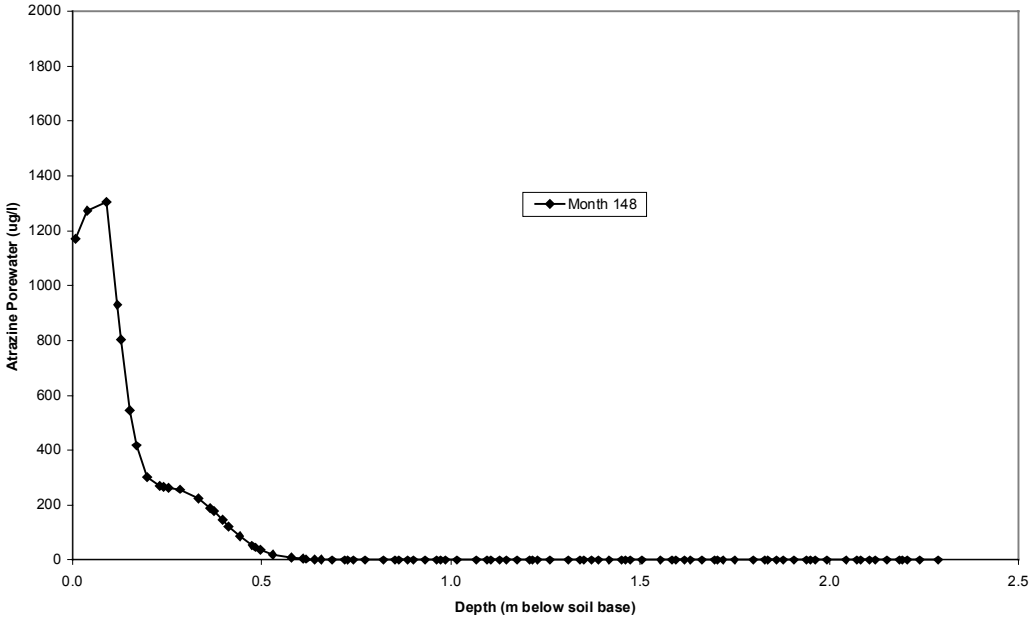


Fig. 76 - Graphical example of PESTGW unsaturated zone output.

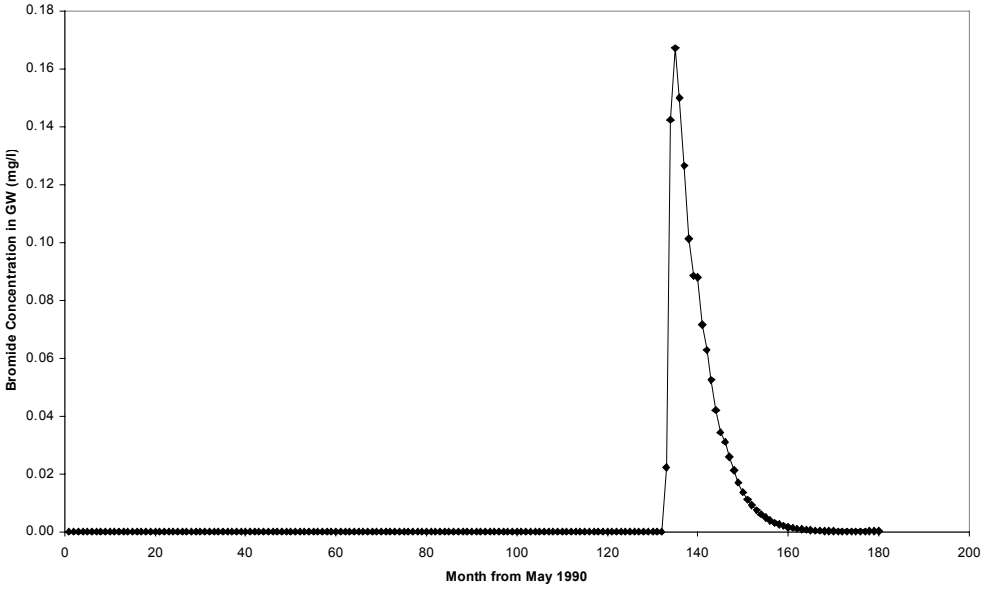


Fig. 77 - Graphical example of PESTGW saturated zone output.

3.4.2. Summary

PESTGW, a screening tool, has been created to predict unsaturated zone porewater pesticide concentrations together with pesticide concentrations within groundwater. In many cases where pesticide impact is being assessed, the data available to conduct groundwater risk assessments are less than those required to undertake reliable 3D modelling. PESTGW may be used to provide a first screening of sites and to support a selection of sensitive sites requiring further assessment and possible intrusive investigations.

4. DISCUSSION OF MODEL DEVELOPMENT AND MODEL REFINEMENT ACTIVITIES

A significant amount of work within PEGASE was dedicated to the refinement and improvement of modelling tools in an effort to further the capabilities of models in the simulation of pesticides to and in the groundwater.

Two root zone models were improved within the scope of the project. A revised version of the preferential flow model MACRO was developed with additional funding from the EU funded APECOP project. Refinements included improvement in the model numerics, replacement of the Brooks & Corey equation by the van Genuchten model, the implementation of subroutines dedicated to kinetic sorption and tillage effects and the addition of a parameter estimation subroutine to aid in the calibration of the model. Pesticide fate routines from the GLEAMS model were integrated into the ANSWERS model. An attempt was also made to implement modifications to ANSWERS to allow the simulation of capillary rise as this feature would have proven useful to simulate data from the Martigny experimental site.

MACRO and ANSWERS were combined to two groundwater flow models (MODFLOWT and FRAC3DVS for MACRO; MODFLOW for ANSWERS), but difficulties in the coupling of the models were experienced in some instances. An operational link was established between MACRO and FRAC3DVS by adapting the latter model to accept inputs from MACRO. A spatialisation scheme for MACRO had to be developed and two different approaches were adopted (a ‘megaplot’ approach and a procedure based on Monte Carlo sampling). The coupling of MACRO and MODFLOWT was achieved through the creation of an intermediate file between the two models which contained recharge data. It should be noted that all couplings between the various models were from the root zone model to the groundwater model only.

Three 3D integrated models were adapted to simulate the water transport and pesticide fate in from the soil surface to and in the groundwater (MARTHE, TRACE and POWER). A range of new subroutines were implemented in the MARTHE model, to account for pesticide degradation (together with temperature and humidity effects on degradation), crop and root development and water and solute uptake by plants. MARTHE was designed from its early days to be a versatile model and a range of options for description of the various processes were therefore added to the model

(*e.g.* five different approaches for accounting for the effect of temperature on degradation, two alternative procedures for simulating plant growth). This allows increased capabilities for the model and the possibility to investigate the uncertainty in the modelling resulting from the use of different conceptual approaches to a given physical, chemical or biological process. A revised upper boundary was added to the water flow TRACE model and the model was adapted to handle soil characteristics and plant growth. Additionally, the model was coupled with the solute transport code 3DLEWASTE. This involved the development of dedicated linking tools and the revision of boundary conditions in the solute transport model. Finally, a simple screening tool with very low input requirements compared to the more complex models, PESTGW, was adapted.

Numerics of the various models were improved as part of the refinement work and running times were greatly reduced in numerous instances. This allows the future potential deployment of advanced modelling activities such as sensitivity and uncertainty analyses or automated model calibration.

The majority of the new modelling tools developed within the project were applied to either reference case studies, numerical solutions or the datasets collected as part of the project (chapter 3).

Chapter 3 -

Application of modelling tools

The numerical models which were either developed or refined within the scope of PEGASE (chapter 2) were applied to a range of datasets to evaluate the capabilities of these new tools. In a first step, new subroutines implemented in a number of models were subjected to a verification process. This involved simulating reference datasets from the literature or comparing model results to analytical solutions. In a second step, the models were used to simulate water transport and pesticide fate either at the scale of the soil profile or the aquifer (regional scale) based on the data collected during monitoring studies (chapter 2). Table 17 provides a listing of subroutine/model evaluation activities which were undertaken within the scope of the project.

Table 17 - Evaluation activities undertaken within PEGASE.

		Numerical solutions	Literature datasets	Bréville	Les Trois Fontaines	Martigny (local)	Martigny (regional)	Zwischenscholle	Lysimeter dataset	Havdrup	Roswinkel
Root zone models	MACRO	•[1]		•		•					
	ANSWERS					•[2]			•		
	PEARL										•[1]
Coupled models	MACRO+FRAC3DVS									•	
	MACRO+MODFLOW							•			
	ANSWERS+MODFLOW							•			
Integrated models	MARTHE	•	•	• (1D & 2D)	• (3D)		• (3D)	• (3D)	•		
	TRACE/TRACE + 3DLEWASTE	•						• (3D)	•		
	POWER			• (2D)							
	PESTGW					•					

[1] Activities not reported in the present report; [2] Modelling discontinued; The HYDRUS model was also evaluated against the local Martigny dataset.

1. MODEL VERIFICATION USING NUMERICAL TESTS, LITTERATURE DATASETS AND HYPOTHETICAL SCENARIOS

1.1. Verification of new vegetation subroutines implemented in MARTHE [BRGM]

1.1.1. Description of the evaluation dataset

The newly integrated crop subroutines of the MARTHE model were evaluated using data from the experimental site of La-Côte-Saint-André (Isère, France), which were collected over the period 1991-1993. Descriptions of the site and of the monitoring and modelling activities are provided by Normand (1996), Normand *et al.* (1997) and Duwig *et al.* (2003).

Monitoring of water fluxes have been performed during the growing season (April to November) during 3 years. Data were collected on a bare plot and on a plot cropped with maize.

The data available were:

- water content at 3 depths (every 10 cm from 10 to 80 cm deep);
- suction at 5 depths (15, 30, 50, 70 and 90 cm deep);
- cumulated bottom drainage;
- Cumulated Actual Evapotranspiration (derived from rainfall, drainage and storage variation);
- and daily rainfall, irrigation and Penman Potential Evapotranspiration.

All the data were provided by LTHE, together with the parameters for the soil characterisation (retention and hydraulic conductivity relations).

1.1.2. Modelling with MARTHE

The maize plot and the bare soil have been modelled separately in 1D. The modelling parameters were as follows:

- vertical discretisation: total depth = 180 cm, cells size = 5 cm except near soil surface 0.5 cm, 1 cm, etc.;
- boundary conditions: no ponding at the soil surface; drainage condition at the bottom of the profile;
- hydraulic conductivity: 4 layers (12, 12, 15 and 15 cm/day); power law for relative hydraulic conductivity;
- retention relation: Van Genuchten relation with m = 1 – 2/n;
- time steps: daily for climatic date; variable time steps for the model (from 0.03 to 1 day).

Crop parameters:

- LeachP development scheme;
- Maximal Crop Cover: 0.9;
- Crop Factor: KC = 1; Root pattern: cylindrical (homogeneous) with a maximal root depth of 76 cm;
- time from germination to maturity: 120 days;
- SWAP stress function: characteristic suctions given as 50 cm, 5 and 80 m.

The period of three years was simulated as a continuous period of 1,096 days, *i.e.* without re-initialising the model at the start of each agricultural season. The total running time for the simulation with MARTHE was approximately 40 seconds with a standard PC (November 2002 specifications).

1.1.3. Modelling results

Only the results for the year 1992 are presented. Results for the other two years are very similar in terms of fit to the data. Figure 78 shows that the cumulated drainage, the actual evaporation and the root transpiration are well simulated by the model even if no calibration was undertaken. Figure 79 presents simulated and measured suctions and water contents at various depths. Again, a good fit to the data was obtained.

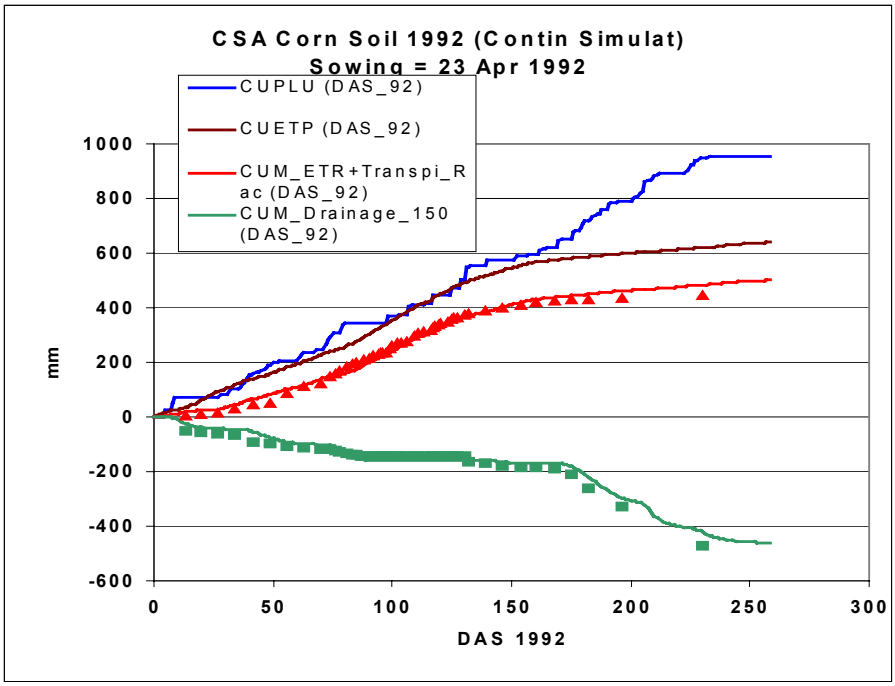


Fig. 78 - Comparison between simulated and measured accumulated PET and drainage for the maize plot in 1992 (symbols = measurements; lines = model predictions). The model runs were uncalibrated.

For comparison purposes, the simulation obtained for the bare soil is shown in Figure 80. The comparison of the two series of simulations stresses the very large influence of the crop when it is most active (100 to 130 days after sowing).

1.1.4. Discussion

Crop development subroutines have been introduced in the MARTHE model. The functionalities introduced for water flow are:

- a more detailed breakdown of evapotranspiration into i) surface evaporation and ii) transpiration by vegetation. This partitioning depends in part on the development of those parts of the vegetation which are in contact with the air (essentially leaves);
- water uptake by vegetation over a variable depth. The uptake is dependent upon root development and vertical root distribution;
- restriction of uptake according to a possible hydric stress experienced by the vegetation.

With regard to the transport of solutes, mass uptake is assumed to occur through root transpiration.

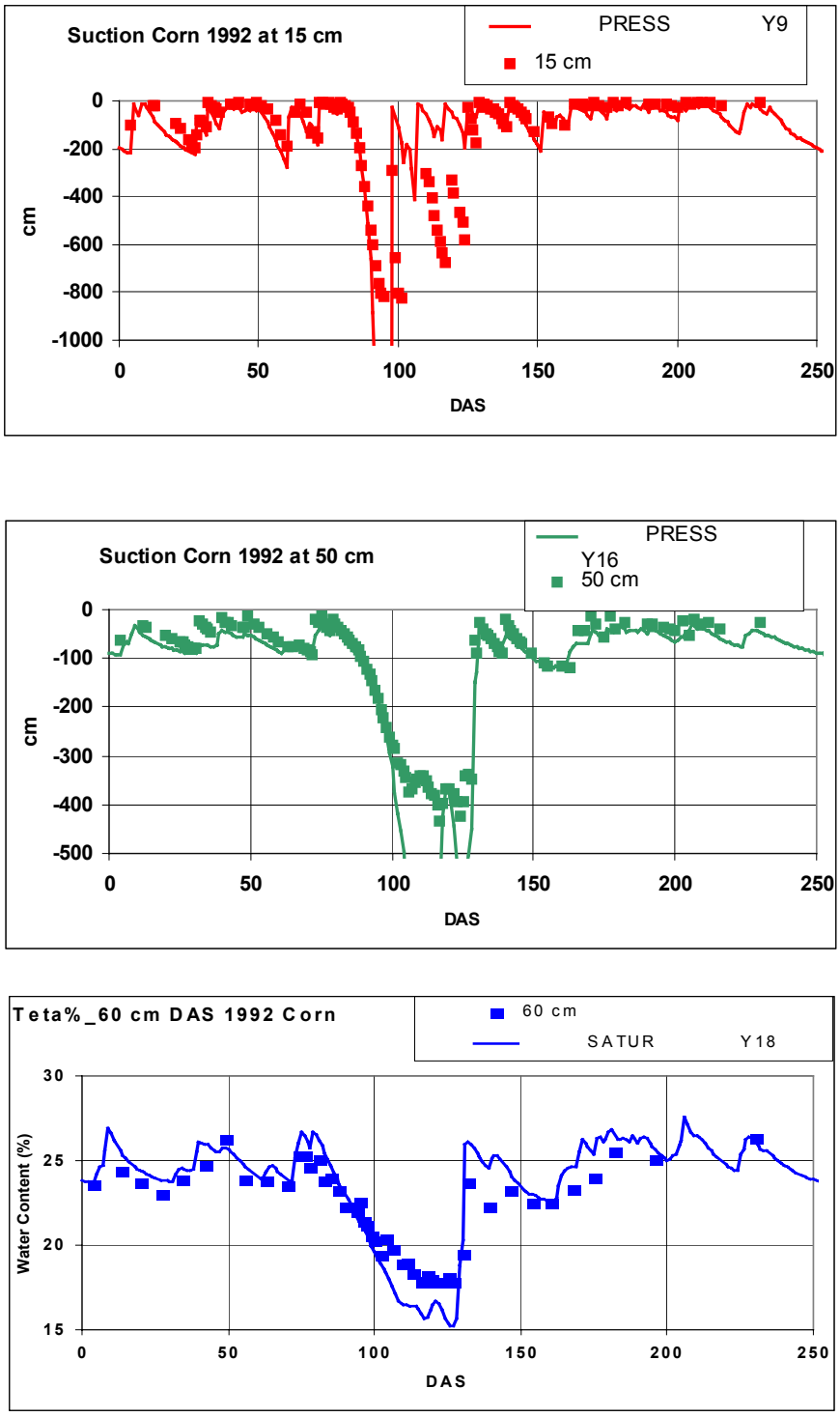


Fig. 79 - Comparison between simulated and measured suction and water contents at various depths for the maize plot in 1992 (symbols = measurements; lines = model predictions).

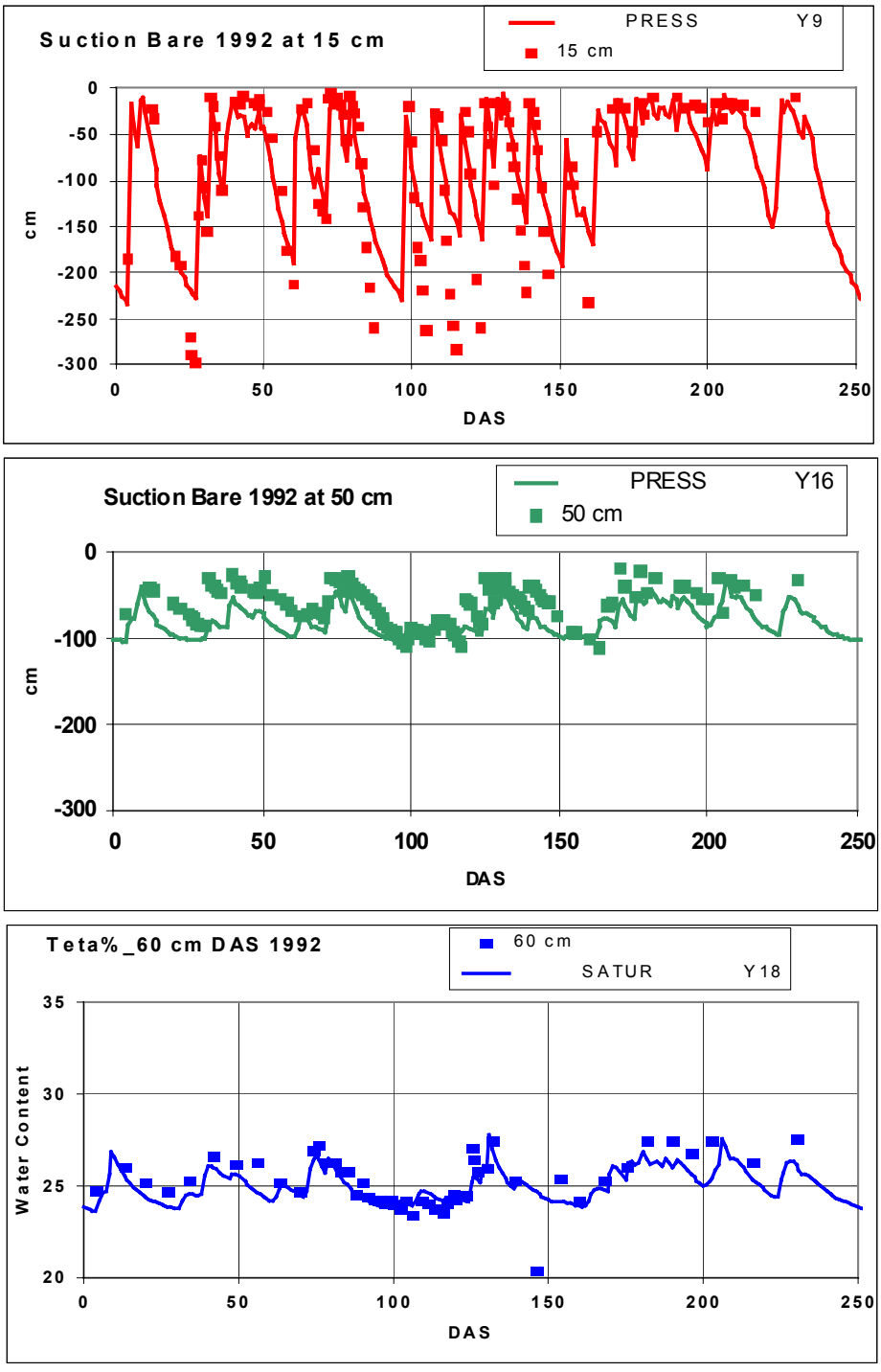


Fig. 80 - Comparison between simulated and measured suction and water contents at various depths for the bare plot in 1992 (symbols = measurements; lines = model predictions).

An evaluation of the newly developed subroutines was undertaken using data from the La-Côte-Saint-André experimental site. The work demonstrated that the new model

functionalities are correctly implemented in the model and may be used in real field applications involving crop covers.

1.1.5. Summary

A range of new functionalities have been added to the MARTHE to allow the simulation of water and solute fluxes in situations where the soil is cropped. Subroutines on plant transpiration, plant and root development, and uptake of water and solutes were added to the model. A validation exercise using data from the La-Côte-Saint-André experimental site demonstrated that the new functionalities have been correctly implemented in the model and may be used in real field applications.

1.2. Verification of new sorption subroutines implemented in MARTHE [BRGM]

The new sorption subroutines implemented in MARTHE were evaluated through 1D and 2D simulations based on three datasets from the literature.

1.2.1. Evaluation through simulations in 1D

- ***Datasets considered***

Two sets of 1D simulations were undertaken: i) a set of simulations described by Zheng and Wang (1998) referring to a problem simulated by Grove and Stollenwerk (1984); and ii) a set of simulations described by Huang *et al.* (1998) referring to benchmarks problems of Goode and Konikow (1989).

Both cases refer to a constant flow through a saturated column of soil. The common physical parameters for both sets of simulations are:

- porosity = 0.37;
- seepage velocity = 0.1 cm/s (10^{-3} m/s);
- bulk density ρ_b = 1,587 kg/m^3;
- concentration of source fluid Co = 50 10^{-6} kg/m^3;
- distance of breakthrough results = 8 cm.

The differences between the 2 sets of simulation are outlined in Table 18:

Table 18 - Differences between the two sets of simulations used for evaluate new sorption subroutines in MARTHE.

Parameter	Zheng & Wang	Huang *et al.*
Decay	0	0 or 10^{-2} or 10^{-3} s^{-1}
Dispersivity	1 cm	0.1 cm
Duration of the pulse	160 s	80 s

The mathematical descriptions of sorption used by the authors are outlined below.

Langmuir:

$$S_M = Q \cdot \frac{K_L \cdot C}{1 + K_L \cdot C}$$

C = volumetric concentration in the liquid phase,
S_M = mass concentration in the solid phase,
Q = total sites for solid phase concentration,
K_L = Langmuir constant.

Zheng & Wang (1998):
Q = 3 10^{-3} μg/g = 3 10^{-9} kg/kg,
K_L = 100 l/mg = 10^5 m^3/kg.

The corresponding MARTHE parameters are:

$$S_V = S_{VMAX} \cdot \frac{C / C_{REF}}{1 + C / C_{REF}}$$

S_V = ρ_b . S_M,
C_{REF} = $1/K_L$ = Reference concentration [kg/m^3]. C_{REF} is the liquid concentration above which the sorption of the solid phase is divided by 2,
C_{REF} =1/KL = 10^{-5} kg/m^3 = 10 [10^{-6} kg/m^3],
S_{VMAX} = ρ_b . Q = Maximal volumetric concentration in the solid phase. S_{VMAX} is the volumetric concentration in the solid phase [kg/m^3] which corresponds to an infinite concentration in the liquid phase,
S_{VMAX} = ρ_b . Q = 4.761 10^{-6} kg/m^3 = 4.761 [10^{-6} kg/m^3].

Huang et al. *(1998)*:
Q =3 10^{-3} g/g = 3 10^{-3} kg/kg,
K_L = 100 cm^3/g = 10^{-1} m^3/kg,
These parameters correspond to the following MARTHE parameters:
C_{REF} =1/KL = 10 kg/m^3 = 10^7 [10^{-6} kg/m^3],
S_{VMAX} = ρ_b . Q = 4.761 kg/m^3 = 4.761 10^6 [10^{-6} kg/m^3].

The reference concentration is extremely large compared to typical values reported in the literature and the value reported in the paper is probably the result of a typing error. It is believed that the true parameters corresponding to the simulations by Huang *et al.* (1998) are the same as those used by Zheng & Wang (1998), namely:

C_{REF} = 1/KL = 10^{-5} kg/m^3 = 10 [10^{-6} kg/m^3],
S_{VMAX} = ρ_b . Q = 4.761 10^{-6} kg/m^3 = 4.761 [10^{-6} kg/m^3].

Freundlich interactions:

Zheng & Wang (1998):
S_M = K_F . C^B,
S_M = mass concentration in the solid phase,
B = 0.7,
K_F = 0.3 μg/g . $(l/mg)^B$ = 0.3 10^{-6} . (1,000 m^3/kg)$^{0.7}$,
= 3.7768 10^{-5} $(kg/m^3)^{0.7}$.

The corresponding MARTHE parameters are:

S_V = K_{FV} . C^B,

S_V = ρ_b . $S_{M,}$

B = Freundlich exponent = 0.7,

K_{FV} = ρ_b . K_F = Volumetric Freundlich constant expressed in $[kg/m^3]^{(1-B)}$,

= 1,587 kg/m^3 . 3.7768 10^{-5} $(m^3/kg)^{0.7}$,

= 5.9937 10^{-2} $(kg/m^3)^{0.3}$,

As the concentrations are expressed in : 10^{-6} kg/m^3.

= 5.9937 10^{-2} /$[(10^{-6})^{0.3}]$. $[10^{-6}\ kg/m^3]^{0.3}$,

= 3.7818 . $[10^{-6}\ kg/m^3]^{0.3}$,

= 3.7818 in the model.

Huang et al. *(1998)*:

B = 0.7,

K_F = 0.3 cm^3/g. The units of K_F were wrong on the original paper as sorption units should account for those of the B exponent. The true expression of K_F is thus:

K_F = 0.3 $\mu g/g$. $(l/mg)^B$ = 0.3 10^{-6} . $(1000\ m^3/kg)^{0.7}$,

= 3.7768 10^{-5} $(kg/m^3)^{0.7}$.

This change in units leads to the same values as those used by Zheng & Wang.

- ***Modelling results***

Eleven simulations were undertaken with the MARTHE model to evaluate the implementation of the non-linear sorption schemes introduced in the model as part of the PEGASE project. The simulations have been undertaken with or without decay, using all transport schemes available in MARTHE, *i.e.* the Finite Differences method (FD), the flux limiter method with Total Variation Diminishing (TVD) and the mass Method of Characteristics (MOC).

For comparison purposes, figures from the simulations by Zheng and Wang (1998) and Huang *et al*. (1998) have been scanned in order to be used as reference. Times are expressed in seconds for the simulations by Zheng and Wang (1998) while those by Huang *et al.* (1998) are presented in pore volumes. As the pore velocity is 0.1 cm/s and the distance is 8 cm, 1 pore volume corresponds to 80 seconds in the figures presented.

Figures 81 to 84 compare MARTHE simulations with the reference simulations. These figures show that:

- MARTHE simulations are very accurate whatever the transport scheme used (FD, TVD or MOC);
- the TVD scheme is optimal and allows the use of coarser grids than the FD scheme;
- although the MOC scheme is satisfactory for Langmuir sorption, the use of the Freundlich equation leads to some oscillations for very low concentrations prior to the breakthrough. This is attributed to the fact that the equivalent retardation coefficient is infinite for a concentration of zero when the Freundlich equation is used with an exponent lower than 1;
- the decay factors are taken into account accurately with both isotherms;
- the mass balance with MARTHE numerical schemes is adequately simulated (error < 1 %).

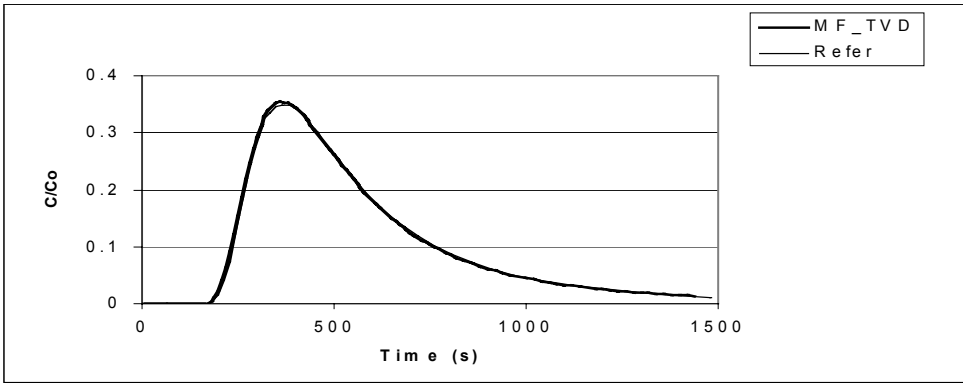


Fig. 81 - Comparison of MARTHE predictions with those of Zheng* et al.** ***(1998) when Freundlich sorption is considered. Thick line = MARTHE; Slim line = Reference.

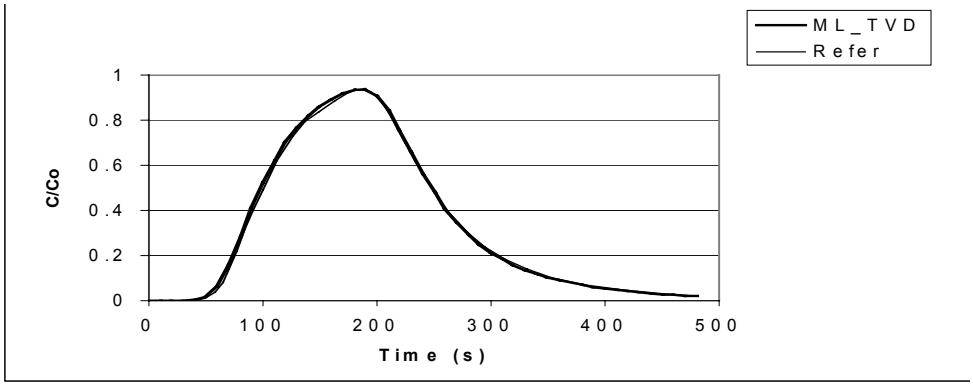


Fig. 82 - Comparison of MARTHE predictions with those of Zheng* et al.** ***(1998) when Langmuir sorption is considered. Thick line = MARTHE; Slim line = Reference.

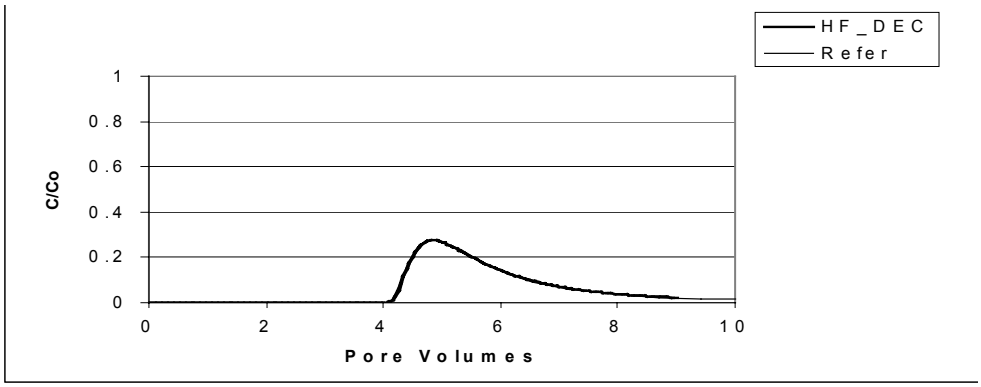


Fig. 83 - Comparison of MARTHE predictions with those of Huang* et al.** ***(1998) when Freundlich sorption and decay are considered. Thick line = MARTHE; Slim line = Reference Freundlich sorption + decay.

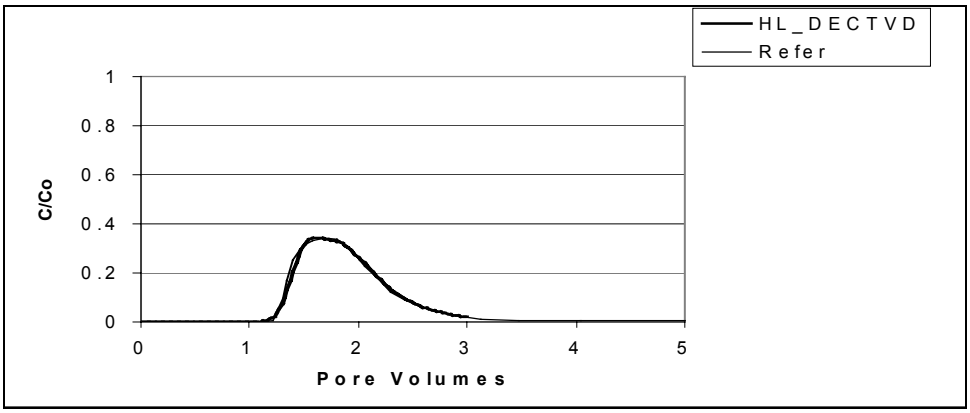


Fig. 84 - Comparison of MARTHE predictions with those of Huang* et al. *(1998) when Langmuir sorption and decay are considered. Thick line = MARTHE ; Slim line = Reference Langmuir sorption + decay.

1.2.2 Evaluation through unsaturated flow modelling

In order to evaluate the implementation of Langmuir or Freundlich sorption isotherms in Unsaturated Zone flows, an exercise modelling adapted from the Vredepeel dataset in the Netherlands (Boesten and Van Der Pas, 2000) was undertaken. The experimental data concerns the 1D simulation of the leaching of bentazone in a 2-m deep overlying an aquifer, as described by Golaz (2001). A mass of 8 10^{-5} kg/m^2 (0.8 kg/ha) of bentazone was applied to the soil surface on 22 November 1990 (day 0). For illustration purposes, a Langmuir isotherm with the following parameter values was assumed:

- C_{REF} = 9 . 10^{-5} kg/m^3;
- S_{VMAX} = 8 . 10^{-5} kg/m^3.

The other parameters used in the modelling were:

Parameter	First 30 cm	Lower than 30 cm
Dispersivity	0.02 m	0.10 m
Degradation Half Life	100 days	100 days

Figure 85 compares the distribution of concentrations in the profile 103 days after application (*i.e.* on 05 March 1991) obtained when Langmuir sorption is assumed or not. It is clear from Figure 85 that sorption has a large effect on predicted profiles of concentration.

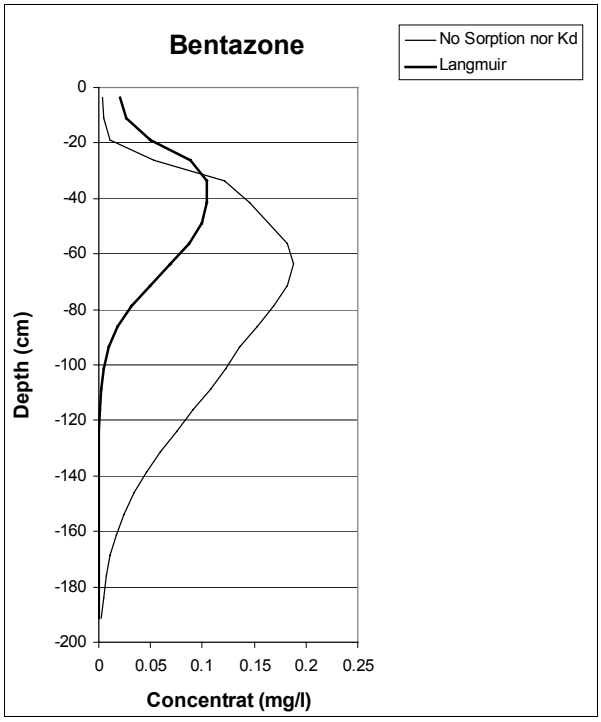


Fig. 85 - Transfer of bentazone in an unsaturated soil with Langmuir sorption and decay (adapted from Vredepeel site).

1.2.3. Evaluation through simulations in 2D

An evaluation test adapted from the "Rocky Mountain Arsenal" test described by Voss (1984) was simulated with MARTHE in steady state. The test region has the following characteristics:

- the study area was approximately 16 km x 20 km;
- the flow was roughly from the North to the South;
- water with a concentration of 1,000 units (ppm) of a hypothetical solute was injected in a lake situated in the northern part of the domain;
- recovery wells were situated in the southern part of the domain.

This test, which integrates a decay process, was simulated without sorption and with a Langmuir sorption isotherm.

MARTHE parameters controlling the transport were:

- decay Half Life = 20 years;
- grid size = 1 km;
- dispersivity : Longitudinal = 500 m,
  Transversal = 100 m ;
- porosity = 20 %;
- C_{REF} = Langmuir Reference Concentration = 100 concentration units;

- S_{VMAX} = Maximal volumetric concentration in solid phase = 120 concentration units.

The steady state concentration plumes obtained with and without Langmuir sorption are presented in Figure 86. The figure clearly shows that in presence of sorption, concentrations of the pollutant are lower and less spread. The aim of this evaluation was to verify the implementation in 2D or 3D of the new subroutines and to demonstrate MARTHE capabilities in steady state. The same simulations in transient state (charts not shown) over a period of 60 years showed that breakthrough in the recovery wells was slower and more progressive when Langmuir sorption was used.

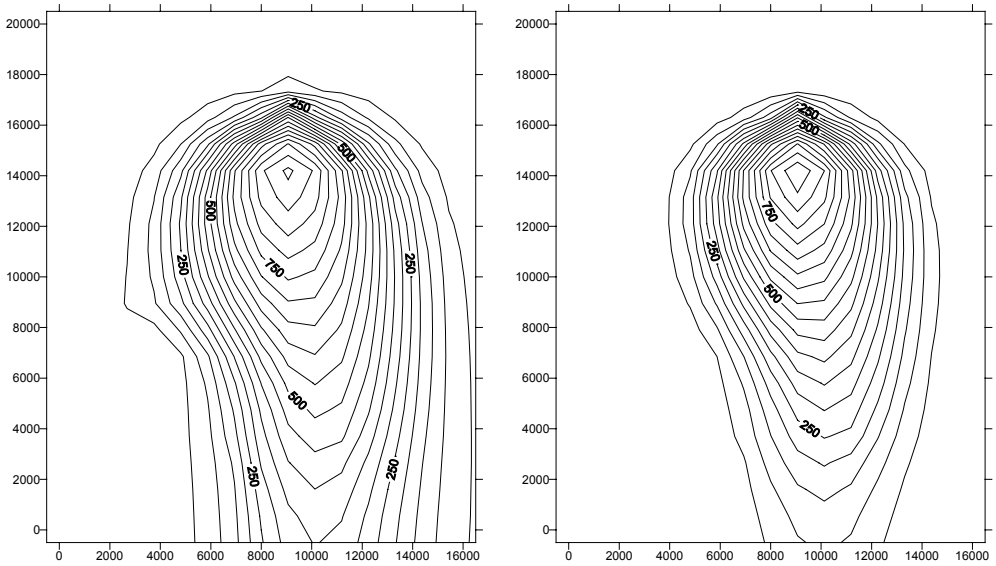


Fig. 86 - Rocky test problem. Transport in Steady State with decay. Left: no interactions; Right: Langmuir sorption.

1.2.4. Summary

Accurate simulation of pesticide fate in the soil and the unsaturated and unsaturated zones by the MARTHE model required the addition of functionalities dedicated to simulating the sorption of compounds to soil and sediment. The two most popular equations used to describe pesticide and nutrient sorption (Freundlich and Langmuir) were implemented in the model and extensively tested using numerical tests and simulations of literature datasets. The evaluation exercise demonstrated that the equations have been correctly implemented in the model.

1.3. Verification of new degradation subroutines implemented in MARTHE [BRGM]

New degradation subroutines were implemented in MARTHE and tested against reference simulations in 2D and 3D.

1.3.1. Evaluation through simulations in 1D

The evaluation exercise was performed using a test scenario described by Van Genuchten (1984). The modelling simulates the three-species nitrification chain:

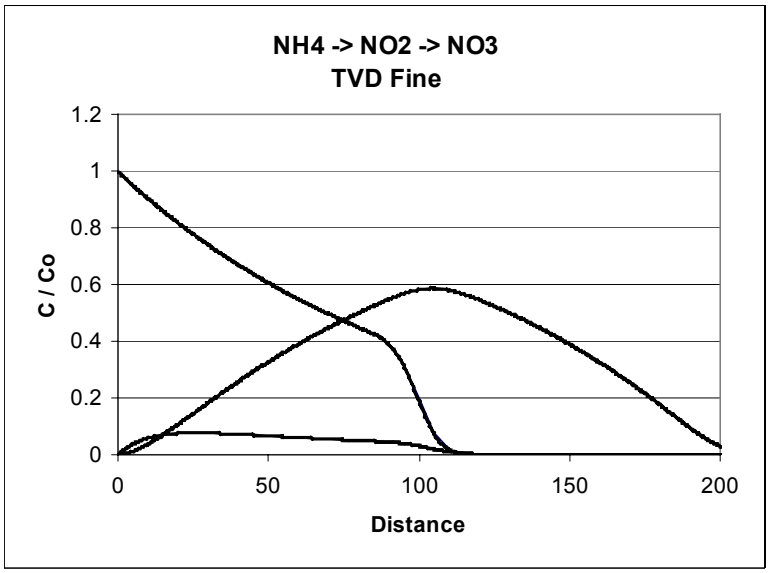
$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$

The experimental set-up which is being simulated is a horizontal column receiving through its left boundary a solution of NH_4^+ that degrades in NO_2^-, which itself degrades in NO_3^-. Initial concentrations of the three species are zero. The parameters of the test are:

- pore velocity = 1 cm/h;
- dispersion coefficient = $5 . 10^{-9}$ m^2/s;
- retardation factors for each product = 2 for NH_4^+; 1 for NO_2^- and NO_3^-;
- decay factors for each product = 0.005 h^{-1} for NH_4^+; 0.1 h^{-1} for NO_2^- and 0 for NO_3^-;
- (Decay Half Life for each product = 138.63 h for NH_4^+; 6.93 h for NO_2^- and infinite for NO_3^-).

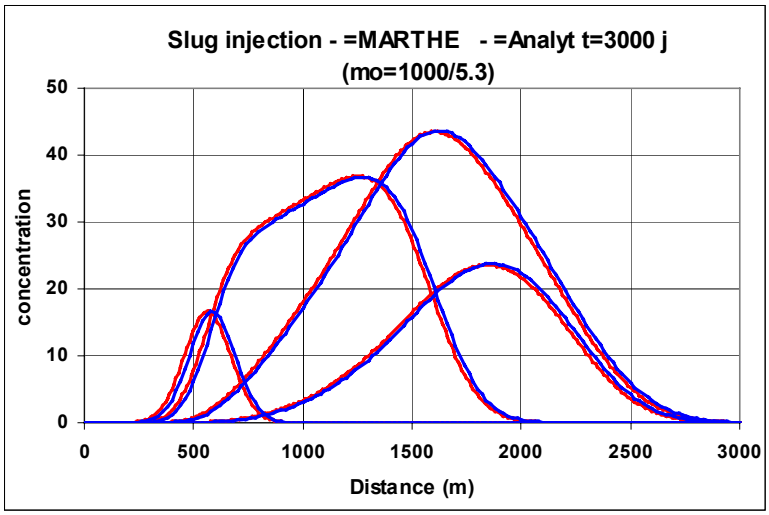
Figures 87 and 88 compare MARTHE simulations with the analytical calculations obtained using the CHAIN code from Van Genuchten (1984). Figure 88 compare MARTHE simulations with Bauer *et al.* (2001) analytical solutions for slug tests injections. Other simulations which are not shown here have been undertaken with parallel schemes for degradation and these provided a good fit to the data.

Figures 87 and 88 show that simulations using MARTHE are very accurate when compared to analytical benchmarks, the error in the mass balance being <0.01 %).



Thick line = MARTHE (TVD scheme); Slim line = Reference.
(The 2 curves are superimposed because the simulation is very close to the analytical solution).

Fig. 87 - Chain first-order reaction of NH_4^+.



Thick line = MARTHE model Simulation; Fine line = Bauer *et al.*, 2000 analytical solution.

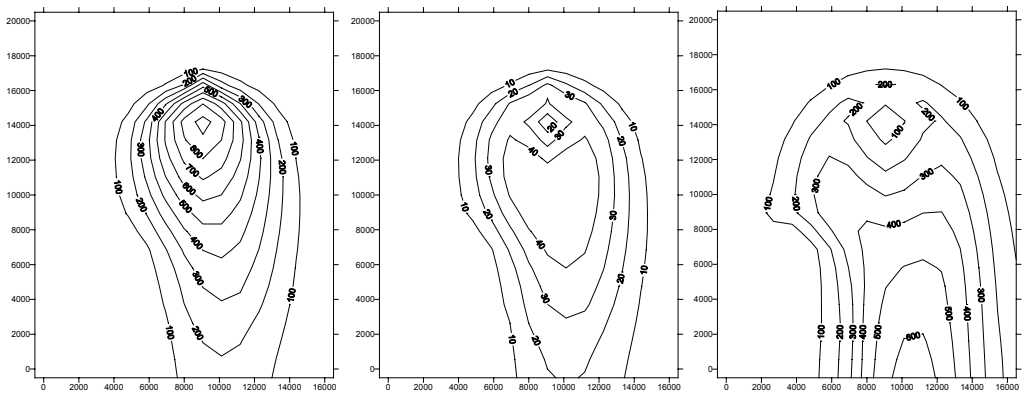
Fig. 88 - MARTHE modelling of degradation with follow up: Slug injection. sequential scheme (after Bauer* et al., *2000). Concentrations of the four members C1 to C4 (from left to right) after 3,000 days.

1.3.2. Evaluation through simulations in 2D

The same reference test adapted from the "Rocky Mountain Arsenal" test described by Voss (1984) has been simulated with MARTHE in transient state. The parameters are the same as those used for the "Rocky Mountain test" with Langmuir sorption (section 1.2. of the present chapter) except for the following:

- movement and fate of 3 compounds with first-order chain reactions;
- simulation in transient state;
- retardation factors for each product = 2 for product 1; 1 for products 2 and 3;
- Decay Half Life for each product = 20 years for product 1; 1 year for products 2 and Infinite for product 3.

Figure 89 shows the effects of the chain degradation. Compound #2 that degrades rapidly (<1 year) is found in much lower concentrations compared to other compounds with larger half-lives.



Product 1 Product 2 Product 3

Fig. 89 - Chain First-Order reaction: Rocky test problem.

1.3.3. Evaluation of the subroutines for the influence on degradation of temperature and humidity

In order to check the implementation of subroutines dedicated to the influence on degradation of temperature and saturation variations, a test adapted from the Vredepeel site (Netherlands; Boesten and Van Der Pas, 2000) was performed. This test concerns the 1D simulation of the leaching of bentazone in soil. Four simulations were performed:

- a reference simulation with a constant decay half life equal to 100 days;
- a simulation where degradation is influenced by temperature;
- a simulation where degradation is influenced by saturation;
- a simulation where degradation is influenced by temperature and saturation.

- ***Reference simulation***

The parameters for this simulation are:

Parameter	Upper 30 cm	Lower than 30 cm
Dispersivity	0.02 m	0.10 m
Rho*Kd (%)	11	0.55
Degradation Half Life	100 days	100 days

The transport scheme is TVD. The simulation period extends from 22/Nov/1990 (day 0) to 10/Mar/1992 (day 474).

Air temperatures were monitored from November 1990 to March 1992. The initial temperature in the 2-m thick soil layer was set to the annual average air temperature for the site (8.3 °C). At each model time step (equal to 1 day), the air temperature measured in the field was assigned to the first cell of the model (depth 3.75 cm). The temperature at the bottom of the soil profile was kept equal to the annual average air temperature throughout the simulation. The reference scenario described above was simulated using LEACHP scheme for correction of degradation according to moisture

contents with the following parameter values: T_min = 3 %, T_max = 8 % and F_sat = 0.6.

- ***Simulation results***

Figure 90 compares the profiles of concentrations obtained on day 103 (*i.e*. on 05/Mar/1991) with and without the activation of temperature and saturation effects on degradation. The effect of temperature correction on degradation (maximum concentration 0.30 mg/l instead of 0.20 mg/l) was larger than that for saturation (maximum concentration 0.22 mg/l instead of 0.20 mg/l). An additive effect was noted when both subroutines were activated.

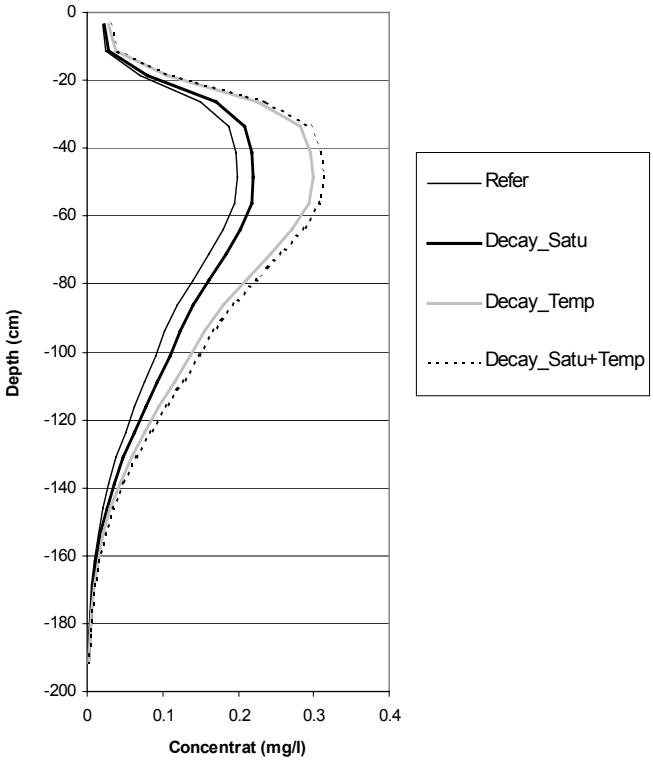


Fig. 90 - Influence of the activation of temperature and saturation corrections for degradation on predicted concentrations of bentazone in the Vredepeel unsaturated profile after 103 days of simulation (MARTHE simulations).

1.3.4. Summary

A description of degradation according to chain and parallel reaction has been introduced in MARTHE. A subroutine to simulate the effect of temperature and moisture variations on degradation was also added to the model. MARTHE new functionalities with respect to degradation were tested against literature datasets and demonstrated the correct implementation of the subroutines in the model.

1.4. Verification of new subroutines implemented in MACRO [SLU]

Fractured moraine clay aquitards represent vulnerable hydrogeological settings for groundwater contamination by pesticides, due to rapid preferential transport in fissures that connect the soil unsaturated zone with underlying coarser-textured aquifer materials (Jørgensen *et al.,* 1998). Such moraine clays are widespread across northern member states of the EU. To simulate such systems, models tools are required that account for preferential flow and transport. The linked preferential flow and transport models MACRO and FRAC3DVS developed in PEGASE (section 2.2. in chapter 2) were used to simulate the fate of the herbicide MCPP in the unsaturated/saturated zone at Havdrup, Denmark (section 6 in chapter 1), with the objectives to evaluate:

- the risk of pesticide contamination of the underlying sand aquifer as a function of MCPP application patterns and uncertainty in key MACRO parameters controlling flow and transport in the unsaturated zone;
- the influence of steady-state vs. transient representations of water flow and pesticide flux at the upper boundary of the groundwater model FRAC3DVS;
- the predicted time-scales for self-remediation of a contaminated aquifer.

MACRO was used in predictive mode to produce 'reasonable' input pulses to FRAC3DVS for different scenarios with respect to application patterns and dosage, based on a qualitative historical knowledge of MCPP use in Denmark. The hydrological parameterization in MACRO was based on a limited calibration to field measurements of water contents (by TDR) and groundwater level, and literature data on MCPP sorption and degradation properties measured in similar soil types.

1.4.1. Modelling

- ***Hydrologic calibration***

Measurements of the water table height and soil water contents by TDR during the two-year period 1999-2000 were used to calibrate the hydrological components of the MACRO model. The calibration procedure was carried out using the MACRO/SUFI tool described in section 1.1. of chapter 2. The parameters included were the total soil porosity in the subsoil, the saturated matrix hydraulic conductivity and an empirical coefficient controlling percolation rates as a function of the water table height. The model efficiency was used to assess the goodness-of-fit of the model (Loague & Green, 1991).

- ***Monte Carlo simulations with MACRO***

A Monte-Carlo approach (see section 2.2. in chapter 2) has been used to evaluate the effects of uncertainty in parameter inputs to MACRO on simulated pesticide fluxes leaving the root zone. For this purpose, daily weather data for the period 1963-2001 (rainfall, temperature and potential evapotranspiration) from a nearby weather station was used as driving data in long-term scenario simulations. A spring-sown cereal crop was assumed, following two different application patterns for MCPP. In the first, a spring application was carried out every third year in the period 1963-1984, and also in 1987, 1991 and 1995. Autumn applications were carried out every fourth year from 1985 to 1993 (a total of 3 applications). For the second application pattern, no autumn

applications were made. Autumn applications of MCPP were banned in 1996 in Denmark. In the simulations, no applications at all were made after 1996, in order to get an idea of the time-scales required for self-remediation of the aquifer. For this purpose, the simulation period was extended to 2100 by repeating the available weather data.

At Havdrup, 4-5 metres of clayey till overlies a local sand aquifer. The groundwater depth varies between 1 and 3 metres below the soil surface. The interface between MACRO and FRAC3DVS was therefore placed at 3 m depth. Three different upper boundaries for FRAC3DVS were created. Two of these represent spatially uniform leaching and percolation through the unsaturated zone:

- spatially variable leaching and percolation whereby the field is divided into 100 cells, where each cell is represented by a randomly selected Monte-Carlo simulation. Latin Hypercube sampling was used to generate parameter distributions based on the data shown in Tables 19 and 20. This data was gathered at a nearby field site in southern Sweden, on a similar soil type (Holman & Hollis, 2001), except for the correlation between the sorption and degradation coefficients, which was based on literature information (Allen & Walker, 1987);
- stochastic (Monte-Carlo) simulations, where the results in i) above are spatially aggregated with respect to leaching and percolation;
- a single deterministic run with average (*i.e.* effective) MACRO parameter values.

Default FOCUS correction factors were used to correct subsoil degradation rate coefficients (*i.e.* 0.5 at 30-60 cm depth, 0.3 at 60-100 cm depth, and zero below 100 cm depth; FOCUS, 1995), while organic carbon content was assumed to decrease logarithmically with depth to 1 m, and was set constant at 1 to 3 m depth. Different Monte Carlo scenarios were simulated to investigate the significance of accounting for both horizontal and vertical spatial correlations between parameters (see Table 21).

Table 19 - Assumed parameter distributions.

Parameter	CV (%)	Mean	Min.	Max.	Distribution
ASCALE (mm)	100	70	5	200	Log-normal
KSM (mm/hr)	50	0.84	0.05	2	Normal
DEG (1/day)	50	0.069	0.034	0.34	Normal
f_{oc} (-)	25	0.021	0.01	0.04	Log-normal

ASCALE: Effective diffusion pathlength.
KSM: Saturated matrix hydraulic conductivity.
DEG: Degradation rate coefficient in topsoil. f_{oc}:
Topsoil organic carbon content (used to calculate the sorption constant).

Table 20 - Assumed parameter correlations.

	ASCALE	DEG	KSM
KSM	-0.31	-	-
f_{oc}	-0.46	-0.56	-0.005

Table 21 - Different Monte Carlo samplings investigated.

Sampling	ASCALE	KSM	f_{oc}	DEG
1	Correlated and constant with depth		Correlated	
3	Uncorrelated and varied Independently for each horizon		Uncorrelated	
6	Uncorrelated and constant with depth		Uncorrelated	

- ***Linked MACRO-FRAC3DVS simulations***

Previous simulations of the fate and behaviour of pesticides in groundwater using FRAC3DVS have usually simplified the upper boundary, by representing the leaching loss from the unsaturated zone as both spatially uniform and also constant in time (*e.g.* a square 'pulse' of constant concentration in a constant water recharge, Jørgensen *et al.,* 2003). This is probably a reasonable representation of the pesticide input to groundwater if the transport process through the soil is 'chromatographic'. However, if the pesticide fluxes leaving the soil root zone are strongly influenced by preferential flow and transport, then it is possible that the evolution of simulated pesticide concentrations in groundwater would be significantly influenced by the highly transient and spatially non-uniform nature of the input fluxes from the unsaturated zone. Coupled MACRO/FRAC3DVS simulations were therefore carried out for a selected twelve-year period (1985-1996) in order to investigate the significance of different representations of the upper boundary in FRAC3DVS. In particular, the significance of accounting for transient boundary conditions was investigated for both recharge rates and pesticide concentrations. A fully transient simulation was compared to two other simulation cases:

- steady-state water recharge calculated as the mean recharge during the simulation period (c. 230 mm/year) combined with transient pesticide input fluxes;
- steady recharge (calculated as above) at a constant pesticide concentration, calculated from the total pesticide leached during the entire simulation period.

The total water recharge and pesticide input in all three cases was therefore equal.

Comparative simulations were also performed for two extreme cases of pore system 'connectivity' at the interface between MACRO and FRAC3DVS:

- water flows and pesticide fluxes simulated by MACRO are lumped for both macropore and micropore domains, and uniformly distributed across the upper surface of FRAC3DVS, irrespective of the location of nodes representing fissures. This is akin to assuming that there is no connectivity between the macropores in the unsaturated and saturated zones. This might be reasonable if the macropores are much more densely distributed in the soil root zone, so that the majority become discontinuous at the boundary (*i.e.* at 3 m depth);
- water flows and pesticide fluxes in macropores at 3 m depth simulated by MACRO are input uniformly to all upper boundary cells bordering to a fissure. The micropore fluxes simulated by MACRO are partitioned equally between all the remaining (matrix) cells. This case assumes a close connectivity between the macropores in the unsaturated and saturated zones.

In all these simulations, FRAC3DVS was parameterised for a subsoil block 1 by 10 m in areal extent. Two continuous fissures were simulated, 5 m apart, in the centre of the block, running parallel to the short side. No flow conditions were assumed around the perimeter of the block except for the local aquifer in the sand layer at 5 to 5.5 m depth. The bottom boundary condition was set as a constant outflow of 80 mm/year, which given an average recharge at the base of the soil root zone of 230 mm/year for the 12-year period, implies a mean lateral outflow in the sand layer of 150 mm/year.

FRAC3DVS simulations of a 40 x 40 m field were also run to investigate the time-scales required for self-remediation of an aquifer contaminated by MCPP. Steady-state

water recharge was used as the upper boundary condition, calculated as the long-term mean water percolation rate simulated by MACRO (= 207 mm/year). Steady downward flow through the aquifer was assured by also setting the outflow rate at 6 m depth to the same value. A simulation was run assuming a transient, but spatially uniform flux of MCPP at the upper boundary, calculated by aggregating the MACRO Monte Carlo simulations.

1.4.2. Modelling results

- ***Calibration***

Soil water contents were adequately simulated following calibration (model efficiencies are all positive, Fig. 91), although the temporal dynamics of the water table position seemed more difficult to capture accurately (Fig. 92). Figure 93 shows the water balance simulated at the site during the calibration year of 1999.

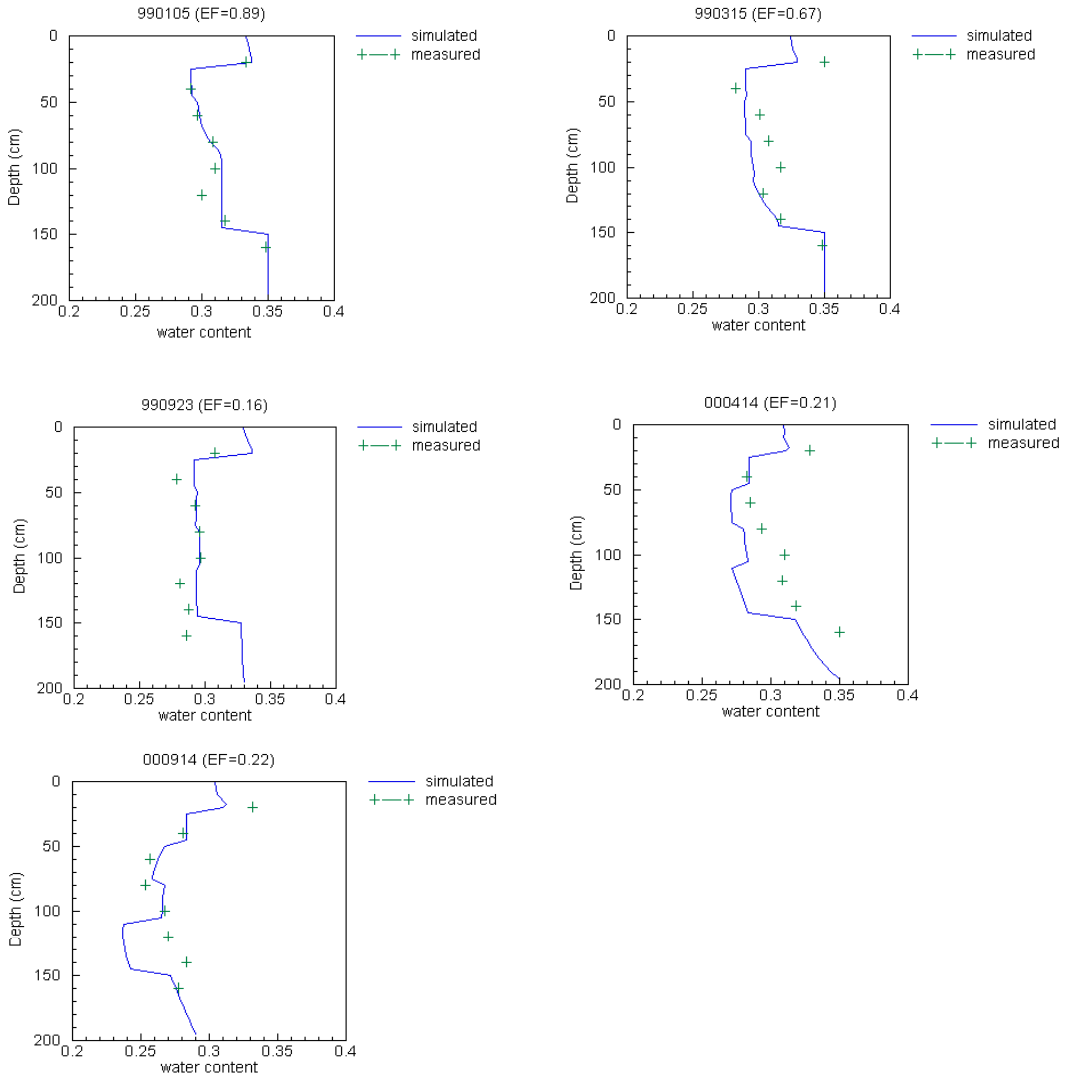


Fig. 91 - Measured and simulated water contents at Havdrup (EF=Model efficiency).

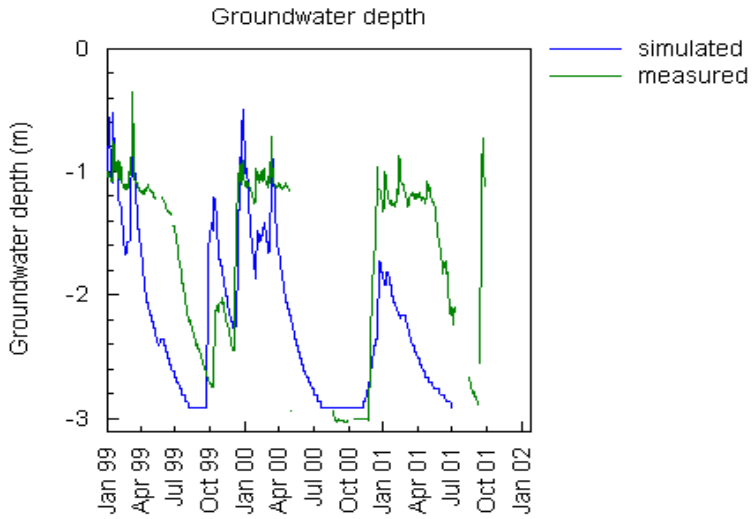


Fig. 92 - Measured and simulated water table positions at Havdrup.

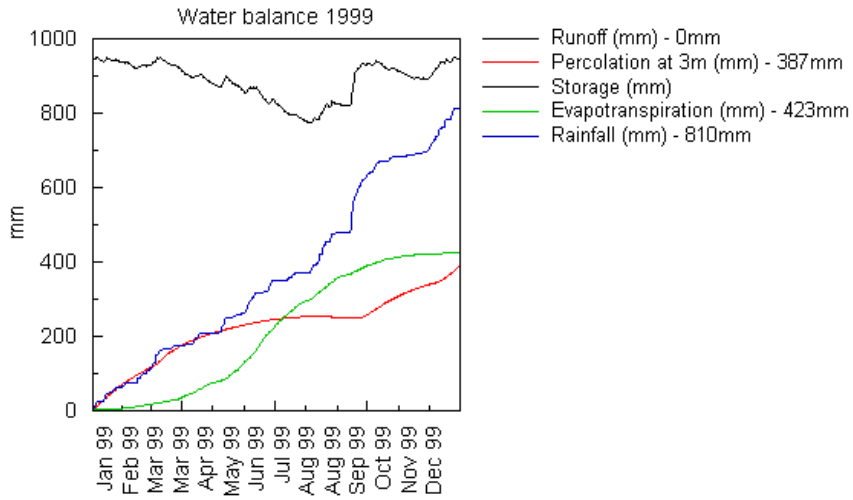


Fig. 93 - Simulated water balance of the unsaturated zone at Havdrup during the calibration year.

- ***Long-term scenario simulations***

Figure 94 demonstrates the temporal pattern of predicted leaching and percolation at Havdrup for the case of a single deterministic simulation, assuming average parameters. It shows that although percolation is fairly constant from year to year, leaching losses vary considerably. The autumn applications simulated between 1985 and 1995 clearly resulted in marked increase in leaching losses.

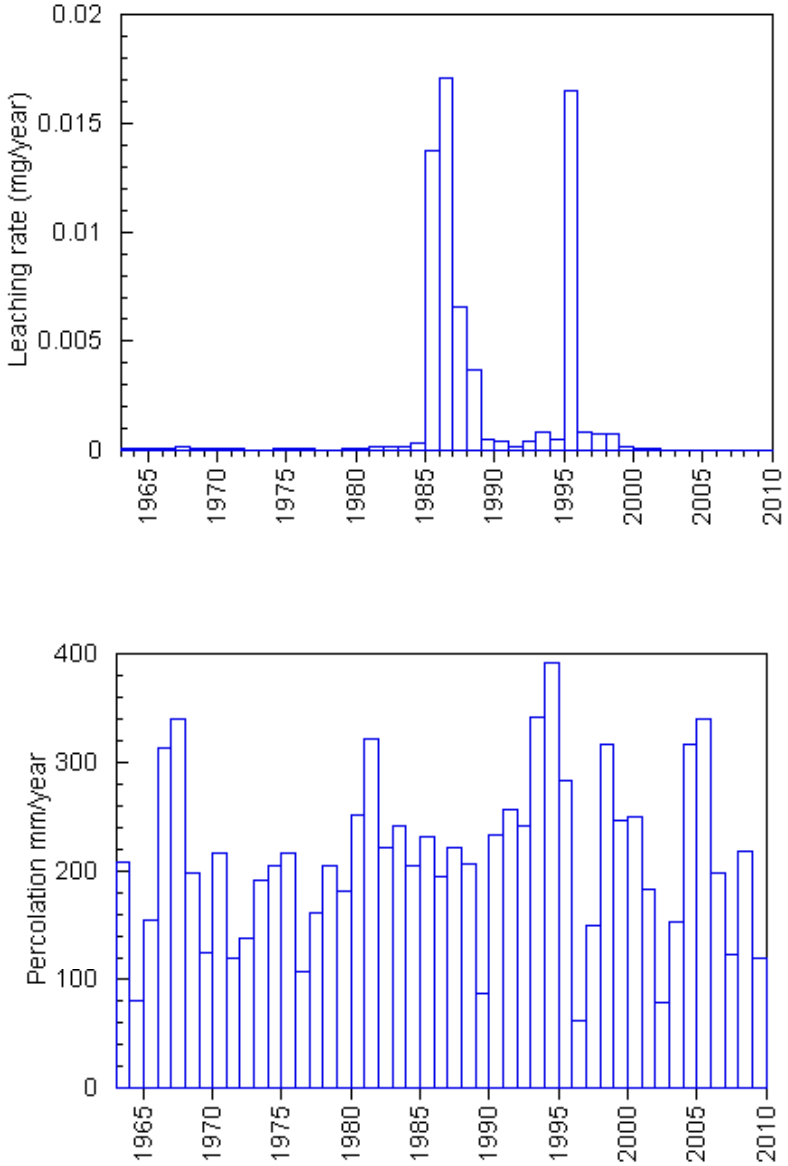


Fig. 94 - Temporal variations in simulated percolation and MCPP leaching for a single deterministic MACRO simulation with 'effective'* i.e. *average parameters.

Figure 95 shows the contrasting results of two of the different Monte Carlo samplings for the first application pattern. It shows that in the case of correlated parameters (sampling 1), leaching is larger (0.12 % of the applied dose vs. 0.07 % in sampling 3), and is also dominated by a few 'hot spots' in the field: less than 5 % of the cells contribute more than 50 % of the leaching. In the case of uncorrelated parameters (sampling 3), leaching is not only smaller, but is also more evenly spatially distributed.

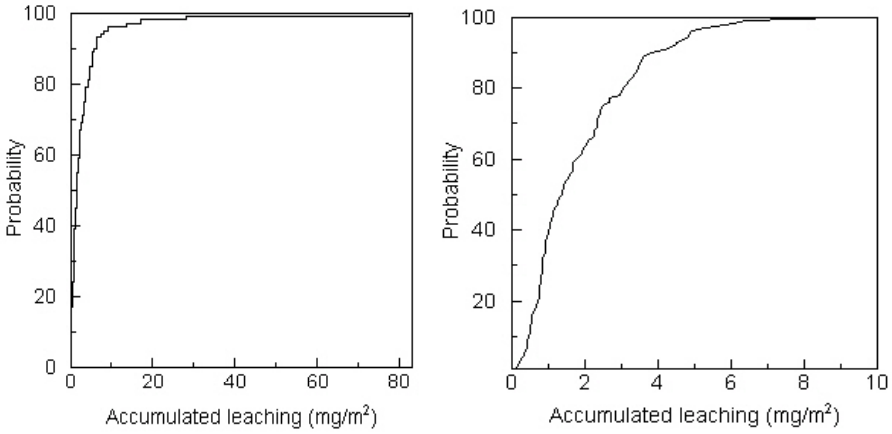


Fig. 95 - Predicted cumulative probability distributions for MCPP leaching for Monte Carlo samplings 1 (left) and 3 (right) for the first application pattern (see Table 22).

Table 22 shows the results for the two different application patterns for Monte Carlo samplings 1 and 3. It shows that the introduction of autumn applications increased predicted leaching by a factor four for correlated parameters (sampling 1) and by a factor seven for uncorrelated parameters (sampling 3). For correlated parameters, ASCALE seems to influence the accumulated leaching slightly more than the parameters DEG (degradation rate coefficient) and KSM (saturated hydraulic conductivity for the matrix) according to the SRRC values (Table 23). For the third sampling, where ASCALE and KSM are uncorrelated and vary independently with depth, the degradation rate coefficient has the largest influence and the influence of ASCALE and KSM decreases. The organic carbon content, f_{oc}, seems to have a relatively small influence on the accumulated leaching for both Monte Carlo samplings.

Table 22 - Percentage of the applied dose leached for different application patterns

Sampling	Pattern 1	Pattern 2 (no autumn application)
1	0.12	0.03
3	0.07	0.01

Table 23 - SRRC (standardized rank regression coefficient) values with respect to accumulated leaching for the different parameters for the first application pattern.

Sampling	ASCALE	DEG	KSM	f_{oc}
1	0.60	-0.48	-0.42	-0.03
3	0.15	-0.51	-0.06	0.01

- ***Linked MACRO-FRAC3DVS simulations***

Figure 96 shows the results of the simulations comparing the three different treatments of the upper boundary fluxes in FRAC3DVS, for the case where the water and pesticide fluxes through macropores and micropores simulated by MACRO at 3 m

depth are combined, and assumed to be distributed uniformly across the upper surface of FRAC3DVS, irrespective of the location of matrix and fissure nodes.

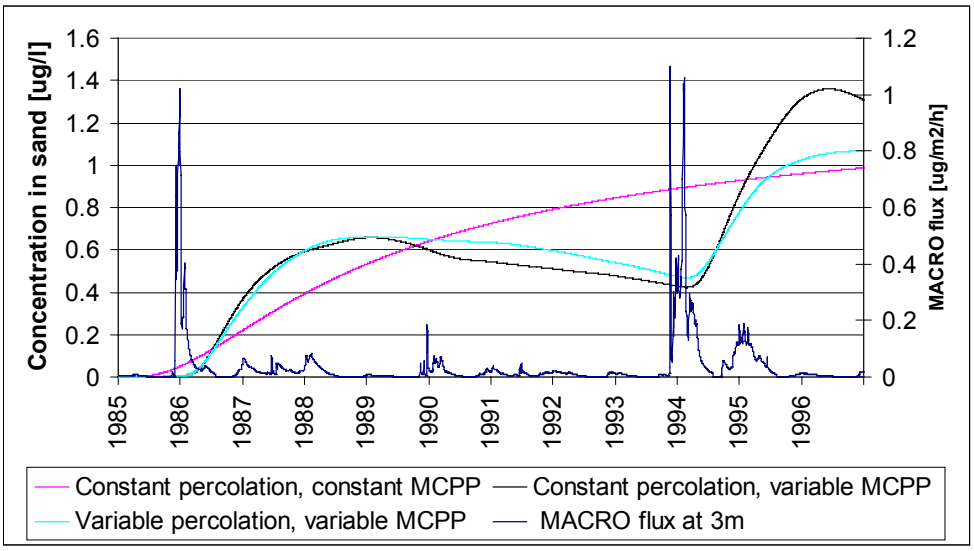


Fig. 96 - Simulated MCPP concentrations at the base of the local sand aquifer at 5.5 m depth, for three different representations of a spatially aggregated flux simulated by MACRO used as the upper boundary condition to FRAC3DVS: constant flow and constant concentration, constant flow and time-variable concentration, and time-variable flows and concentrations. Macropore and micropore fluxes simulated by MACRO are combined and distributed uniformly across all FRAC3DVS cells.

Figure 96 shows the typical smooth response of pesticide concentrations to a 'square-pulse' type of constant upper boundary condition (Jørgensen *et al.,* 2003). The fully transient simulation shows fluctuations of simulated pesticide concentrations in the local sand aquifer in response to the highly transient nature of the input fluxes from the unsaturated zone. Simplifying the flow problem by assuming steady water flow, while maintaining transient pesticide fluxes, provides acceptable simulation results compared to the fully transient case (Fig. 96). This is a practically useful result for larger-scale problems, since steady-state water flow simulations are much faster than fully transient simulations.

Figure 97 shows the effect of the different assumptions concerning vertical connectivity of macropore fluxes between MACRO and FRAC3DVS, for fully transient simulations. Somewhat surprisingly, there is no great difference in the evolution of simulated MCPP concentrations at the base of the sand layer between the two cases. It might be expected that the time-course of pesticide concentrations in the aquifer would be more dynamic when the macropore fluxes leaving the soil root zone are directed towards FRAC3DVS cells bordering the two fissures, due to a stronger preferential transport of MCPP through the till aquitard between 3 and 4.5 m depth. However, this was not the case, perhaps due to a 'damping' of macropore fluxes due to diffusion exchange with the till matrix at 3 to 5 m depth, or mixing in the sand layer itself. Since the bottom boundary condition for water flow was set to a constant 80 mm/year, Figure 97 also shows that the total loss of MCPP to deeper groundwater is smaller in the case of

strong connectivity of macropore fluxes between models. This is because more of the pesticide is lost instead in lateral discharge in the sand layer.

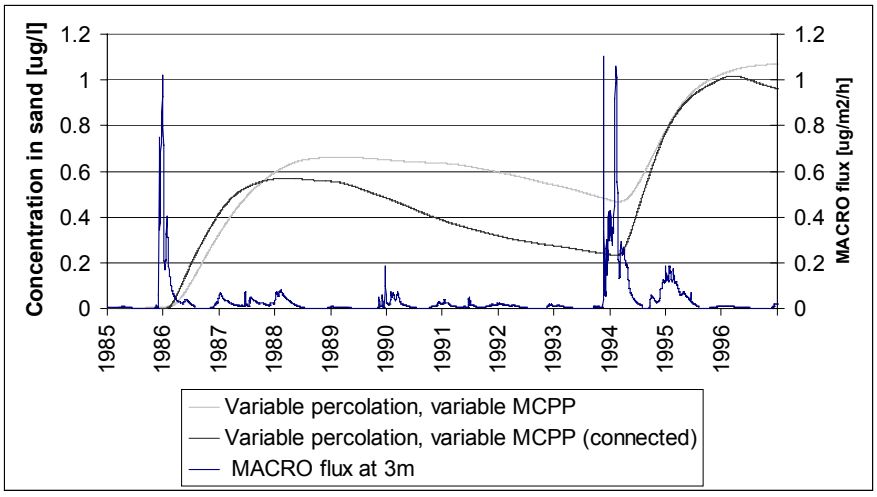


Fig. 97 - Simulated MCPP concentrations at the base of the local sand aquifer at 5.5 m depth, with a single 'effective parameters' MACRO simulation used as the upper boundary condition to fully transient FRAC3DVS simulations: comparison of connected and disconnected macropore fluxes.

Figure 98 shows the MCPP concentrations in the local sand aquifer predicted by FRAC3DVS for the field-scale (40 x 40 m) simulation, using the spatially aggregated pulse from MACRO as the upper boundary condition, with a constant recharge rate and a transient MCPP flux that is distributed uniformly across the upper surface. A maximum concentration of 0.87 μg/l is reached, and the model predicts that it will take ca. 20 years after banning the use of this product for the concentration to decrease below the EU drinking water limit (= 0.1 μg/l).

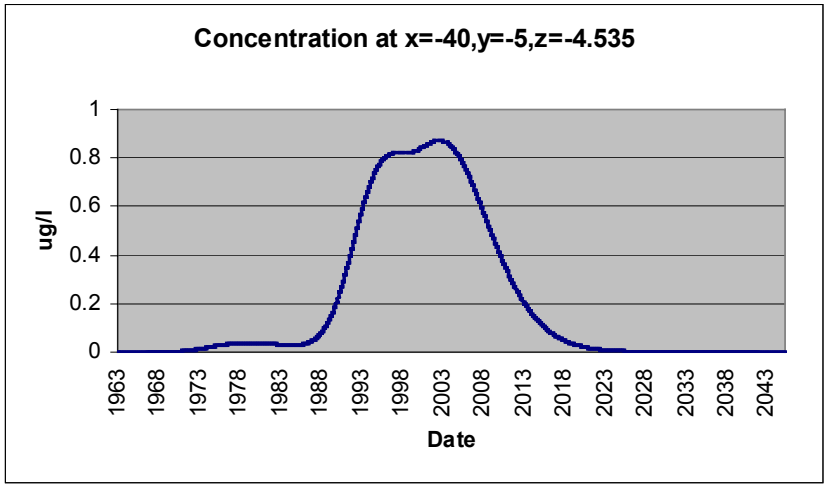


Fig. 98 - Long-term simulation of MCPP concentrations in the local sand aquifer at 4.535 m depth, at the downstream end of a 40 x 40 m field.

1.4.3. Discussion and conclusions

From these simulations, it can be concluded that:

- large variations in predicted leaching may result from parameter variations at the field scale, although it is unclear whether it is important to take this uncertainty and variability into account. The significance of these spatial variations will depend on the scale of the 'hot-spots' compared to the density of fissures in the aquitard;
- assumptions made about the vertical parameter variation and correlation seem to be important. The variability of key soil physical and hydraulic parameters strongly influences leaching, especially when correlations are explicitly considered, both across the field, and with depth in the soil. For the uncorrelated case, leaching was most sensitive to variation in degradation rates;
- autumn applications of MCPP starting in the mid-1980's are an important reason for observed groundwater contamination by this compound. The time required for self-remediation of shallow groundwater contaminated by MCPP (*i.e.* for concentrations to decrease below the EU drinking water limit) was ca. 20 years. Since autumn applications were banned in 1996 in Denmark, one should expect contaminated aquifers to be useable again in about 10 years from now;
- assumptions with respect to the connection between the two models can have a significant influence on the simulated time evolution of pesticide concentrations in shallow groundwater. An assumption of steady recharge from the unsaturated zone (by averaging flows predicted by MACRO) seems adequate and useful from the practical point of view, since steady-state simulations are considerably faster than transient ones. However, simulations showed that pesticide concentrations in shallow groundwater can show considerable fluctuations in response to the highly transient fluxes leaving the unsaturated zone of macroporous soils. Thus, the constant concentration upper boundary condition, commonly used in groundwater modelling, may give misleading estimates of the time-scales required for self-remediation of contaminated aquifers. Somewhat surprisingly, assumptions concerning the degree of connection between macropore fluxes in the two models seemed less critical. More research is needed to understand the reasons for this lack of sensitivity.

1.4.4. Summary

A 'loose-linked' modelling tool comprising the one-dimensional dual-permeability model MACRO and the three-dimensional groundwater model FRAC3DVS was applied to a macroporous soil-groundwater system in fractured clayey till at Havdrup, Denmark. The objectives were to identify the main controls on leaching through the unsaturated zone and the subsequent evolution of pesticide concentrations in shallow groundwater, including the expected time-scales for self-remediation of contaminated aquifers. The soil hydrological component of the MACRO model was first calibrated against measurements of soil water content and water table fluctuations during two years. MCPP was then used as test substance in scenario simulations, focusing on the significance of accounting for i) spatial variation in soil properties, ii) temporal variations in water and pesticide fluxes leaving the soil root zone, and iii) the assumed degree of connectivity of macropore fluxes across the interface between the models. Both of these models account for preferential flow and transport processes, but with different conceptual approaches. MACRO treats macropores as a 'lumped' flow region, while

FRAC3DVS describes flow and transport in individual fractures that are explicitly defined in geometric terms. A 'one-way' file transfer from MACRO is used to define the upper boundary conditions for water and pesticide fluxes in FRAC3DVS.

Monte Carlo simulations with MACRO showed that large variations in predicted leaching may result from parameter variations at the field scale ('hot spots'), and that assumptions made about the vertical parameter variation and correlation also seem to be important. The variability of key soil physical and hydraulic parameters controlling macropore flow strongly influences leaching, especially when correlations are explicitly considered, both across the field, and with depth in the soil. For the uncorrelated case, leaching was most sensitive to variation in degradation rates. The long-term scenario simulations confirmed that autumn applications of MCPP beginning in the mid-1980's were the main reason for the observed groundwater contamination by this compound. The time-scales for self-remediation of shallow groundwater contaminated by MCPP, defined as the time taken for concentrations to decrease below the EU drinking water limit, were of the order of ca. 20 years.

Simplifying assumptions concerning the connection between the two models can have a significant influence on the simulated time evolution of pesticide concentrations in the groundwater. An assumption of steady recharge from the unsaturated zone seemed adequate, although transient pesticide fluxes should be preferred. Surprisingly, assumptions concerning the degree of connection or correlation between macropore fluxes in the two models seemed much less critical.

2. APPLICATION OF MODELLING TOOLS AT THE BRÉVILLES SITE

The Brévilles catchment has been extensively monitored for water and pesticide fluxes over a period of three years (section 1 in chapter 1). Soil, geological and meteorological data collected at the site were used to simulate water, bromide and pesticide fluxes using the modelling tools developed within the scope of PEGASE. The predictions of the various modelling tools were compared to observed data.

2.1. MARTHE modelling in 1 dimension [BRGM]

The modelling in one dimension was aimed at: i) demonstrating the capability of the MARTHE to simulate flow and solute transport in soil layers; ii) evaluating the influence on model predictions of selected model parameters such as the geometry of the column (depth of the soil column, thickness of the mesh) and crop parameters; iii) determining a level of simplification of the system which would give a reasonable fit to the data (context of model parsimony); and iv) predict acetochlor concentrations without recurring to model calibration.

Simulations were undertaken for two agricultural plots within the basin. Simulation results for water flow and solute transport are presented for one plot (Calcisol) only using water, bromide and pesticide leaching data for the year 2000.

2.1.1. Conceptual model and MARTHE parameterisation

The one-dimensional model is constituted by a column of 40 cm of soil overlaying 32 m of homogeneous limestone. The impact on simulations of using various column depths and mesh sizes was studied.

Boundary conditions. Daily rainfall and Evapotranspiration (ET0) were applied in the top mesh. A unit gradient condition was fixed on the deepest mesh.

Geometry. The soil column is constituted of two 20-cm thick horizons (38-1 and 38-2). The surface of the column was set to 1 m^2.

Initial conditions. The simulation was started on 01/01/2000 with initial water contents set to observed values on 26/04/2000 in the soil and to an arbitrary water content of 25 % in the limestone.

Time step. Calculation time steps were automatically adjusted by MARTHE between 0.02 and 0.5 day. These boundary limits were selected to obtain a good convergence of the model should numerical difficulties be encountered and to allow a fast computation when convergence is easily obtained.

Cropping. The maize crop was sown on 11/04/2000 and harvested on 15/10/2000.

Bromide application. Bromide is often considered to be an inert tracer for water movement. A total of 1.997 g/m² of bromide was applied to the soil surface on 19/04/2000 (day # 110). Longitudinal dispersivity was set to 2 cm in the soil layers and to 10 cm in the limestone on the basis of other modelling activities undertaken on the same plot.

Unsaturated zone parameters. Soil water retention curves [h(θ)] were obtained by fitting the Van Genuchten law to the measured data using the RETC software. The Mualem transformation from h(θ) to K(h) was used as no data were available to support a direct parameterisation of the K(h) relationship. Saturated permeability (Ksat) was measured on-site using the constant head method. Limestone parameters were taken from previous simulations for the same experimental plot. Unsaturated zone parameters used in the modelling are presented in Table 24**.**

Table 24 - Soil and subsoil parameters used in the modelling.

Horizon	38-1	38-2	Limestone
Depth (cm)	0 to 20	20 to 40	32 m
Ksat (m/s)	2.95E-05	2.17E-05	6.00E-06
θr (%)	10	10	20
θs (%)	36.5	30	30
α	22.13	1.27	0.2
n	1.169	1.247	2

2.1.2. Modelling results

MARTHE predictions were compared to the experimental dataset which was constituted of water contents and bromide concentrations in 16 soil samples taken at five depth intervals on six different dates (from day 117 to day 454). Predicted volumetric water content and bromide concentrations (in mg/kg of soil) were compared to the average of the 16 observations. The variability of the measured data was significant and was therefore incorporated in the evaluation of modelling results. Model results are presented in the form of chronological series for a given depth (2.5, 7.5, 15, 25, 35 cm) and profiles at two particular dates (day 117, one week after application, and day 270, towards the end of the summer period).

The reference simulation considered a 32-m column divided in 1cm-thick meshes in the 50 first centimetres and increasing progressively towards the bottom of the column. The total number of soil meshes was 103. Computation time was <3 minutes on a 1-GHz Pentium III computer.

Figures 99 to 101 show uncalibrated MARTHE predictions for water contents. Measured humidity data for the top layer were found to be highly variable during the day and thus cannot be adequately simulated on the basis of daily precipitation data. Daily data are considered to be useful for predicting water contents from a depth of ca. 5 cm except when rainfall events with large intensities are experienced. The results demonstrated the general ability of the model to simulate water flow and transport in soil and in the underlying limestone in variably saturated conditions.

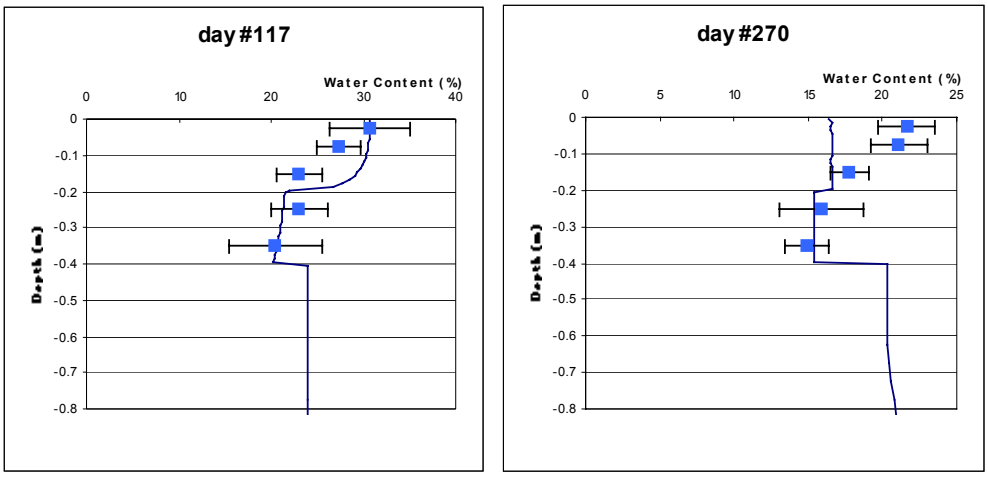


Fig. 99 - Simulated water content profiles at day 117 and day 270 (squares = observations; lines = model predictions).

The transport computation was coupled to flow computation in the modelling. Bromide concentrations in the soil were calculated for those dates for which measurements have been made in the field. Large concentrations of bromide in the soil were observed shortly after harvesting and these were attributed to the presence and possible remobilization of bromide in vegetal debris. These values were removed from the evaluation dataset. Model predictions for bromide concentrations are compared to field observations in Figures 102 to 104.

The simulations did not provide a perfect match to the observed data. Still, predicted data were usually in the range of observed values and the simulation of concentration peaks was considered to be satisfactory. Since measured parameters and observation data carry a significant uncertainty and very little calibration of the model was undertaken, it is considered that MARTHE is capable of adequately simulating the transport of bromide in this Calcisol.

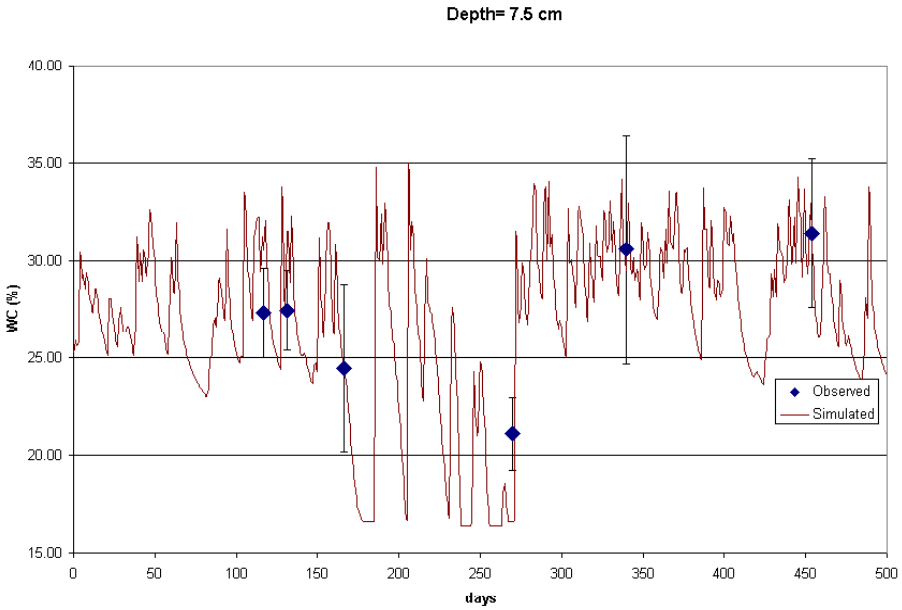


Fig. 100 - Simulated water content time series and observed values at 7.5 cm depth.

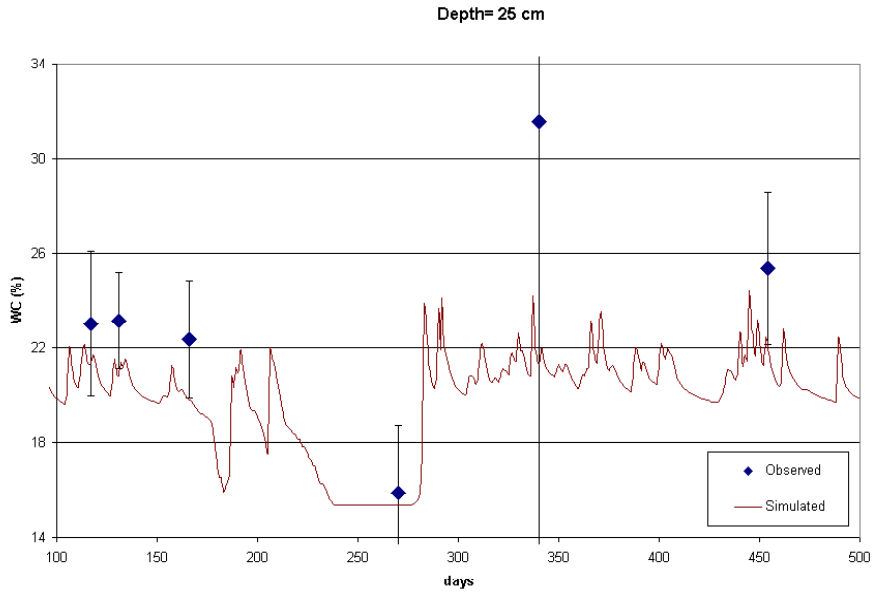


Fig. 101 - Simulated water content time series and observed values at 25 cm depth.

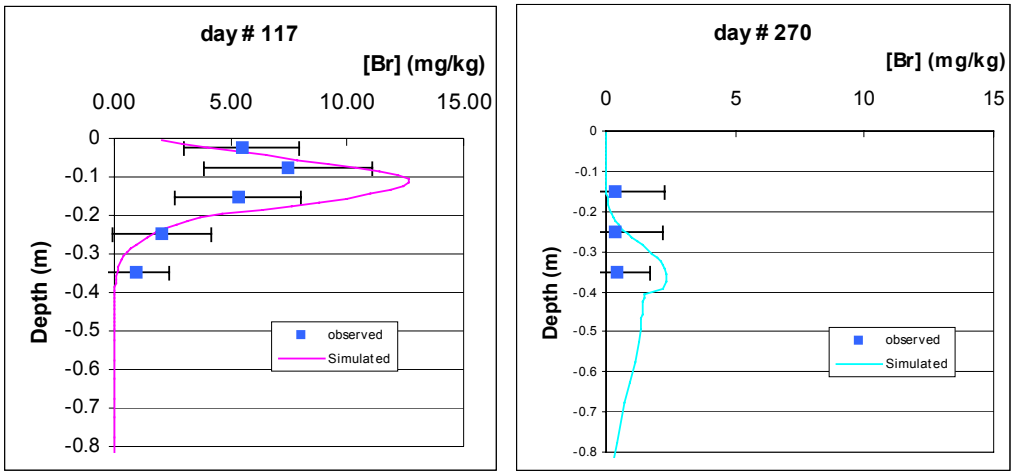


Fig. 102 - Simulated bromide concentration profiles at day 117 and day 270.

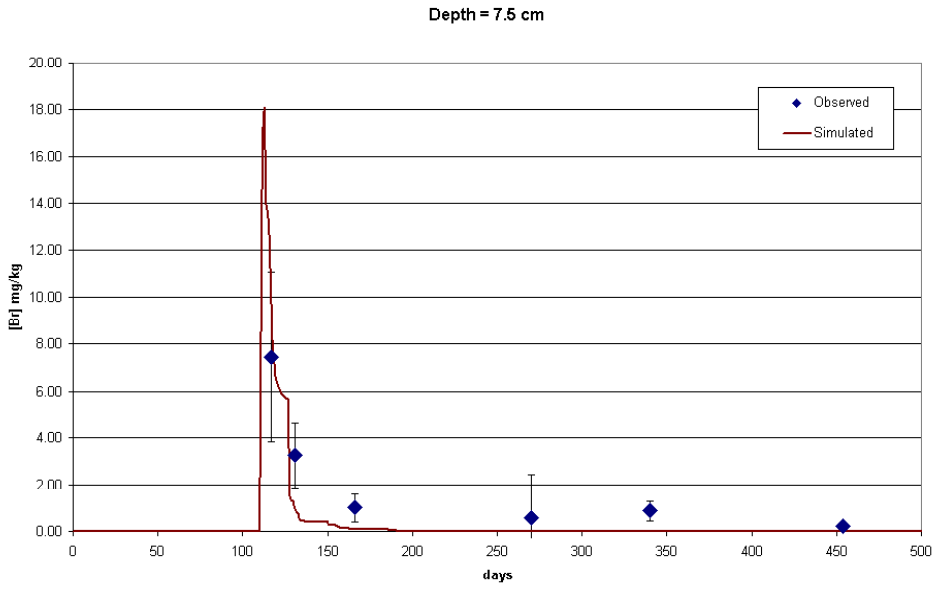


Fig. 103 - Comparison between model predictions and observed values for bromide concentrations at 7.5-cm depth.

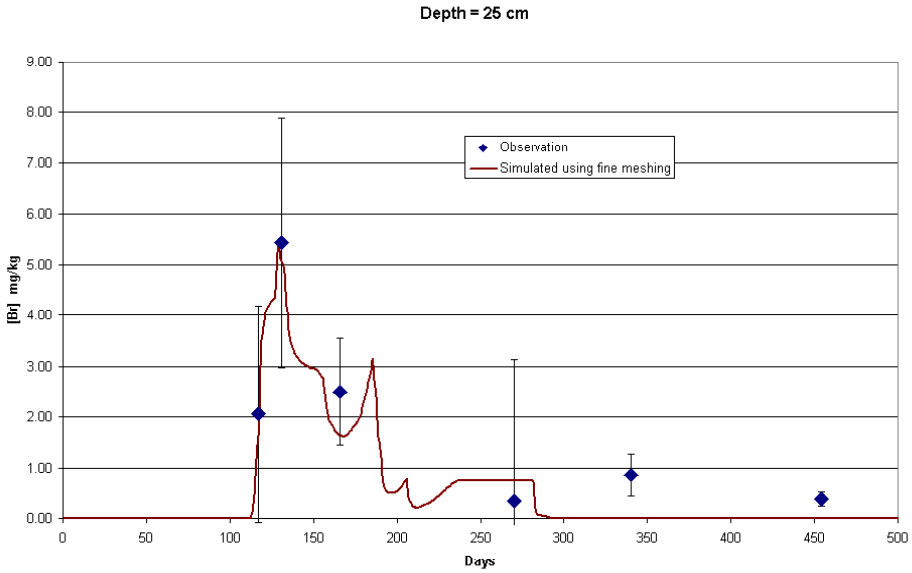


Fig. 104 - Comparison between model predictions and observed values for bromide concentrations at 25-cm depth.

2.1.3. Sensitivity analysis based on simulated bromide concentrations

Values for a range of model parameters were altered from the initial scenario to identify the governing parameters in the simulations and to investigate the potential impact of simplifications of the modelling system. Results from these investigations are presented below.

- Depth of simulated column: simulations with deep and shallow columns were found to be very similar provided that the boundary condition was properly set (Unit gradient). A column of 100 cm was found to be appropriate for simulating the evolution with time of water contents and concentrations in the first 40 cm (soil zone). Reducing the size of the column simulated provides a way to reduce computer time.
- Mesh size: water contents in the profile were found to be adequately simulated using a mesh of 5 or 10 cm (see above). Using a meshing of 1-cm thickness for each mesh in the top soil resulted in significant differences with regard to predicted bromide concentrations (Fig. 105). Bromide moved faster down the profile in a model with wide meshes compared to a model with a finer meshing. This is due to wider meshes creating artificial dispersion. This observation is of particular interest as the refining of mesh size carries a significant computer time cost, in particular when dealing with 2D and 3D models.
- Influence of stones on soil parameters: this test aimed at investigating the effect on predicted water contents of stones. Given that the “calcisol” horizon is constituted of ca. 10 % of stones, comparisons were made between simulations which consider stones as inert (*i.e.* stones do not contribute to any storage of water) and simulations which consider stones to play an active role in water storage. Accounting for the role of stones in storing water did not provide any significant improvement in the goodness-of-fit.

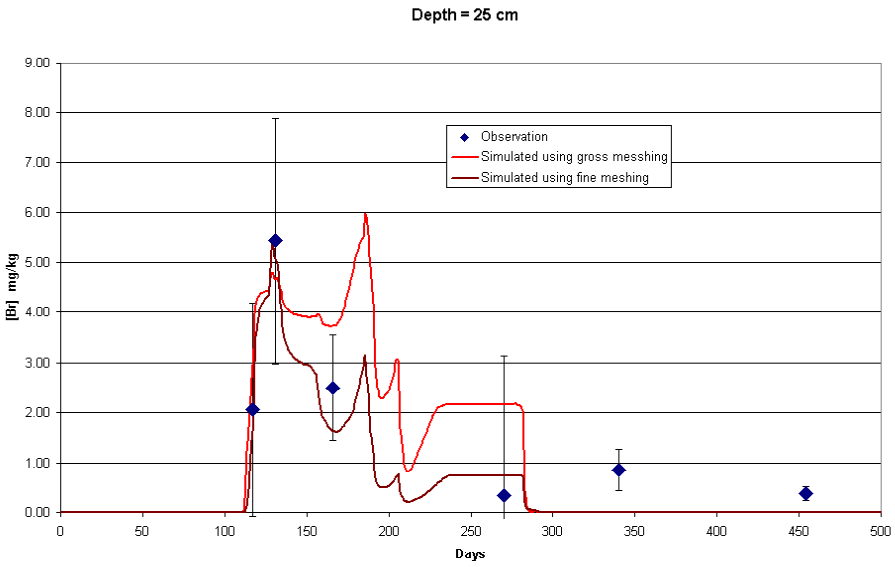


Fig. 105 - Influence of the size of the mesh on predicted bromide leaching.

- Simplification of the two horizons into one: amalgamating horizons can be a useful way to decrease time requirements for model computations. The first two horizons were aggregated in a single one using an equivalent retention law. Although the results were acceptable for the simulation of water contents, predictions for solute transport were negatively affected.
- Influence of crop parameters: accounting for water uptake by plants during dry periods was necessary to improve the fit to experimental data. Extensive testing resulting in the selection of a particular crop development scheme and of adequate Kc values for maize.

2.1.4. Acetochlor simulations

Sorption and degradation parameters were estimated on the basis of laboratory data generated for samples of a similar soil type. A Koc value of 155 ml/g was assumed for acetochlor. Sorption values used in the modelling are presented in Table 25. MARTHE uses a parameter called RHOKD to describe the potential for sorption, which is defined as the product of the sorption coefficient k_d by the density of the soil.

The half life of acetochlor was estimated from laboratory measurements using soils sampled in the field between 0 and 25 cm depth.

Table 25 - Sorption coefficients used in the modelling.

Horizon	foc (%)	k_d (ml/g)	density (g/ml)	RHOKD (%)
38-1	2,14	3,32	1,08	358
38-2	1,21	1,87	1,14	214
Limestone	0,001	0,0015	2,4	0,37

Table 26 - Measured half life for acetochlor.

Soil	Temperature (°C)	DT50 (days)
Calcosol	25	3.5
	15	8.42

Degradation was assumed to be affected by temperature (Arrhenius coefficient γ = 0.097) and water content (Walker parameter β = 0.7) in the modelling. Acetochlor was analysed in soil samples taken over a range of depths on day 117 and 166 (*i.e.* 7 and 56 days after application) and these field data were compared to model predictions.

The initial simulations based on the sorption and degradation parameters above resulted in an over-estimation of measured concentrations. A higher k_d value and a higher degradation rate were then applied to the first 5 cm of soil and results were significantly improved (Fig. 106). Information gained through the 1D modelling was used in subsequent modelling activities in two and three dimensions.

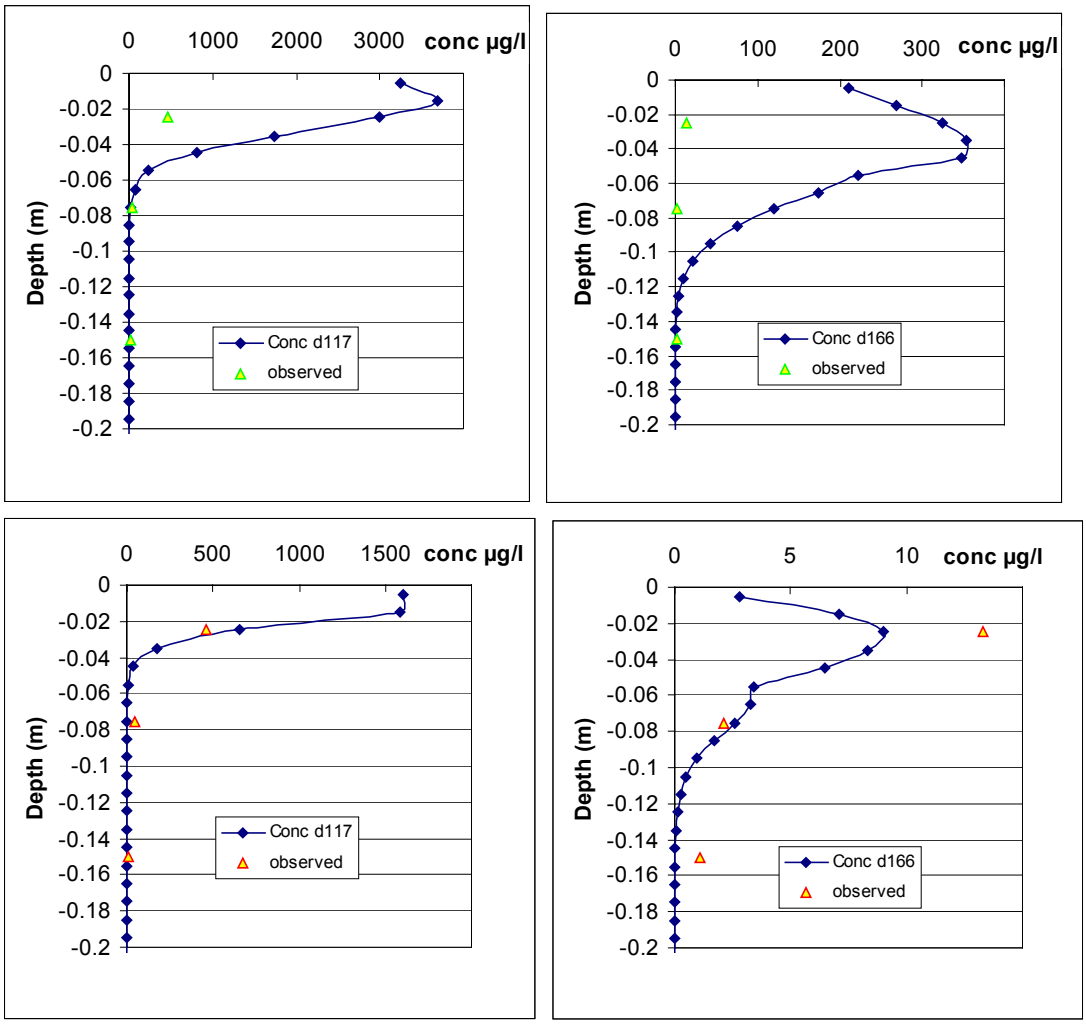


Fig. 106 - Acetochlor profiles in the Calcisol, 7 (left) and 56 (right) days after application. Top = without calibration. Bottom = after modification of Kd and DT50 in the first 5 cm.

2.1.5. Conclusions

One-dimensional modelling of the leaching data collected at Brévilles demonstrated that the MARTHE model is able to simulate the order of magnitude of pesticide transfer in soil provided that the following conditions are met:

- meteorological data on a daily (or shorter) time step;
- a fine discretisation, to adequately simulate solute and pesticide concentrations;
- calibration of kd and DT50.

These conditions required for the success of the modelling in 1D may have serious implications in 2D and 3D modelling as they all lead to an increase in computer time.

2.1.6. Summary

The 1D modelling of the data collected at the Brévilles catchment aimed at gaining hands-on experience with the new functionalities implemented in the MARTHE model. Water flow and bromide transport were initially simulated without recurring to model calibration and model predictions were compared to field data. A range of tests were undertaken to evaluate the influence of variations in model parameters on predictions. The numerical testing demonstrated that model predictions are particularly sensitive to the mesh size and that no simplification of the vertical discretization could be carried out. The model was also used to predict concentrations of acetochlor in soil 7 and 56 days after pesticide application. Overall, MARTHE was found to be able to simulate water flow and bromide and acetochlor transport although model calibration was needed to achieve a good fit to the pesticide data.

2.2. MARTHE modelling in 2D [BRGM]

Two approaches to 2D modelling of the Brévilles site were undertaken: i) 2D saturated modelling aiming at checking the global consistency of aquifer parameters; and ii) 2D variably saturated modelling of a cross section across the catchment.

Modelling the flow in saturated steady state conditions did not present any specific difficulties and a good agreement was obtained between measured data and MARTHE predictions for recharge, water level in piezometers (except for one particular piezometer situated close to a geological fault) and discharge at the gauging station. The fitting to the data was improved by considering two permeability zones in the catchment on the basis of pumping test measurement (Fig. 107).

Piezometer level measurements in the field demonstrated that the aquifer has a strong inertia with respect to changes in water levels. These strongly buffered water levels, could not be replicated through modification of hydrogeological parameters even when very large coefficients of water storage (30 %) were used in the modelling. Since recovery occurred rapidly during pumping tests, it was hypothesized that significant storage was occurring in the unsaturated zone. Consequently, modelling efforts were focused on the simulation of a cross-section across the basin, considering both the saturated and the unsaturated zone.

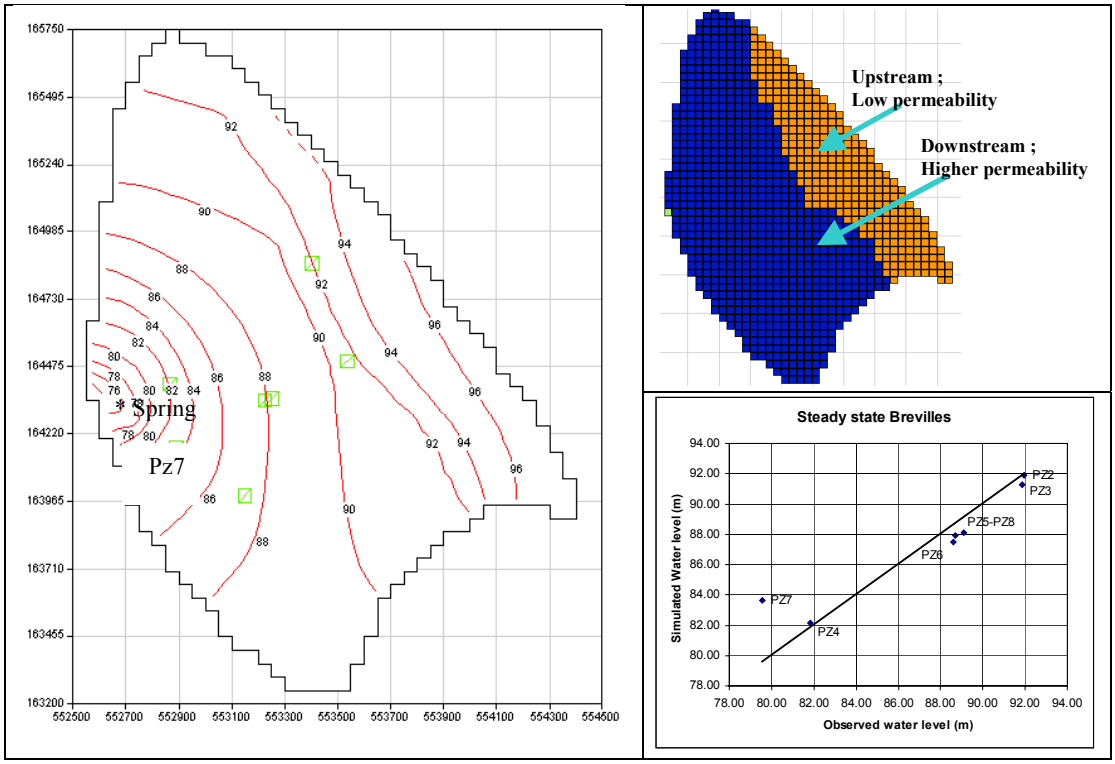


Fig. 107 - 2D saturated model: Simulated head, permeability zones and correlation observed vs. simulated water level.

2.2.1. Methods for the 2D cross section modelling

The 1.65-km long cross section is a straight line in the East-West direction of a flow path extending roughly from PZ3 to the spring and passing through Pz5 and Pz8 (Fig. 108). The grid is composed of 33 50-m wide regular meshes and 12 layers (9 layers for the first metre of soil, 1 layer for the limestone and 2 layers for the sandy aquifer) (Fig. 109). Boundary conditions to the East and to the West were set to no-flow. The aquifer being unconfined, water was allowed to overflow at any place in the catchment. Daily rainfall and potential evapotranspiration were provided to the model and the computational time step was automatically adapted by MARTHE.

Three different soil zones (UCS2 to UCS4) were considered on the basis of the soil map of the catchment. Each of these zones was represented by a soil profile with 2 or 3 horizons. For the nine vertical layers, the parameters of the van Genuchten law selected for the modelling are presented in Table 27.

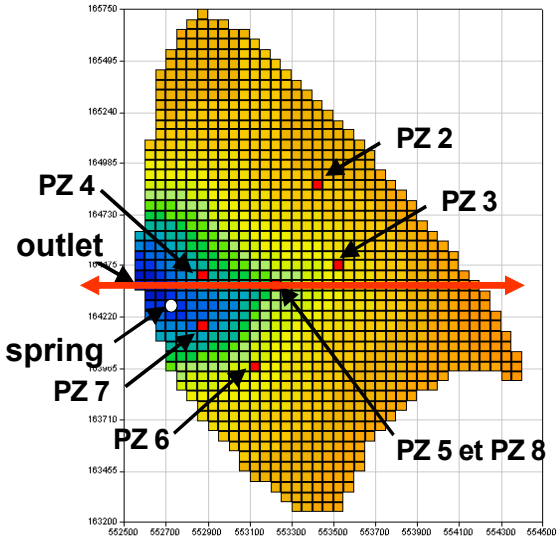


Fig. 108 - Location of the 2D cross section across the basin.

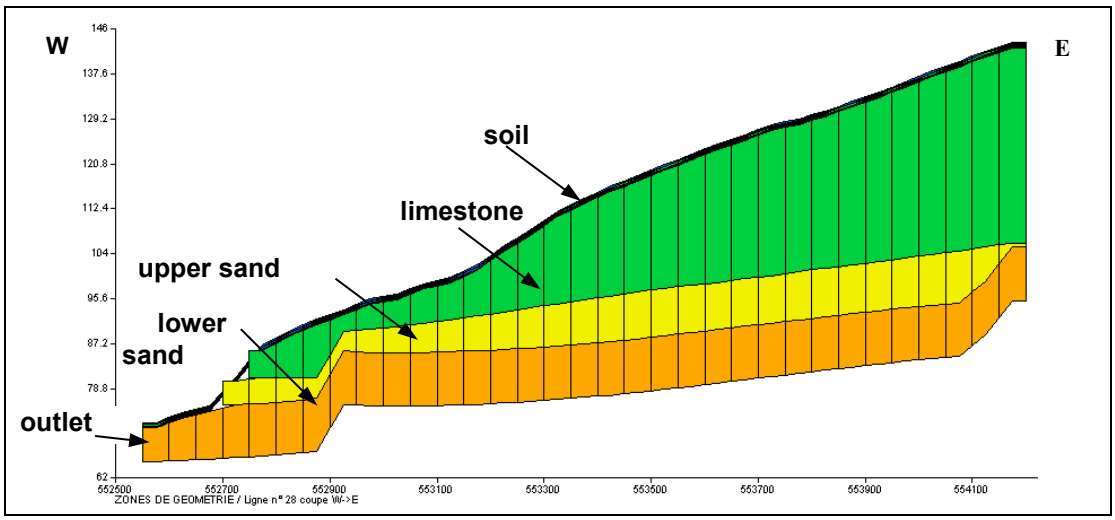


Fig. 109 - 2D cross section across the Brévilles basin.

Table 27 - Van Genuchten parameters for the unsaturated zone.

Layer	Thickness (m)	θs (% vol)	θr (% vol)	α (m^{-1})	n	Ks (m/s)
UCS2 : Calcosol/ Rendosol	0.26	35.0	8.0	0.175	1.224	2.97E-05
	0.14	41.3	8.0	2.697	1.131	1.84E-05
UCS3 : Calcisol/ Rendisol	0.26	41.2	8.0	22.000	1.167	2.95E-05
	0.06	31.0	8.0	1.274	1.247	2.17E-05
UCS4 : Colluvions	0.3	34.6	8.0	2.841	1.201	4.96E-05
	0.72	41.2	8.0	8.468	1.177	4.96E-05
Limestone	29 (avg)	30.0	6.0	0.050	2.000	1.00E-06
Cuise sands	6 (avg)	27.1	6.0	0.011	1.588	1.00E-04
	10	30.9	6.0	0.011	1.417	1.50E-05

2.2.2. 2D modelling results

Figure 110 provides a comparison between measured and simulated water levels in the piezometer Pz 5 located in the middle of the basin. The calibration of unsaturated zone parameters did not improve model performance in simulating the absence of seasonal fluctuation of water levels. In an effort to improve model performance, several hypotheses were made to try to store more water in the unsaturated zone and regulate percolation to the saturated zone. Simulating the presence of a 3-m layer of marls and accounting for more detailed lithological information for the limestone acquired during the drilling did not result in a significant improvement in the goodness-of-fit.

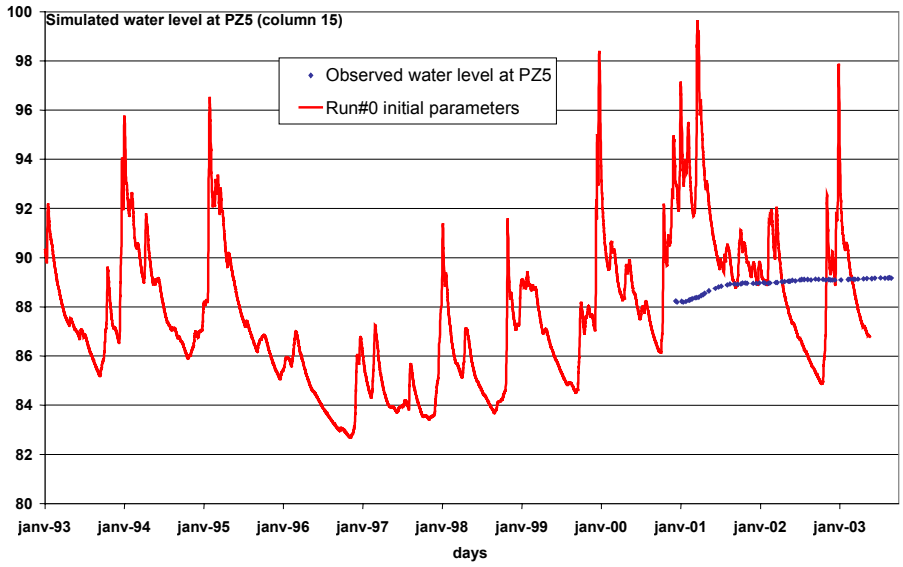


Fig. 110 - Transient MARTHE simulations showing important seasonal variations (red line) while negligible variations in the water levels have been observed in the field (blue dots).

In an attempt to improve model parameterisation, values for all unsaturated zone parameters were modified within acceptable bounds either systematically (one-at-a-time sensitivity analysis) or randomly (Monte Carlo sampling). None of the simulations undertaken provided a simultaneous improvement in water level variations, global hydraulic gradient to the spring and altitude of the water levels.

2.2.3. Discussion and conclusions

The simulations undertaken in 2D demonstrated the difficulty in modelling the behaviour of the Cuise sand aquifer using a deterministic approach. Investigating a large number of combinations of values for the unsaturated zone parameters did not result in the simulation of an attenuated input signal to the saturated zone. Reconsidering the conceptual model (*e.g.* by changing the boundary shapes at boundary conditions) did not improve model performance.

Two explanations may be put forward to explain the poor fit to the data. First, the conceptual model supporting the description of the hydrological functioning of the basin

may be inadequate. Further investigations will be undertaken in the field to try to confirm / infirm the current conceptual model used. Secondly, the laboratory data which were used to support the parameterisation of the model may be inadequate for simulating the behaviour of the groundwater basin at large scale. Although these data provided satisfactory simulations at the scale of the soil column, further characterisation might be needed to obtain valuable simulations at larger scales. Integrating information on soil and unsaturated layers in a less deterministic way (*e.g.* by allowing parameters to be varied outside the range of laboratory experimental values) would probably lead to a better fit to the field data. However, the potential for extrapolation using a model parameterised in such a way may also be questioned.

2.2.4. Summary

The conceptual model for the hydrological functioning of the Brévilles groundwater basin was first evaluated using a simple monolayer 2D model in steady state. The modelling then focused on 2D simulations using a vertical cross section along a flow path. The cross section flow model integrates information on geological layers and soil horizons with variably saturated conditions and the climate. In transient state, the testing of a large number of combinations of input parameters did not allow a satisfactory representation of the hydraulic behaviour of the aquifer.

2.3. Modelling with MACRO [SLU]

Fissured chalk and limestone represent especially vulnerable hydrogeological settings for pesticide contamination, since only shallow soils overly the fractured rock, which itself may be prone to rapid preferential transport of pesticides in the fissures. Fractured chalk and limestone is widespread throughout Europe, and especially important drinking water aquifers are located across large areas of the Paris and London basins. Significant atrazine contamination of these aquifers at levels above the drinking water standard is sometimes reported (Chilton *et al.,* 1995) and it is important to fully understand the mechanisms by which this contamination arises. In the deep unsaturated fissured chalk vadose zone in southern England, isotope profiling combined with investigations of rock hydraulic properties indicate that at some locations recharge processes are dominated by flow in the porous chalk matrix with steady downward percolation rates of ca. 0.5 to 1 m/year, while at other locations, fissure flows during periods of heavy rain seem to contribute significantly to the recharge (Welling and Cooper, 1983; Darling and Bath, 1988; Geake and Foster, 1989). The key factors determining whether recharge is either matrix dominated or influenced by fissure flow were shown to be the saturated hydraulic conductivity of the chalk matrix (of the order of 0.5 to 5 mm/day) and the depth of soil overlying the chalk (Geake and Foster, 1989), since a deeper soil cover resulted in the dissipation of macropore flows before they reach the fissured chalk. Recently, Haria *et al.* (2003) demonstrated the importance of the depth of the unsaturated chalk vadose zone in controlling the generation of fissure flow. At downslope locations with shallower water tables, the chalk matrix remained close to saturation due to the effects of the ‘capillary fringe’, and this led to more frequent activation of flow in the fissures, compared to upslope locations with deeper water tables. Jarvis (2002) hypothesized that preferential flow in the soil root zone may be significant even when matrix processes dominate transport from the base of the root zone to the groundwater. This is because the attenuation of agrochemical transport by sorption and degradation is generally much weaker in deep vadose zones and groundwater

compared to soil (section 7 in chapter 1, Pothuluri *et al.,* 1990; Moreau and Mouvet, 1997).

Application of a mechanistic model able to simulate preferential flow and transport could prove useful in furthering our understanding of the mechanisms controlling pesticide leaching through these fissured rock systems. No attempts to model these processes in a coupled soil/fissured rock system have been published to our knowledge. Chilton *et al*. (1995) compared LEACHP model predictions with measured atrazine profiles in the English chalk, but LEACHP does not account for the possible occurrence of fissure flow. The upgraded version of the MACRO model developed in PEGASE (section 1.1. in chapter 2) was therefore used to investigate the controls on atrazine leaching through a luvisol overlying unsaturated fractured limestone at Brévilles, France (section 1 in chapter 1).

2.3.1. Methods

A two-stage modelling procedure was adopted. The model was first parameterised through a combination of direct measurements and calibration using data obtained from field sampling and measurement campaigns at the 'luvisol' field site. In the second stage of the modelling procedure, long-term Monte Carlo 'scenario' simulations were run to investigate the controls on atrazine leaching through the combined soil/fissured limestone sequence, based on an assumed application pattern, and accounting for uncertainty in several key input parameters for both the soil and rock. Two different depths to groundwater were considered. As a qualitative 'reality check', the simulated flux concentrations at the base of the profile were compared to atrazine concentrations measured in piezometers and at the spring in the Brévilles catchment.

- ***Model parameterisation for the soil root zone***

Parameters of the van Genuchten (1980) function were derived by least-squares fitting to measured water retention data, while saturated hydraulic conductivity was also based on measurements (Table 28).

Table 28 - Physical and hydraulic parameters for the luvisol.

Horizon	θ_s (%)	θ_b (%)	θ_w (%)	α (m^{-1})	N	K_s mm h^{-1}	n*	γ (g cm^{-3})
0-30 cm	41	32	13	2.4	1.14	40	4	1.58
30-60 cm	44	36	16	3.1	1.14	43	4	1.46
60-90 cm	42	36	21	2.6	1.09	45	4	1.46
90-100 cm	42	39	22	2.3	1.09	45	4	1.46

θ_s saturated water content — θ_b saturated matrix water content
θ_w wilting point — α, N shape parameters in the van Genuchten equation
K_s saturated hydraulic conductvity — n* kinematic exponent — γ bulk density

Four solute transport parameters were calibrated against bromide leaching data obtained from field experiments carried out in two years (2000 and 2001): the solute dispersivity in the matrix, the stream concentration factor controlling uptake into the plants, and two key parameters controlling the strength of macropore flow, namely the saturated matrix hydraulic conductivity and the effective diffusion pathlength. The SUFI routines incorporated into MACRO5.0 were used for this calibration (section 1 in chapter 2, Abbaspour *et al.,* 1997).

Atrazine first-order degradation rate constants for the luvisol at Brévilles estimated from rates of CO_2 evolution in laboratory incubation experiments (see section 7 in chapter 1) seemed very small in comparison to those normally reported in the literature. The reason for this is not clear, but it may be because the initial concentrations used were quite small (L. Clausen, pers.comm.). A half-life in the topsoil of 50 days for atrazine at optimum soil moisture and 20°C based on data in the literature was selected. Degradation rate coefficients in the subsoil were calculated based on the default FOCUS multiplication factors of 0.5 at 30 to 60 cm depth and 0.3 at 60 to 100 cm depth. The sorption K_f values were set to 2.42 and 1.07 cm^3/g in the topsoil and subsoil respectively, based on the measured batch data obtained at the site (see section 7 in chapter 1).

- ***Monte Carlo simulations for the soil/limestone sequence***

For each scenario, a total of 150 Monte Carlo simulations were run for the complete soil/limestone sequence. The simulation scenarios represented three different degrees of macropore flow in the soil root zone and two groundwater depths (15 and 31 m respectively).

Four parameters characterizing the physical and hydraulic properties of the limestone were treated stochastically, namely the porosity and saturated hydraulic conductivity of the limestone matrix, the van Genuchten α parameter for water retention in the limestone matrix, and the 'effective' half-spacing between fissures, *d*. For the latter parameter, only qualitative information was available to support the choice of parameter distribution, namely observations from borehole drillings that fissuring is quite dense in the limestone underlying the Brévilles catchment. A log-normal distribution was assumed with a mean of 2 m and a standard deviation of 1 m. A limited amount of quantitative data was available to support the parameterisation of the three remaining hydraulic parameters. The van Genuchten function was fitted to measured water retention curves for the limestone to derive 15 individual values of the shape parameters α and *N* and the matrix porosity $\theta_{s(m)}$ (the residual water content was set to zero). *N* did not vary much and was therefore fixed at the mean value. Both α and $\theta_{s(m)}$ were found to be log-normally distributed and weakly correlated (r = 0.125). The fitted parameter values were used to estimate means and standard deviations of the distributions (see Table 29), which were then sampled using the Latin hypercube method, accounting for their correlation (Janssen *et al.,* 1992). The saturated matrix hydraulic conductivity is related to α and $\theta_{s(m)}$ by (Miller & Miller, 1955; Hoffman-Riem *et al.,* 1999):

$$K_{s(m)} = k_o \, \theta_{s(m)} \, \alpha^2$$

where k_o is a composite parameter, estimated here from the mean measured values of $K_{s(m)}$, α and $\theta_{s(m)}$. The stochastically generated values of α and θ_s were then used together with this estimate of k_o (= 0.057 m^3 h^{-1}) to generate a distribution of $K_{s(m)}$ values. The fissure porosity in the limestone was fixed at 1 %, and the total saturated hydraulic conductivity of the limestone (*i.e.* including the fissures) was assumed equal to 3,600 mm h^{-1}.

Table 29 - Distributions of physical/hydraulic parameter values for the limestone.

Parameter	Distribution	Mean	St.dev.	Max.	Min.
$\theta_{s(m)}$ (m^3 m^{-3})	Log-normal	0.103	0.036	0.247	0.081
α (m^{-1})	Log-normal	0.0365	0.070	0.187	0.0013
$K_{s(m)}$ (mm h^{-1})	Log-normal	0.039	0.069	0.381	1.02×10^{-5}
D (m)	Log-normal	2	1	5	0.5

The atrazine degradation rate coefficient was set to zero in the limestone, based on the lack of degradation observed in the one-year incubation experiments carried out at Brévilles (section 7 in chapter 1). Sorption K_f values were set to 0.09, 0.05 and 0.03 cm^3 g^{-1} at depths of 1 to 3, 3 to 6 and 6 to 8 m respectively. Sorption was found to be negligible in the limestone at depths below 8 m (section 7 in chapter 1).

The simulations were run from 1958 to 2002. Atrazine applications were assumed to take place every 4 years starting in 1963, at a dose of 2 kg/ha until 1991, and thereafter at 1 kg/ha. An initial condition of drainage equilibrium in the entire profile was assumed. Since the profiles were rather deep, a long warm-up period (5 years) for the hydrological component of the model was considered appropriate. A pressure head of zero was set at the bottom boundary. Driving data consisted of daily potential evapotranspiration (calculated from 10 day averages) and hourly rainfall data obtained by stochastically disaggregating daily data according to the method described by Olsson (1998). Parameter values for the stochastic disaggregation were taken from an analysis of high time resolution rainfall data from southern England (Gunther *et al.,* 2001). Stochastically generated hourly rainfall data was used, since the generation of non-equilibrium macropore flow is known to be strongly influenced by rainfall intensity (Jarvis, 2002).

2.3.2. Modelling results

- ***Hydrology and non-reactive transport in soil***

Reasonable simulations of the soil water content profiles at the Luvisol site were obtained (see Fig. 111). This gives confidence that the simulated water balance is also reasonable, which is important for the subsequent transport modelling.

For bromide transport, best-fit values of 1.5 cm and 0.61 were obtained for solute dispersivity and the uptake concentration factor respectively. The outcome of the calibration procedure was, however, inconclusive with respect to the extent of macropore flow occurring at the site. Figure 112 shows a 2D response surface of the goal function for the two calibrated parameters, the saturated matrix conductivity K_b and the effective diffusion pathlength d. It shows a large degree of insensitivity across a wide range of values for d and K_b and no clear global minimum. In fact, two smaller 'best-fit' areas are apparent, one at large values of d and small values of K_b, which would imply strong macropore flow, and one at small values of d (with K_b insensitive), which implies conditions of physical equilibrium without macropore flow.

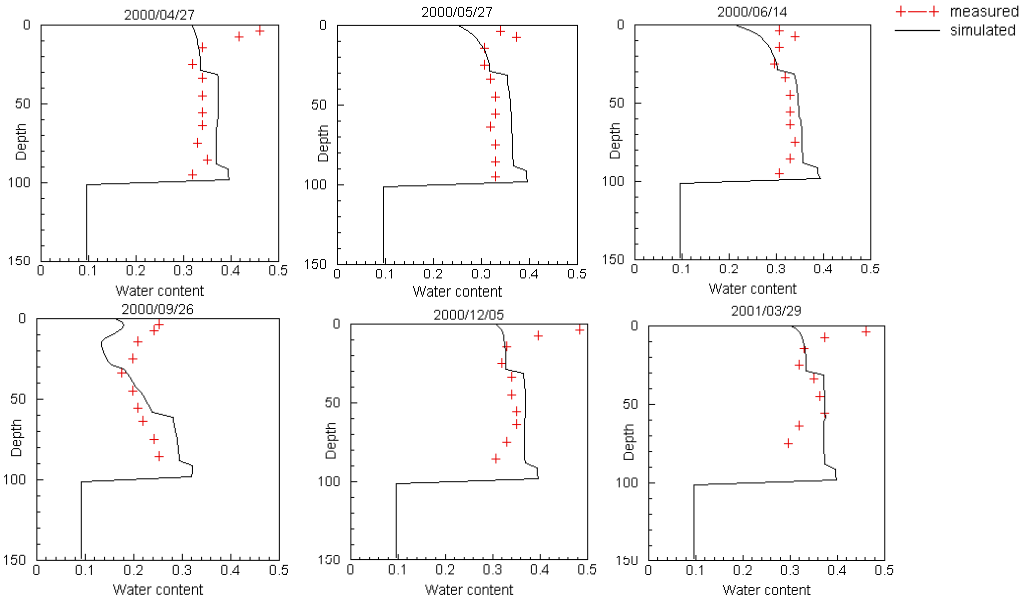


Fig. 111 - Measured (crosses) and simulated (line) soil water contents at Brévilles for the Luvisol, in the measurement campaign of 2000.

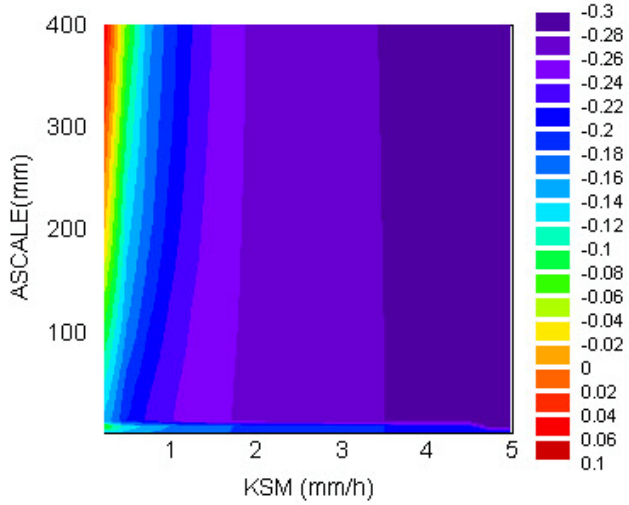


Fig. 112 - Response surface of the goal function for the effective diffusion pathlength (ASCALE) and the saturated matrix hydraulic conductivity (KSM). MACRO5.0 simulations of the bromide leaching experiments in 2000 and 2001.

This inconclusive result is due to the data used to condition the model. Some of the individual measured bromide resident concentration profiles indicated the occurrence of macropore flow while others suggested convective-dispersive transport (Fig. 113), and other profiles (here termed 'Intermediate') could not easily be classified. Even though the model could be successfully calibrated against the mean resident concentration profile using a single 'effective' parameter set (see Fig. 113), it was considered that these results were probably not physically meaningful. An attempt was therefore made to sort the profiles into two groups (with and without macropore flow), prior to calibrating separately against the mean profile for each group, but this did not

prove successful. Instead, three alternative scenarios intended to cover a broad range of preferential flow behaviour in the soil root zone were defined: a simulation without macropore flow, where convective-dispersive transport is assumed to dominate (d = 1 mm, K_b = 2 mm h^{-1}), a simulation with very strong macropore flow (d = 230 mm, K_b = 0.1 mm h^{-1}), and an intermediate situation with moderate macropore flow behaviour (d = 50 mm, K_b = 1 mm h^{-1}).

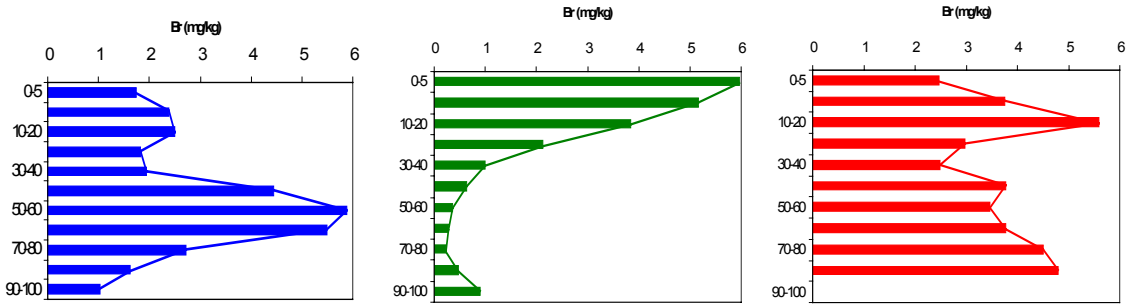


Fig. 113 - Selected individual resident concentration profiles for bromide, 21 days after application in 2000, representing situations of convective-dispersive transport (left), strong macropore flow (centre), and 'Intermediate' flow (right).

- ***Atrazine leaching***

Figure 115 illustrates the effects of the depth to groundwater on atrazine concentrations predicted in recharge, for the case of strong macropore flow in the soil. In the simulations shown in Figure 115, the limestone was treated deterministically, assuming average values of θ_s, α and $K_{s(m)}$ (Table 30).

Figure 115 shows that the pattern of leachate concentrations is 'peakier' in the case of shallow groundwater, with the fissure flow 'signals' being less dampened. Otherwise, there is very little effect on the overall level of leachate concentrations, despite the large difference in thickness of unsaturated limestone assumed in the simulations. This is reinforced by Figure 116 which shows that the main difference in leached amounts lies in the longer 'lag' period before leaching starts in the case of the deeper groundwater. The total leaching was predicted to be 0.5 % of the applied amount in the case of shallow groundwater.

The reason for the lack of influence of the extent of the capillary 'fringe' on leaching is explained in Figure 117, which shows that the uppermost layer of the limestone matrix remains virtually saturated for both the shallow and deep groundwater cases. This is due to the water retention characteristics of the limestone, which in contrast to the chalk studied by Haria *et al.* (2003), is maintained close to saturation even at very large tensions (see Table 29).

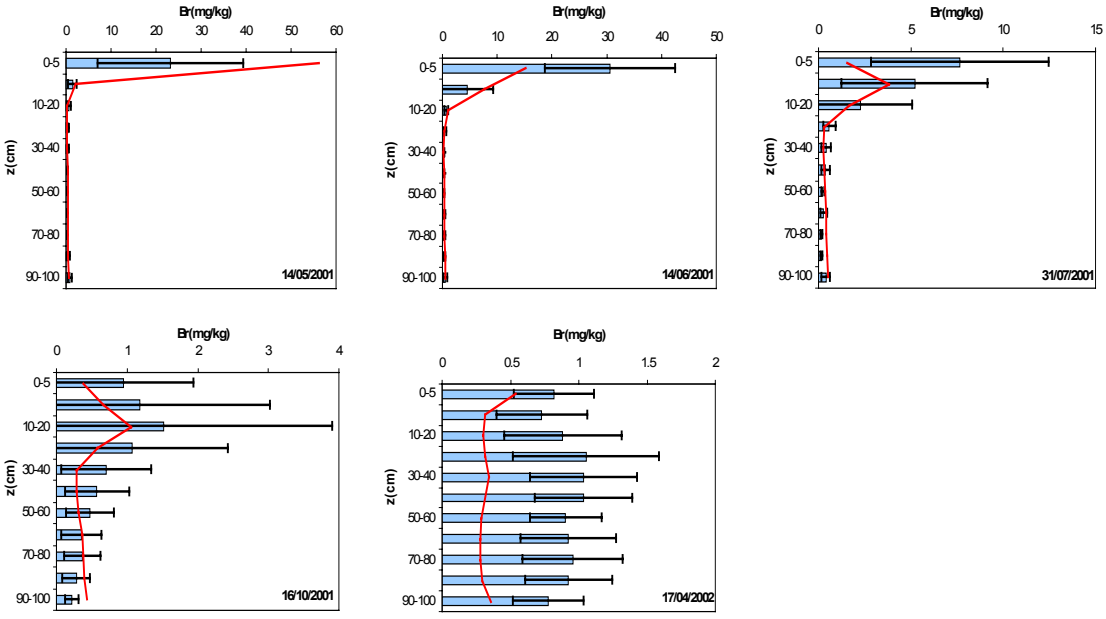


Fig. 114 - Measured (bars) and simulated (lines) bromide concentration profiles in the Luvisol, 2001. Note the change of scales on the x-axes.

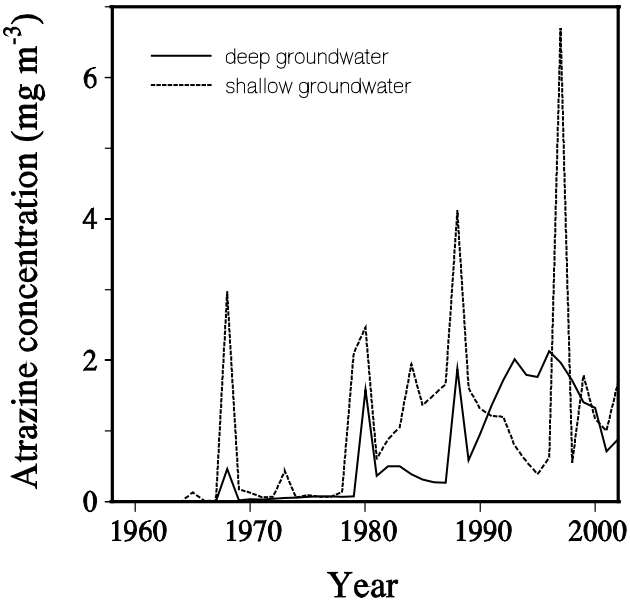


Fig. 115 - Effect of groundwater depth on simulated average yearly flux concentrations of atrazine entering groundwater (strong macropore flow case) for deterministic simulations*, i.e. *average physical/hydraulic properties have been assumed.

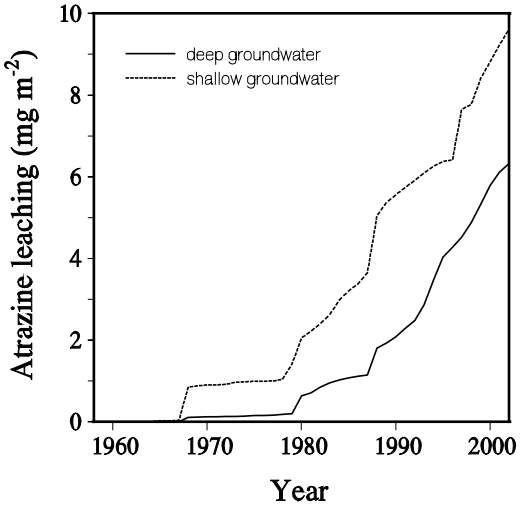


Fig. 116 - Accumulated atrazine leaching predicted for deep and shallow groundwater, with zero degradation assumed in the limestone.

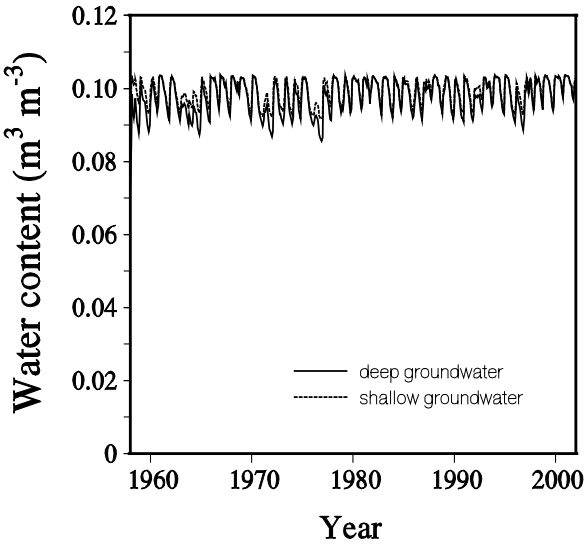


Fig. 117 - Simulated water contents in the uppermost layer of limestone at 1.05 m depth, in the cases of deep and shallow groundwater.

Figure 118 also shows that the atrazine concentrations predicted in recharge water for the average case are of a similar order of magnitude (ca. 1 μg/l on average during the latter part of the simulation) as those recorded in groundwater samples and at the spring at the Brévilles site (ca. 0.2 μg/l is recorded on average at the Brévilles spring, section 1 in chapter 1). This is at least a qualitative indication that the conceptual model and its parameterisation for the soil-limestone sequence at Brévilles are quite reasonable.

The deterministic simulations for the cases of 'intermediate' macropore flow and convective-dispersive transport were very similar, with no measurable atrazine concentrations reaching the base of the soil profile at 1 m depth. This implies that the uncertainties with respect to both the appropriate conceptual model of the leaching mechanisms operating in the Luvisol, and its parameterisation, are highly critical.

The results of the Monte Carlo analysis for the case of strong macropore flow in soil and deep groundwater are shown in Table 30. The overall r^2 value of the multiple regression between inputs and outputs was 0.96 for ranked data, which indicates the existence of monotonic relationships that allow for unequivocal interpretation. The saturated matrix water content was not significantly correlated to the model outputs. Of the remaining three parameters, the saturated matrix conductivity in the limestone was ranked as most significant (Table 30), followed by the fissure spacing.

Table 30 - Partial rank correlation coefficients between model outputs (total atrazine leaching loss) and stochastic input parameters (with deep groundwater and 'strong' macropore flow in the soil).

Parameter	Partial rank correlation coefficient
Saturated matrix conductivity	-0.37
Half crack spacing	0.22
Van Genuchten α	0.17

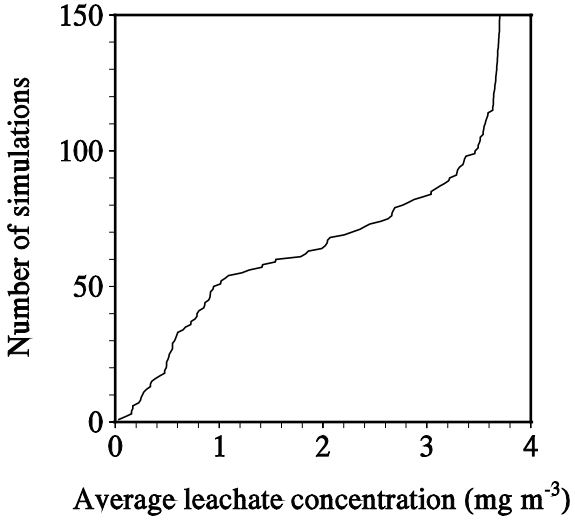


Fig. 118 - Distribution of average atrazine concentrations entering groundwater (deep groundwater case, 'strong' macropore flow in soil).

For the same scenario, Figure 118 shows the distribution of average atrazine concentrations entering groundwater (deep groundwater case). These concentrations have been calculated simply as the total leaching divided by the total water percolation for the entire simulation period, including the period prior to atrazine applications. For comparison, the average leachate concentration produced by the simulation using average properties was 0.75 μg/l, which as expected, is much smaller than the 50th

percentile concentration (= 2.63 μg/l) predicted in the stochastic approach. It is also interesting that the distribution of simulated leachate concentrations appears to be slightly bimodal in nature, presumably related to the presence or absence of significant preferential transport in the limestone.

One difficulty in interpreting these results is that significant quantities of atrazine remain stored in the limestone at the end of the simulation period, which must sooner or later leach to groundwater, since zero degradation was assumed. In this case, the nature of the transport processes operating in the limestone should only influence the pattern of leaching (*e.g*. the degree of attenuation of peak concentrations), and not the total amount leached. In this respect, it can be noted that the laboratory incubation studies were carried out for one year. With very long half-lives, it is quite possible that atrazine mineralisation may not be detectable even after one-year. For example, half-lives of 20 and 10 years imply 3 and 7 % degradation respectively after 1 year. These values may be within the margins of experimental error. The results of the Monte Carlo analysis could therefore change significantly if atrazine does in fact degrade in the limestone, even with a half-life as long as 10 to 20 years. This is because the transport times of atrazine through the unsaturated zone are as long as this, for a significant number of the Monte Carlo simulations. Even though many studies confirm the general lack of atrazine degradation capacity in aerobic aquifers, and also in unsaturated chalk (Johnson *et al.,* 2000), several other experiments have indicated a potential for atrazine degradation. For example, in one extreme case, Issa & Wood (1999) found degradation half-lives for atrazine of ca. 6 months in English chalk aquifer material. Based on model calibrations, Levy and Chester (1992) derived a half-life of ca. 10 years for atrazine degradation in an aerobic sandy aquifer, while McMahon *et al.* (1992) estimated a half-life of ca. 3 years in similar aquifer material based on short-term incubations.

It is recommended that the Monte Carlo simulation exercise should be repeated, using an assumed distribution for atrazine half-life in the limestone, based on literature data and also allowing for a sufficiently long period of 'self-remediation' of the unsaturated limestone, without atrazine applications at the surface.

2.3.3. Conclusions

The main conclusions that can be drawn from this work are:

- the flow and transport processes occurring in the soil, especially the presence or absence of macropore flow, will largely control the leaching losses of atrazine. The nature of the transport process through the deep unsaturated, fractured, limestone (*i.e.* whether or not preferential flow and transport is significant) also influences the temporal patterns of leaching losses, but should be less important for the total loss when degradation is negligible. With non-negligible degradation, the saturated hydraulic conductivity in the limestone matrix will probably be the most important vadose zone parameter controlling leaching, although more research is needed to confirm this suggestion;
- leaching of atrazine was predicted to be negligible in the absence of macropore flow in the soil. With 'strong' macropore flow in the soil, predicted concentrations of atrazine entering groundwater averaged 1 μg/l, compared to concentrations of ca. 0.2 μg/l recorded on average at the Brévilles spring.

- changing the depth of the water table from 15 to 31 m had little influence on simulated leaching losses, since the uppermost layers of the rock matrix remained largely water saturated in both cases.

2.3.4. Summary

The upgraded one-dimensional dual-permeability model MACRO was used to simulate atrazine leaching through a Luvisol-unsaturated limestone sequence at Brévilles, France. The objectives were to identify the main controls on pesticide leaching through shallow soils overlying fissured limestone. MACRO was first calibrated to bromide transport experiments carried out during two years at the Brévilles site. No unequivocal calibration was possible, and significant uncertainty remained concerning the correct conceptual model to describe solute transport through the soil. Some individual resident concentration profiles indicated the occurrence of macropore flow, while others indicated convective-dispersive transport. Three scenarios were therefore constructed representing 'strong' macropore flow, 'intermediate' macropore flow, and convective-dispersive transport.

Scenario simulations were carried out for leaching of the maize herbicide atrazine for the period 1958 to 2002. No site-specific information on historical atrazine usage in the catchment was available, so a typical use pattern was assumed, with atrazine applied every 4 years starting in 1963, at a dose of 2 kg/ha until 1991, and thereafter at 1 kg/ha. Four physical/hydraulic properties of the limestone were treated as stochastic parameters in Monte Carlo simulations. Two depths to the water table were considered, 15 and 31 m.

For 'intermediate' macropore flow and convective-dispersive transport in the soil, no detectable leaching of atrazine was simulated. In the case of 'strong' macropore flow, simulated atrazine concentrations entering groundwater reached ca. 1 μg/l assuming average properties in the limestone, compared to measured concentrations at the spring at Brévilles of ca. 0.2 μg/l. Processes occurring in the soil exerted the main control on leaching losses, especially the presence or absence of macropore flow. With respect to vadose zone properties, the stochastic analysis suggested that the saturated hydraulic conductivity of the limestone matrix appears the most important, followed by the fissure spacing.

2.4. Modelling with POWER [LTHE]

Due to the late development of POWER, the simulation of the Brévilles dataset reported in the present report should be considered as a preliminary exercise. The majority of the input data concerning the subsoil, in particular the hydraulic characteristics and the spatial repartition of geological layers, were not considered in the modelling. Consequently, some hypotheses have been made for the subsoil configuration. The simulation was limited to water movement although further work on pesticide leaching in Brévilles will be undertaken.

2.4.1. Data analysis and parameter estimation

- ***Pre-processing of upper layer***

Since the concept of POWER is based on discretisation into Representative Element Columns (RECs), where each REC is represented by uniform soil, slope and land use, whatever its shape and surface, a pre-processing of available data had first to be made to define the distribution of REC within the catchment. First, maps of elevation, slope and drainage network were built by the use of a Digital Elevation Model (Fig. 119).

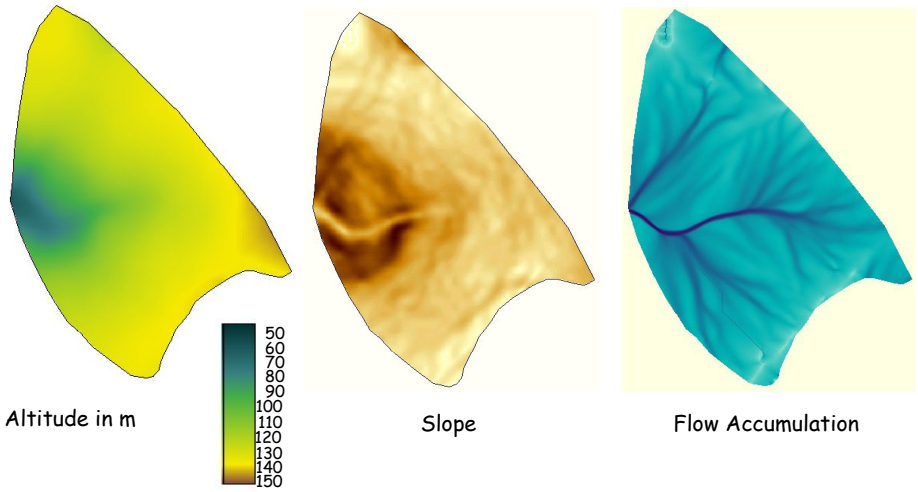


Fig. 119 - Pre-processing from the Digital Elevation Model.

Secondly, the maps of soil, soil hydraulic conductivity (obtained by pedotransfer functions), infrastructure and land use were built (Fig. 120). Finally, the distribution of RECs was obtained by superposition of all previous maps (Fig. 121). The Brévilles site was represented by a total of 277 RECs.

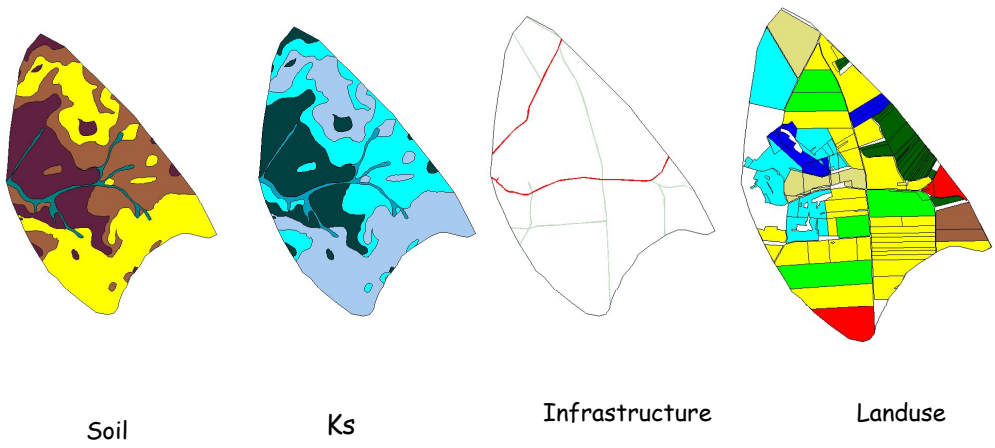


Fig. 120 - Input data for REC.

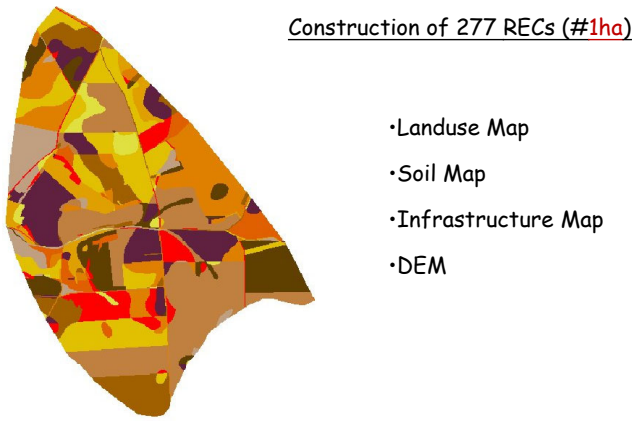


Fig. 121 - Discretisation of the landscape in RECs.

- ***Subsoil***

Information concerning spatial distribution and textural properties (to induce hydraulic parameters with the use of pedotransfer functions) was only available for the soil, with a thickness ranging from 0.5 to 1 m. Information concerning the subsoil was limited to that obtained when the seven piezometers were drilled. These piezometers are located on a transect. The information was mostly visual and did not allow the determination of hydrodynamic parameters. The three dimensional distribution of the subsoil was simulated with 4 layers reported on Figure 122, corresponding to two transects across the catchment. Bedrock information was obtained through BRGM (Fig. 123).

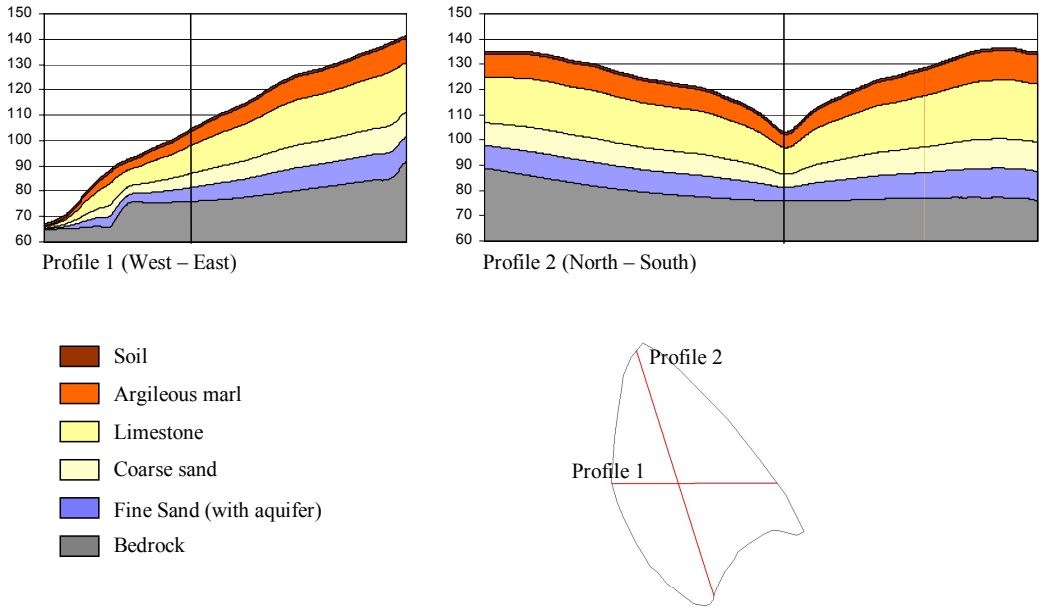


Fig. 122 - Simulated geology considered in the modelling.

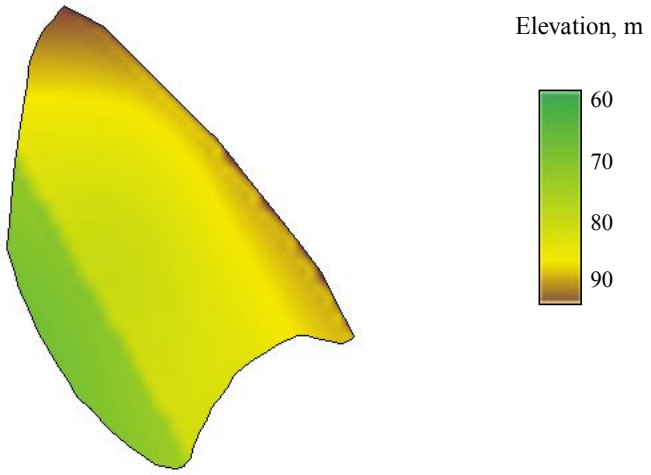


Fig. 123 - Simulated bedrock considered in the modelling.

In order to run the simulation, each layer was defined by the relationship between hydraulic conductivity K and water content θ, and the relationship between soil water pressure h and water content θ. In both cases the phenomenological relationship used in POWER are those defined by Brooks & Corey (1964), namely:

$$K(\theta) = K_s\ (\theta/\theta_s)^{\eta} \quad (1)$$

$$h(\theta) = h_e\ (\theta/\theta_s)^{\lambda} \quad (2)$$

Consequently five parameters had to be determined for each layer:

- K_s, the saturated hydraulic conductivity (m/s);
- θ_s, the saturated water content (m^3/m^3);
- h_e, the air entry value (m);
- η and λ, the shape parameters of the relationships $K(\theta)$ and $h(\theta)$.

In the absence of direct measurements, the parameters were estimated by the use of pseudo-empirical relationships, which typically result from multiparameter correlation which relate parameter values to texture, density, organic matter, etc. These types of relationships are only valid for soil and cannot be used for rock, most particularly for fracture rocks such as limestone which are particularly abundant on the Brévilles catchment. Also, the conceptual model POWER is based on Richards' equation which is not suitable for simulating water flow in fractured limestone. Geological layers were replaced by corresponding soil layers. The fractured limestone horizon was assimilated to coarse sand, and the argileous marl horizon to clay. The parameters used in equations 1 and 2 were inferred from the GRIZZLI database (Haverkamp *et al.,* 1998) and from the recent work of Haverkamp *et al.* (2003a, b). They are presented in Table 31.

Table 31 - Hydrological properties used in the modelling.

	Layer1 Top Soil	Layer 2 (Marl) Clay	Layer3 (limestone) Coarse sand	Layer 4 Gravel	Layer 5 Fine sand
K_s, m/s	$1.\ 10^{-5}$	$1.6\ 10^{-7}$	$1.5\ 10^{-5}$	$2.4\ 10^{-5}$	$9.1\ 10^{-6}$
θ_s, m^3/m^3	0.35	0.41	0.2	0.27	0.3
h_e, m	0.15	0.7	0.01	0.15	0.1
η	24	8.3	3.7	3.7	4.7
λ	0.1	0.2	0.5	0.33	0.36

2.4.2. Modelling results

The intrinsic quality of numerical simulation is dependent upon three basic criteria:

- the conceptual capacity of a model to reproduce the simulated problem;
- the adequacy of initial and boundary conditions with those met in the real case;
- the adequacy of internal parameters with those corresponding to the study.

In the present case, criterion #1 has been previously checked by comparison between analytical and numerical solutions. Criteria #2 and #3 could not be satisfied as little information on the initial water contents and pressure heads and on transport parameters was integrated into the modelling. Given the strong non linearity of the flow equation, this implies that no proof of the validity and unicity of the solution can be provided.

The simulation was therefore intended as a way to demonstrate that the programme runs properly and to obtain some information concerning the possibility of water transfer (and consequently some transport of pesticide) from the soil to the aquifer. The modelling was undertaken for the year 2001 with a daily time step and the following assumptions:

- hydrostatic equilibrium above the water table (initial condition);
- no flow at the bedrock level;
- land use corresponding to observations (when available);
- hydrometeorological input corresponding to observations.

No percolation to the water table was simulated along the two transects considered. Without being a proof of validity, this information is compatible with the fact that almost no change in watertable depth was observed in the field (section 1 in chapter 1).

Let's consider 2 RECs corresponding to extreme conditions: REC134 with bare soil (in fact no information concerning land use) and REC 122 with winter wheat. Figure 124 presents results for cumulative mass balance computed on a yearly basis at one hour time step, values of cumulative rainfall, cumulative infiltration and cumulative evapotranspiration in the first layer (soil). Similarly, the evolution of water content profiles for the same situation is provided at four times (t0, 30 March, 30 June and 30 September) in Figure 125.

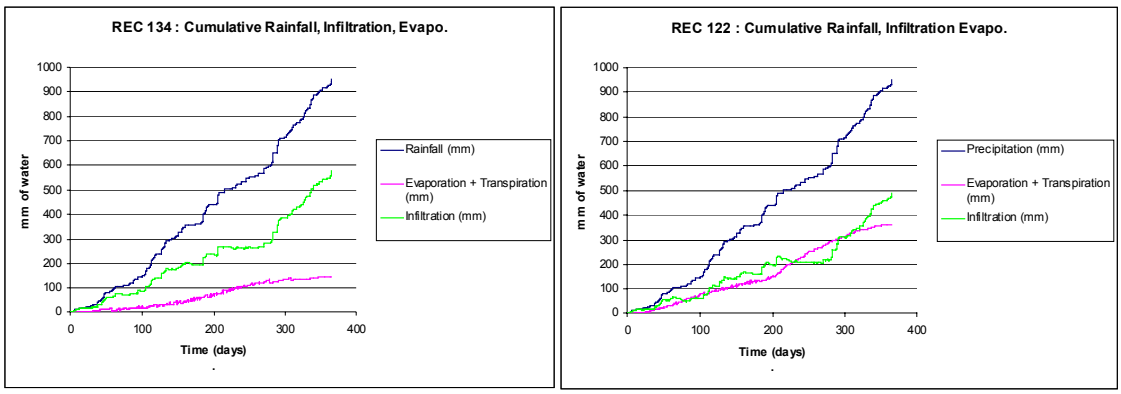


Fig. 124 - Cumulative mass balances for two extreme RECs.

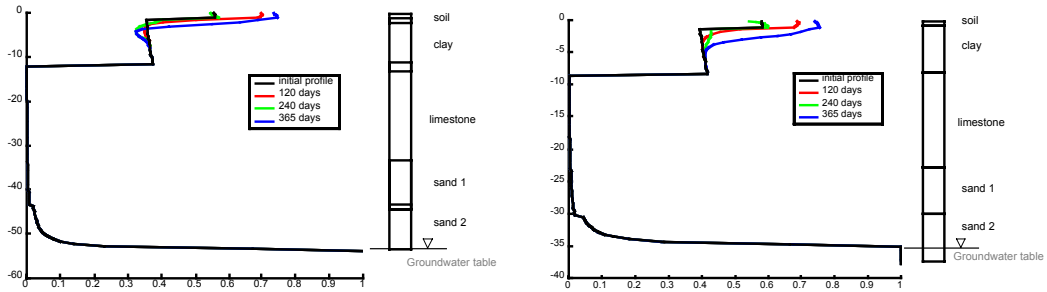


Fig. 125 - Degree of saturation as a function of depth for two extreme RECs at four times.

The following information could be deduced from the modelling:

- the marl layer, simulated as a clay layer, acts probably as an important buffer against water movement. During this first year of simulation, the transport of water was limited to the upper horizon. Due to the extraction of water by crop roots, the cumulative infiltration in the second layer (marl) was much lower in the REC with crop (REC122) that in the REC with bare soil (REC134);
- the initial condition (hydrostatic) is probably too severe and could be considered to be unrealistic. The selection of alternative conditions would require the availability of additional data;
- the modelling suggests that it would take several years for a pesticide to be transported by convection to the groundwater.

2.4.3. Conclusions

The results obtained in the present exercise raised some questions with regard to the pertinence of this simulation. Two important points ought to be raised. First, the choice of using a model accounting for transport in the unsaturated zone instead of a classical groundwater model is extremely sensitive to i) the pertinence of initial and boundary conditions; and ii) the representativeness of transport parameters. In the present modelling exercise, little information was available on these two aspects. Secondly, the

conceptual model used for transport in the soil unsaturated zone (Richards' equation implemented in the POWER code) is based on the assumption of a continuous media, such as soil. The model is not designed to represent the physics of transport in fractured material, such as fractured limestone. The use of POWER on this type of fractured catchment is therefore questionable.

2.4.4. Summary

The computer code POWER was used to simulate water movement using data from the Brévilles catchment. The simulation was intended as a way to i) demonstrate that the programme was running properly and ii) obtain some information concerning the possibility of water transfer (and consequently some transport of pesticides) from the soil to the aquifer. Results suggest that transport of pesticides to the groundwater is unlikely. The modelling was hindered by the fact that little on-site information was used to parameterise the model and by the fact that POWER is not designed to simulate water and solute fluxes in fractured subsoil material such as that encountered at Brévilles.

3. APPLICATION OF MODELLING TOOLS AT THE ZWISCHENSCHOLLE SITE

Modelling of the Zwischenscholle dataset was organised in the form of a ring test between the different modelling groups.

3.1. Modelling using TRACE and 3DLEWASTE [FZJ]

The main objective of the 3D modelling of water and pesticide transport at the Zwischenscholle test site was a final evaluation of the modified TRACE/3DLEWASTE model according to the modifications described in section 2 in chapter 2. The data presented in section 3 in chapter 1 was used to parameterise the model wherever possible. A notable exception is the use of a simplified soil map characterized by four representative soil profiles due to the fact that the soil map 1:5000 was not completely available in a digital format. These soil profiles represent the underlying spatial structure of soils on the 'Zwischenscholle'. The textural variety of the representative profiles, however, was chosen to be rather extreme instead of averages (Table 32).

Table 32 - Selected properties of the four representative soil profiles and the aquifer.

profile	horizon	θ_s [$m^3\ m^{-3}$]	θ_r [$m^3\ m^{-3}$]	α [m^{-1}]	n [-]	K_s [$m\ d^{-1}$]	thickness [m]
fore	1	0.461	0.048	2.102	1.3414	0.0743	0.06
	2	0.358	0.082	4.319	1.3286	0.0168	1.00
agr1	1	0.463	0.045	2.155	1.3447	0.080	0.23
	2	0.392	0.041	1.602	1.3529	0.0320	0.28
	3	0.359	0.074	1.416	1.3021	0.0170	1.35
agr2	1	0.395	0.044	2.040	1.3381	0.0491	0.20
	2	0.298	0.069	4.160	1.3289	0.1102	1.00
agr3	1	0.382	0.056	11.215	1.3528	1.3769	0.25
	2	0.314	0.053	9.328	1.3994	0.8914	0.10
aquifer		0.184	0.001	10.000	2.1000	404.12	variable

Three out of these representative profiles represent cropped soils, one profile is assumed to be representative for forest soils found on the 'Zwischenscholle' test site. Soil hydraulic properties of the four representative profiles were derived using one set of pedotransfer functions (section 3 in chapter 1). Using these basic data, TRACE/3DLEWASTE was applied to simulate the transport of isoproturon (IPU) at the test site 'Zwischenscholle' for a ten-year period (from 12/1983 to 12/1993).

3.1.1. Material and methods

The simulation of water and pesticide transport was run on a 3D flow domain with dimensions x = 7,200 m, y = 2,800 m and variable thickness in the z direction. The grid size in the x and y directions was 200 m. In the z direction, a variable grid resolution was selected for reasons of numerical stability. A fixed sequence of element thickness was used for the upper 1.3 m. From top to bottom, the number of elements and their thickness was 5 x 0.01 m, 5 x 0.05 and 10 x 0.1 m, respectively. For the aquifer, the thickness of the finite elements was variable, depending on the depth of the aquifer base. Another 15 elements were used to fill the space between the aquifer base and the bottom of the fixed discretisation of the unsaturated zone. Thus the geometry consists of 19,980 nodes in 17,640 elements. The geometry of the upper model boundary is given by the digital elevation model (section 3 in chapter 1).

At the bottom of the flow domain, an impermeable boundary representing the aquifer base was imposed. At the top of the domain, the atmospheric boundary condition linked to the plant module was applied while for the vertical sides of the domain a 'global Dirichlet' boundary condition was applied. Here the interpolated groundwater levels were used to define the heads (see section 3 in chapter 1 for details). Urban regions were treated as partially sealed surfaces. Assuming a sealing of 30 % of the area resulted in a reduction of precipitation and potential evapotranspiration to a value of 70 % of the original values.

To simulate solute transport, impermeable boundary was assumed at the bottom of the flow domain. At the top, only downward solute flux into the model domain was allowed. For upward solute fluxes the upper boundary was impermeable. At the vertical boundaries, a zero-gradient Neumann boundary condition was applied.

Table 33 presents isoproturon transport parameters selected for the modelling. The decay constants and the K_d of the soil were taken from a database while the K_d of the aquifer was taken from the results of the experiments carried out in the framework of PEGASE (section 7 in chapter 1). The longitudinal dispersivity for the aquifer was scaled up from the results of Vereecken *et al.* (2000).

Table 33 - Transport properties of isoproturon used in the modelling.

	K_d [$m^3\ g^{-1}$]	α_L [m]	α_T [m]	decay [d^{-1}]
soil	0.853E-06	0.0045	0.00045	0.0347
aquifer	0.265E-06	154.0	15.4	0.0022

K_d=distribution coefficient, α_L = longitudinal dispersion, α_T=transversal dispersion.

3.1.2. Results

Figure 126 shows actual evapotranspiration and the location of four randomly selected points of the 'Zwischenscholle'. The actual evapotranspiration for the period 12/1983 to 11/1993 of the cropped locations was quite close to each other, while the actual evapotranspiration of the forest location was clearly higher. Around 750 mm/y was estimated for the forest, whereas the agricultural locations ranged between 400 and 450 mm/y.

The large deviation in actual evapotranspiration between the forest and the arable land was also visible in Figure 126. The large actual evapotranspiration of the forest surrounding the research centre could be clearly distinguished for the years 1, 5 and 10 (1984, 1988 and 1993 respectively). The years 1 and 5 can be characterized as rather wet years, with high amounts of precipitation and slightly smaller amounts of actual evapotranspiration compared to the other years. The year 5 had the smallest actual evapotranspiration during the simulation period, whereas year 10 was one of the years with the highest actual evapotranspiration. For this year, actual evapotranspiration were up to 800 mm/y in the forest. The spatial structure of the actual evapotranspiration outside the forest was determined by the spatial distribution of the crops for the relevant year (see section 3 in chapter 1, Fig. 127).

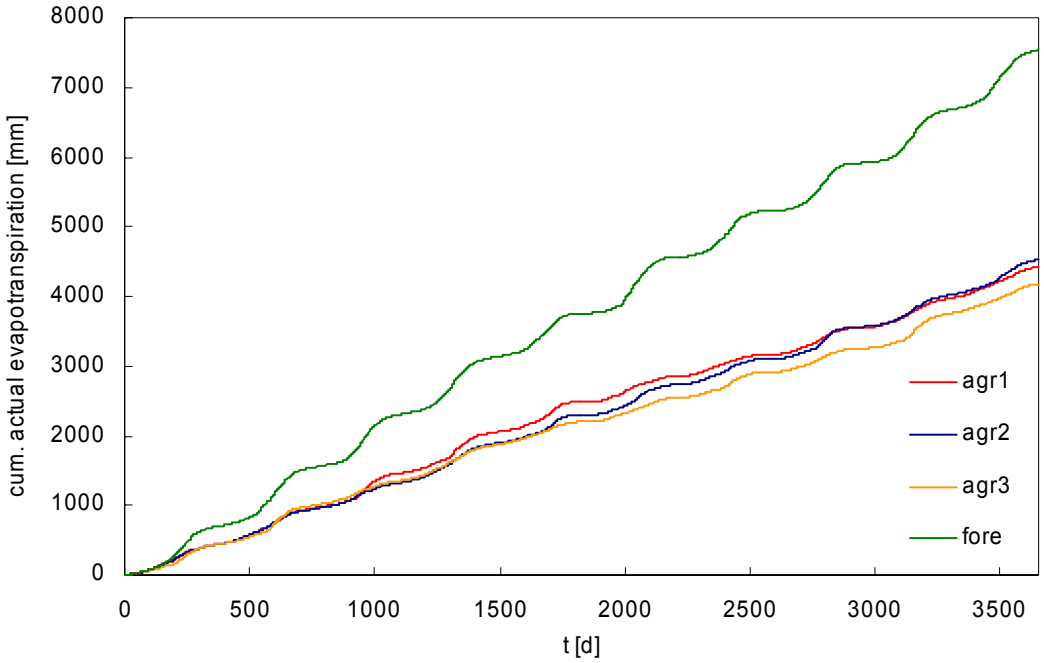


Fig. 126 - Cumulative annual actual evapotranspiration and location of the four selected points for the ten-year modelling period (12/1983 – 11/1993).

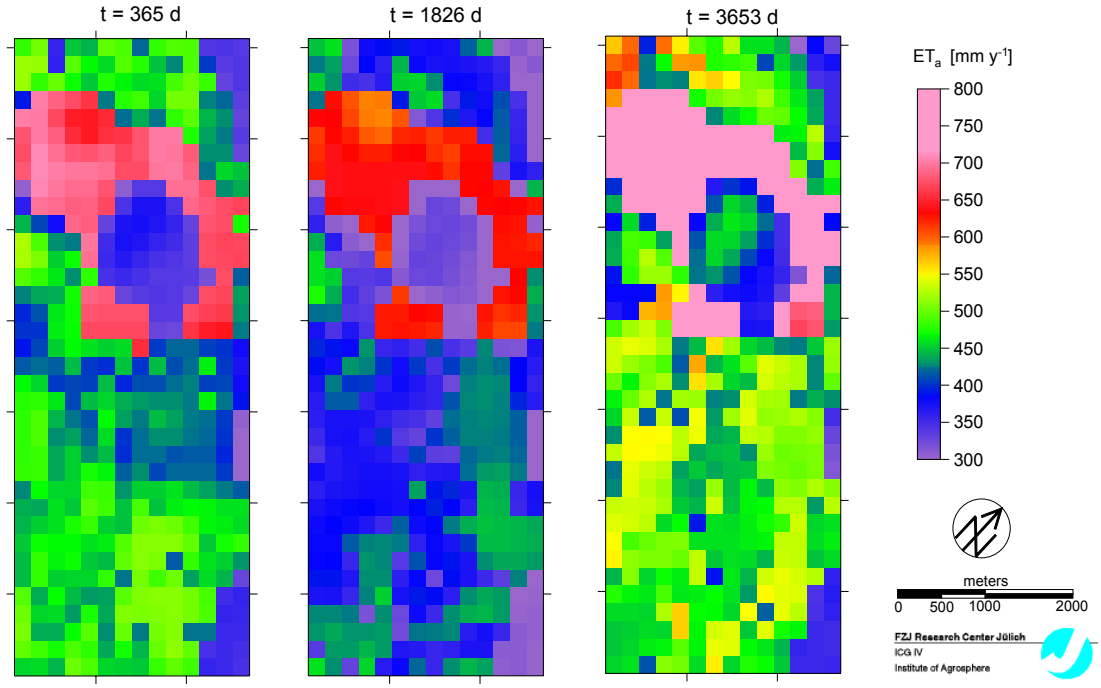


Fig. 127 - Cumulative actual evapotranspiration 1, 5 and 10 years after the start of the model (12/1983).

The calculated groundwater levels for the years 1, 5 and 10 differed only very slightly (see Fig. 128). The influence of the meteorological conditions during single years on the ground water levels of the 'Zwischenscholle' test area was rather small. The estimated groundwater levels reproduced the general flow direction northeast. Figure 128 shows steep gradients for the southwestern corner of the model area, which may be due to the imposed boundary conditions. In order to check the estimated groundwater levels of the model a comparison with measured groundwater levels was done (see Fig. 129). Time series of the measured groundwater levels of those wells, which are located close the four selected locations ('agr1'-'agr3' and 'fore', see Fig. 129) were compared to the calculated levels of the closest located model node. The root mean square errors for the model results and the wells 20111, 20232, 20255 and 20244 were 0.408, 0.678, 0.335 and 0.424, respectively. Figure 129 also shows that the deviations between the model and the measurements were much smaller than the deviations between the different measured locations. TRACE also reproduced the temporal course of the groundwater levels well. Year 5 (1988) showed the highest groundwater levels for the wells 20232, 20255 and 20244, which was well reproduced by TRACE.

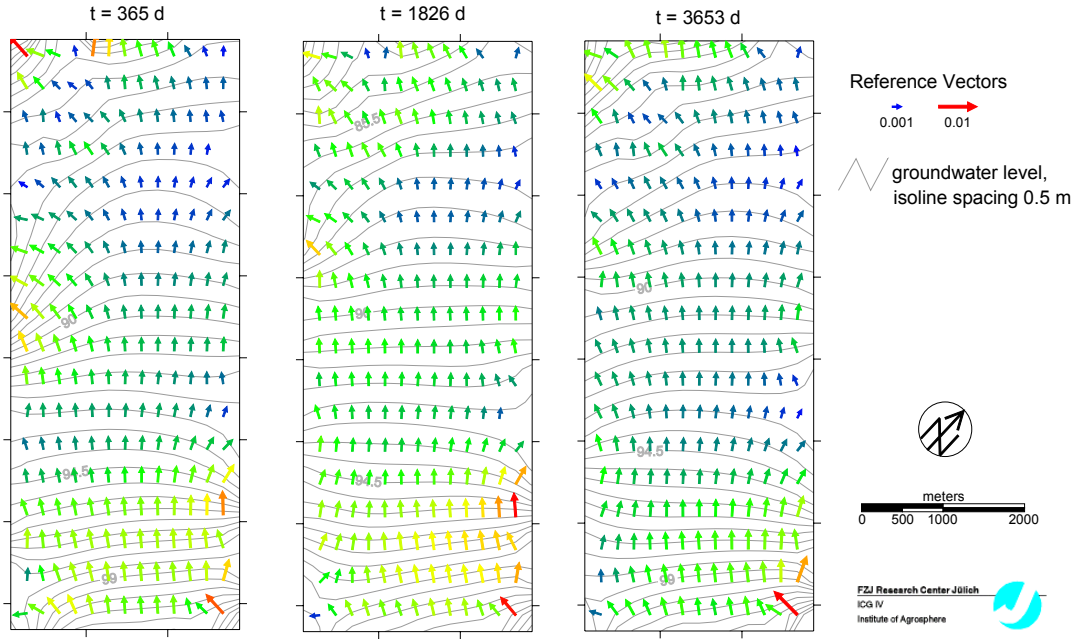
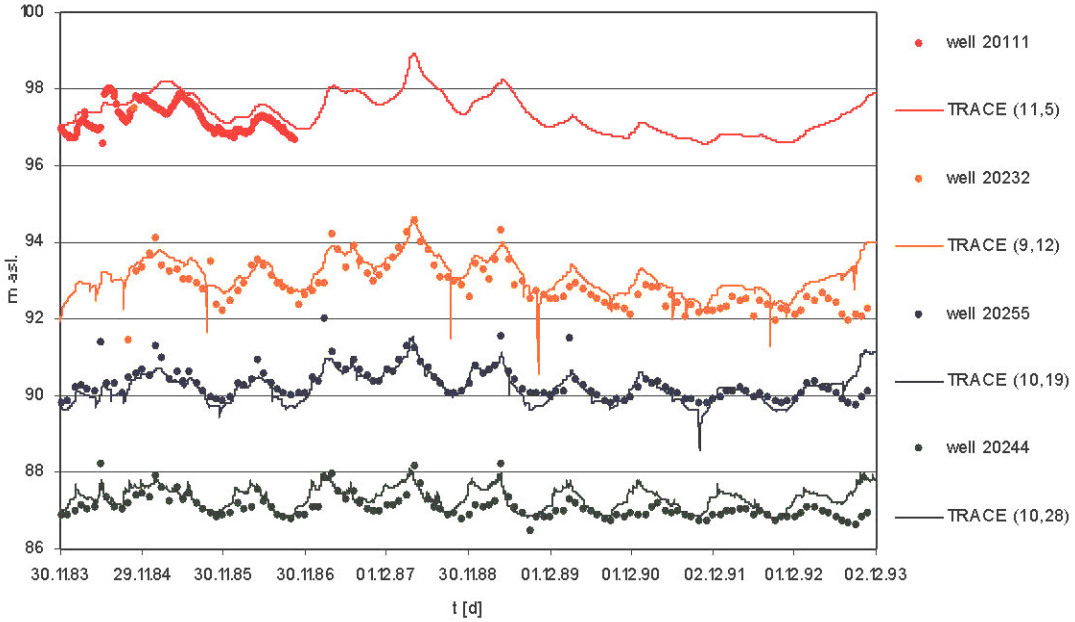


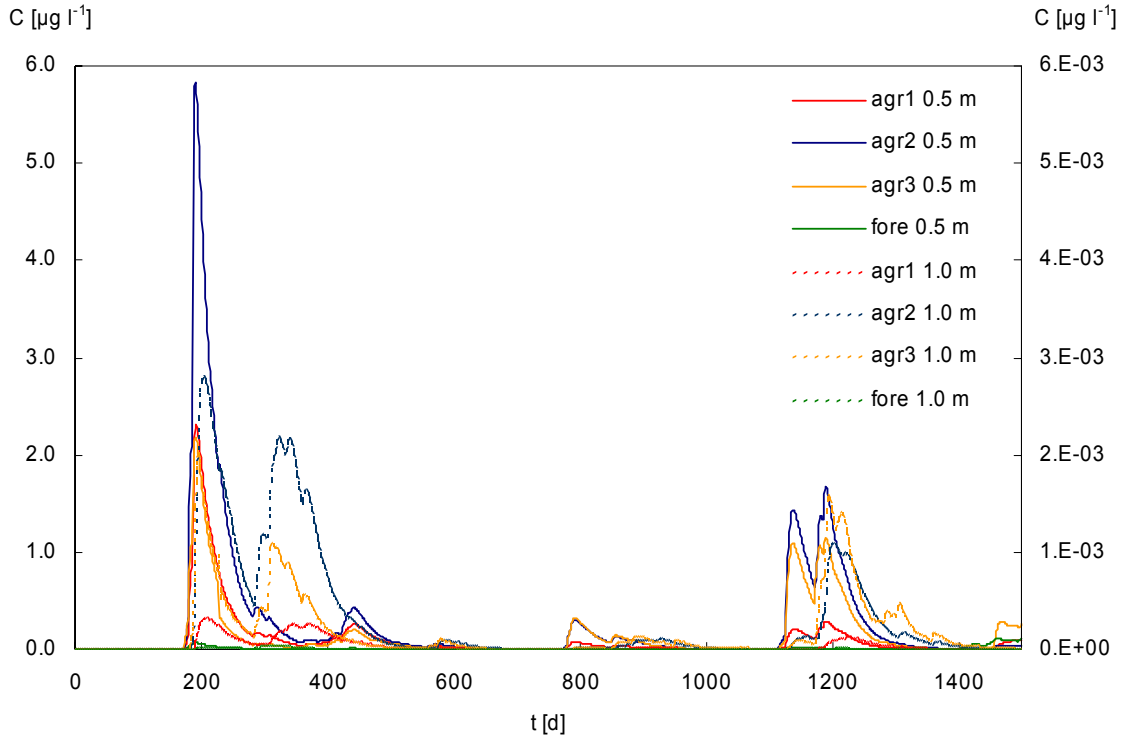
Fig. 128 - Groundwater levels and flow directions 1, 5 and 10 years after the start of the model (12/1983).



The measured groundwater levels are given as solid lines, the model results are given as points.

Fig. 129 - Comparison between measured and simulated total head [m above sea level] for the four locations selected.

The sound estimation of pesticide leaching from soil is a precondition for modelling pesticide transport in groundwater. The estimated breakthrough curves of IPU in the soil of the selected four locations are shown for the first 1,500 days in Figure 130. The highest peak concentration among the four selected locations at the depth of 0.5 m below soil surface was found for location 'agr2' with a concentration of 5.83 µg/l at day 202. The first application of IPU was at day 122. For the same location at the depth of 1 m the peak concentration was found only 24 days later, but at a much lower concentration. The later applications at day 351, 714, 1081 and 1441 showed smaller peaks at 0.5- and 1-m depth than the first application, due to the fact that the first year was a rather 'wet' year with large downward fluxes. The forest location only showed significant - but still very small - concentrations at a depth of 1 m between 1,400 and 1,500 days (see Fig. 131), which was caused by an upward movement of groundwater into the unsaturated zone. In general the concentrations found in the soil were rather small due to the short half-life of IPU considered in the modelling (Table 33).



The solid lines refer to the left y-axis, the dashed lines refer to the right y-axis.

Fig. 130 - Estimated breakthrough curves for IPU 0.5 and 1.0 m below soil surface for the four selected locations. Notice the change of scale for the y-axis.

Concentrations in the groundwater after one year were also very small and were found at only one location (see Fig. 131). Peak concentrations of about 6.0E-6 µg/l were found at one 'hot spot', located under the representative soil profile 'agr3', which is characterized by a thin soil layer with relative high saturated hydraulic conductivities (see Table 32). Detectable concentrations in the groundwater were thus mainly affected by the soil physical properties and the soil thickness.

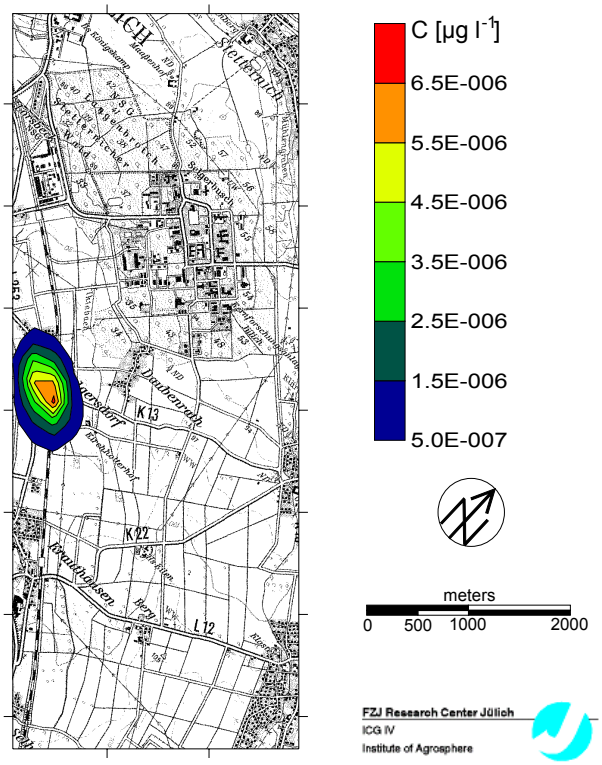


Fig. 131 - Concentrations of isoproturon in groundwater averaged in the z-direction 365 days after the start of the simulation (12/1983).

3.1.3. Discussion

The TRACE/3DLEWASTE model provided reasonable and consistent results on the transport of IPU in soil and groundwater for the 'Zwischenscholle' test site. The evaluation of the estimated groundwater levels with measured piezometric heads showed a good agreement between model and measurements, which was the result of a sound modelling approach in combination with a well defined vertical boundary condition. The evaluation showed that, there is no need to improve the data or the degree of complexity concerning the hydraulic properties of the aquifer. Still, the groundwater levels were the only model output for which an evaluation was possible. An evaluation of the estimated spatial structures of evapotranspiration, soil moisture and pesticide concentrations would have been very helpful. A clear lack of validation in particular for the processes linked to the unsaturated zone remains.

Model simulations also revealed the importance of the unsaturated zone which appears to function like a protective buffer for the groundwater. The largest concentrations in groundwater were estimated for the areas where a thin and permeable soil layer was assumed. Instead of using the four representative soil profiles, further model runs should be based on the more complex soil map 1:5,000, as this map contains the best soil data available. Another possible development would be the use of longer time series for meteorological conditions. This would allow model runs for the period extending from 1983 to 2003 to be undertaken, which would allow the validation of predicted pesticide concentrations in groundwater against measured values.

3.1.4. Summary

The main objective of the 3D modelling of the Zwischenscholle test site was a final evaluation of the modified TRACE/3DLEWASTE model. A simplified soil map consisting of four representative soil profiles was generated and used for the modelling. The model simulations provided reasonable and consistent results for the transport of isoproturon (IPU) in soil and groundwater. The largest concentrations of IPU in groundwater were estimated for the areas where a thin and permeable soil layer was assumed, which stresses the importance of process specification in the unsaturated zone. An evaluation of the estimated groundwater levels with the help of measured piezometric heads provided a good agreement between model predictions and measured data. A lack of validation, in particular for the processes linked to the unsaturated zone like evaporation, transpiration and soil water flux, remains. Overall, the TRACE/3DLEWASTE model was successful in describing the long-term transport of IPU at the regional scale.

3.2. Modelling using MARTHE [BRGM]

The versatile 3D groundwater model MARTHE was improved as part of the PEGASE project to allow the simulation of the fate of pesticides from the soil surface to and in groundwater (section 3.1. in chapter 2). The new version of the code was used to simulate water fluxes and isoproturon transport at the Zwischenscholle experimental site.

3.2.1. Modelling methods

The Jülicher Zwischenscholle test area (22.2 km^2) is located in North Rhine - Westphalia (Germany), 7 km south-east of the Forschungszentrum Jülich (FZJ) research centre, in the southern part of the lower Rhine Embayment. The first unconfined aquifer consists of Quaternary Rhine and Maas sand and gravel sediments (Klosterman, 1992). The base of the aquifer is constituted by the Reuver clay. The aquifer thickness varies from 15 m in the south-west of the monitoring area to 35 m in the north-east. The main groundwater flow direction is from south-east to north-west.
The Zwischenscholle dataset generated by the FZJ group consists of:

- initial conditions: type of soil, soil topography, lower boundary of aquifer, initial water table elevation;
- boundary conditions: daily rainfall and PET time series from 1/12/1983 to 30/11/1993, land use scenario (annual spatial distribution of crop cover with dates of sowing, harvesting and pesticide application), monthly values of groundwater depth on the four sides of the simulated area.

Four representative soil profiles were selected for the modelling. Physical properties for these four soil profiles are presented in Table 34. The parameters of Van Genuchten functions for water release and unsaturated conductivity curves (Table 35) were calculated using the pedotransfer functions of Rawls and Brakensiek (1985). The topography of the model was obtained from a digital elevation model. The aquifer formation was described with homogenous hydraulic parameters and was bound at the bottom by substratum interpolated from existing well data. The initial condition of

groundwater level in the studied area in December 1983 was interpolated from the groundwater levels in observation wells located on the Juelicher Zwischenscholle.

Table 34 - Selected properties of soils in the Zwischenscholle area.

Horizon name	Depth (cm)	Clay (%)	Silt (%)	Coarse (%)	C_{org} (%)	Porosity (cm^3/cm^3)
Agr1	0-22.5	11	78.5	0	0.87	0.5094
	22.5-50	10	78.5	0	0	0.434
	50-185	21	66.5	0	0	0.434
Agr2	0-20	13	78.5	27.5	0.87	0.5094
	20-120	19	37.5	27.5	0	0.434
Agr3	0-25	13.5	26.5	27.5	0.87	0.5094
	25-35	10	23.5	27.5	0	0.434
Fore	0-6	12	78.5	0	4.24	0.51
	6-106	19	37.5	0	0	0.44

For clay and silt, % is the mass of the fraction < 2mm; for coarse, % is the mass fraction of the total soil.

Table 35 - Parameter values of Mualem/VanGenuchten equation (m = 1-1/n).

Horizon name	Depth (cm)	θ_s (cm^3/cm^3)	θ_r (cm^3/cm^3)	α (1/cm)	n -	K_s cm/d
Agr1	0-22.5	0.4634	0.0447	0.02155	1.3447	8
	22.5-50	0.3922	0.0408	0.01602	1.3529	3.2
	50-185	0.3585	0.0743	0.01416	1.3021	1.7
Agr2	0-20	0.3952	0.0441	0.0204	1.3381	4.9
	20-120	0.2975	0.0691	0.0416	1.3289	11
Agr3	0-25	0.3819	0.0598	0.11215	1.3528	137.6
	25-35	0.3143	0.0532	0.09328	1.3994	89.1
Fore	0-6	0.4607	0.0479	0.02102	1.3414	7.4
	6-106	0.3583	0.0818	0.04319	1.3286	16.8
Aquifer	variable	0.184	0.01	0.1	2.1004	3.8e+4

Potential evapotranspiration (PET) was calculated for 10 years on a daily time step using the Penman/Monteith (1975) approach using measured data on air temperature, humidity, wind speed and radiation.

Land use at the site was assessed through aerial photographs taken in 1999 which allowed the digitisation of the most recent land parcel boundaries. The various types of land use were used to generate scenarios by randomising the distribution of vegetation covers while keeping constant the mean proportion of every crop of the arable land. Crop covers considered were forest, partially sealed surface, maize, potatoes, winter wheat, sugar beet and pasture.

The Juelicher Zwischenscholle area is characterised by both forest and agricultural land use. The western part of the study area is mainly covered by deciduous forest with small patches of mixed forest, coniferous forest and urban land use. The eastern part of the area is dominated by agriculture. Detailed information about crops (type, date of seed and harvest, yield, intermediate crops, cultivation) and pesticides (type, quantity, date of application) used in the last 3-10 years was obtained by interviewing a total of 25 farmers. Knowledge about the distribution of crops in the past was used in the stochastic generation of annual land use for the area.

Isoproturon (IPU) was selected for the modelling because of this pesticide was detected in groundwater for some wells of the Zwischenscholle test site during the 3 sampling campaigns in 2000-2002. IPU was assumed to be applied to winter wheat

in the autumn of each year at a rate of 1.75 kg/ha. An application in the spring was also considered in the year 1984 at a rate of 1.5 kg/ha.

Groundwater levels in 500 observation wells located on the Juelicher Zwischenscholle were used to generate i) a fixed head (Dirichlet) boundary condition along the model limits with a monthly time step; and ii) the initial condition of groundwater level in the studied area in December 1983.

The MARTHE model which simulates three dimensional water, heat and solute transfer in unsaturated and saturated zones (Thiéry, 1993, 1994) was used for the modelling. The hydrodynamic module solves Richards' equation with a finite volumes algorithm. Water retention and hydraulic conductivity functions can be described by homographic, power, logarithmic/exponential or Van Genuchten laws. Solute transport which is described by the convection dispersion equation can be solved by four different methods (finite differences, total variation diminishing, method of characteristics or random walk method) depending on the type of problem encountered (predominance of convection or dispersion). With regard to reactive solutes, MARTHE can handle a range of processes including sorption with linear, Langmuir or Freundlich isotherm assuming instantaneous equilibrium between liquid and solid phases, degradation with first-order kinetics which can depend on depth, temperature and water content, chain reactions and water uptake by plants (Thiéry, 2002; section 3.1. in chapter 2).

The study area was divided into a cell-centred grid with 15 columns, 37 rows and 12 layers. For consistency purposes, the spatial data available in 14x36 format were extended with the available data on boundary conditions by duplicating the last column and last row. The prescribed head boundary condition was applied on a monthly basis to cells along the edges of the model. Cells for which the centre was located below the prescribed head were restricted in the vertical direction. The recharge applied to the surface was calculated on the basis of daily values of precipitation and potential evapotranspiration. The groundwater table in December 1983 was used as the initial condition. The application of IPU was simulated using Dirac's condition of instantaneous mass injection to the cells of the top layer.

The retention law and the unsaturated conductivity law modified Van Genuchten's equations were selected in the following form:

$$\Theta_{(h)} = \Theta_r + \left(\Theta_s - \Theta_r\right) \cdot \left[1 + \left(\frac{h}{h_t}\right)^{1/b_t}\right]^{b_t - 1}$$

$$K_{(h)} = K_s \sqrt{\frac{\theta - \theta_r}{\theta_s - \theta_r}} \cdot \left\{1 - \left[1 - \left(\frac{\theta - \theta_r}{\theta_s - \theta_r}\right)^{\frac{1}{1-b_t}}\right]^{1-b_t}\right\}^2$$

with $h_t = \frac{1}{\alpha}$ [L] is the suction for half saturation and $b_t = \frac{1}{n}$ [-].

The effect of vegetation was introduced in the computation by accounting for transpiration of crops, water uptake by roots and restriction of uptake according to the state of hydric stress of vegetation. Crop parameters were taken from the literature (Feddes *et al.,* 1974; FOCUS, 2000). In an effort to limit the loss of water from the system in the winter through transpiration, forests and pastures were assumed to

germinate in the spring, to reach maturity at the beginning of the summer and to be harvested at the beginning of the winter. A reduction of 70 % was applied to the rainfall and potential evapotranspiration in the partially sealed areas.

3.2.2. Modelling results

Simulation results allowed the study of the vulnerability of the Zwischenscholle aquifer to contamination by pesticides in two ways: i) by analysing time series of selected hydrological and chemical parameters (*e.g.* actual evapotranspiration, vertical flux, water content, groundwater level, pesticide concentration and leaching) at selected locations within the basin; and ii) by making spatial distribution maps of these parameters for specific dates.

Four locations (P1, P2, P3 and P4; Fig. 132), each characterised by a different soil type, were selected for further analysis. Statistics for selected MARTHE outputs are presented in Table 36.

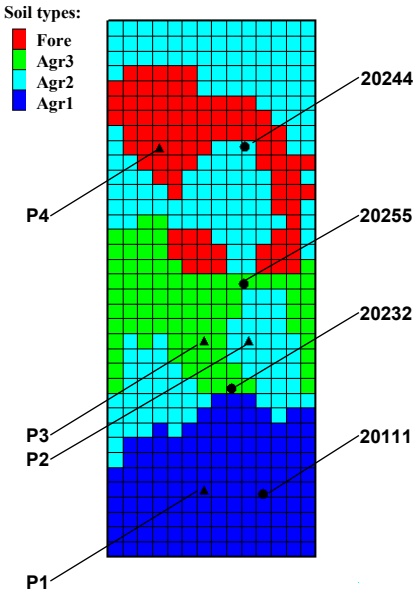


Fig. 132 - Location of the simulation points (P1 to P4) and the observation wells used for model evaluation.

There was no significant variation in actual evapotranspiration between the four locations and actual evapotranspiration never exceeded the value of potential evapotranspiration prescribed in the model. Compared to the other locations, P4 presented a unique behaviour in terms of vertical fluxes of water at 1 m depth with the smallest values (apart from negative data which characterise upward flow). Water contents close to residual values were simulated at a depth of 50 cm for point P3. These small values were attributed to the shallowness of the soil (35 cm thickness) and to the presence of a very permeable underlying aquifer formation. Maximum values of IPU leaching at 1 m depth varied from 0.013 % of the quantity applied (for the deepest soil profile P1) to 0.264 % (for the shallowest soil P3).

Table 36 - Statistics for selected MARTHE predictions in the four locations selected.

	P1 (Agri1)	P2 (Agri2)	P3 (Agri3)	P4 (Fore)
Annual cumulative actual evapotranspiration [mm]				
Maximum	587.85	580.79	515.50	619.28
Minimum	419.83	417.09	393.48	370.12
Mean	496.05	470.52	444.56	485.30
Median	494.50	445.47	445.98	466.96
Standard deviation	49.58	54.07	39.53	66.31
Annual cumulative vertical flux at 1 m depth [mm]				
Maximum	299.38	329.70	415.67	189.53
Minimum	130.33	173.35	144.00	-141.06
Mean	204.19	232.11	266.11	102.48
Median	200.51	224.81	255.14	149.50
Standard deviation	54.42	51.40	77.32	103.50
Water content [vol/vol] at 0.5 m depth				
Maximum	0.392	0.298	0.054	0.358
Minimum	0.137	0.102	0.010	0.257
Mean	0.306	0.216	0.021	0.337
Median	0.320	0.222	0.021	0.358
Standard deviation	0.054	0.038	0.005	0.029
Annual cumulative IPU leaching at 1 m depth [micro g/m^2]				
Maximum	23.09	77.63	462.10	0.09
Minimum	0.00	0.01	110.36	0.00
Mean	6.41	14.89	270.73	0.04
Median	0.04	1.96	230.18	0.04
Standard deviation	9.31	26.70	132.25	0.03
IPU concentration [micro g/l] at 0.5 m depth				
Maximum	3.908	8.938	2.209	0.000
Minimum	0.000	0.000	0.000	0.000
Mean	0.290	0.401	0.912	0.000
Median	0.000	0.000	0.830	0.000
Standard deviation	0.734	1.184	0.444	0.000

Evaluation of the performance of the model could only be undertaken through a comparison between predicted and measured groundwater elevation in selected observation wells (Fig. 133) as no pesticide monitoring data were available for the period simulated. The seasonal variation of water table was predicted accurately although the model displayed a tendency to over-estimate water levels. Statistical indices (Table 37) demonstrated that the best predictions were obtained for the well located in the centre of the basin (# 20255; Fig. 133).

Table 37 - Statistical indices for model evaluation.

Well no	20244	20255	20232	20111
RMSE	0.398	0.346	0.764	0.488
CRM	-0.003	-0.001	-0.005	-0.004
CD	0.994	1.342	1.402	0.474
EF	-0.233	0.450	0.079	-0.688

RMSE – Root Mean Square Error, CRM- Coefficient of Residual Mass, CD – Coefficient of Determination, EF – Efficiency.

Predicted pesticide concentrations can be tentatively compared to concentrations measured during the monitoring period although the modelling (1983-1993) and monitoring (2000-2002) periods do not overlap. IPU was detected in only 3 occasions (0.07, 0.08 and 11.8 μg/l) above the detection limits of 0.05 μg/l in the 57 groundwater samples taken within the area simulated. Both the most frequent (< 0.05 μg/l) and the maximum (1.28 μg/l) simulated isoproturon concentrations in the groundwater after 10 years of isoproturon application were in line with observations.

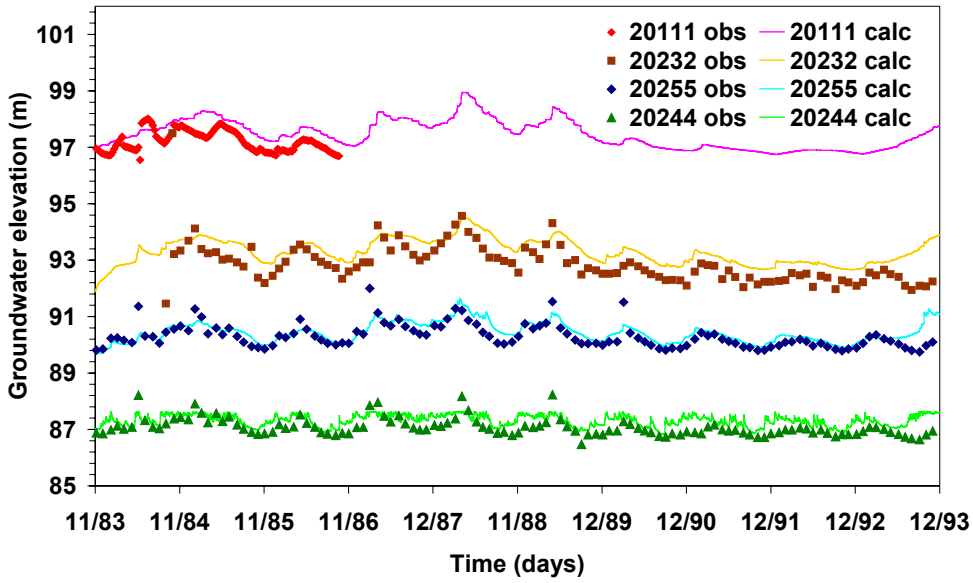


Fig. 133 - Groundwater elevation [m] in observation wells.

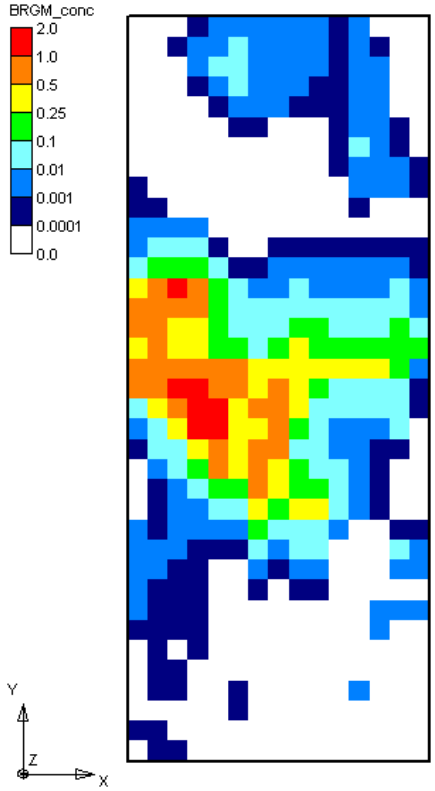


Fig. 134 - IPU concentration [µg/l] in groundwater after 10 years.

3.2.3. Discussion and conclusions

The comparison between MARTHE predictions for water table elevation in selected observation wells and measured data demonstrated a good agreement with the data, which suggests an adequate selection of boundary conditions along the model limits. The impossibility to conduct an evaluation of the model using pesticide concentrations should not discredit the simulations undertaken or the model itself. Simulated concentration of IPU in groundwater (most frequent value: < 0.05 μg/l; max 1.28 μg/l) fell in the range of measured concentration although the modelling and monitoring periods are different. This achievement is remarkable considering that the modelling integrated significant simplifications with regard to the subsoil.

The present simulations confirmed that MARTHE should be considered as an efficient and useful tool for modelling complex three-dimensional systems. The simultaneous solving of the transport of water and solute at each time step is a strong incentive to using this model for simulation of water fluxes and pesticide fate in aquifers when compared to alternative methodologies such as the coupling of 1D root zone models with 3D groundwater models.

3.2.4. Summary

Modelling of water movement and pesticide transport to and in groundwater in the Zwischenscholle area was undertaken using the 3D model MARTHE. Newly developed features of the model such as the possibility to correct degradation for the effects of temperature and humidity variations were used in the modelling. Comparison of model predictions against water table elevation measured in a number of observation wells showed a relatively good agreement between model predictions and the data. Predicted concentrations of IPU in groundwater were of the same order of magnitude as those measured on the site 10 years later. MARTHE was found to be an efficient and useful tool for modelling water fluxes and pesticide fate in complex 3D systems under real field conditions.

3.3. Modelling using ANSWERS and MODFLOW [LTHE]

The Zwischenscholle modelling was intended to be used by LTHE as the basis for the development of the coupling between ANSWERS (transport of water and pesticides in the soil-crop- atmosphere continuum) and the MODFLOW and MT3D models (transport of pesticides in the groundwater). The coupling of the three models could not be achieved as explained in section 2.4. in chapter 2 and the contribution of LTHE was thus limited to the following points :

- for the unsaturated zone of soils: 10 years of simulation (daily time step, watershed scale) of the water balance (evapotranspiration and downwards flow to the groundwater), changes in soil water contents, and pesticide transport from the root zone to the groundwater. Annual land use was automatically generated on the basis of the crop rotation schedule for Zwischenscholle;
- for the groundwater: estimation of the groundwater level determined in each peak cell, estimation of the net flow from the unsaturated zone. For a grid of 504 peak

cells, the total simulation time was less than 2 hours for the 10-year period (Pentium 4 PC).

3.3.1. Local comparison

- ***Transport in the soil***

The first example considered concerned the simulation of isoproturon concentrations at a particular peak cell (point #3). The modelling was carried out during the period extending from December 1987 to November 1988 where the crop was winter wheat and an application was made in the autumn of 1987. Figure 135 shows variations in pesticide concentrations at 1.0 m depth. There was a clear correlation between winter rainfall and the peaking of isoproturon concentrations.

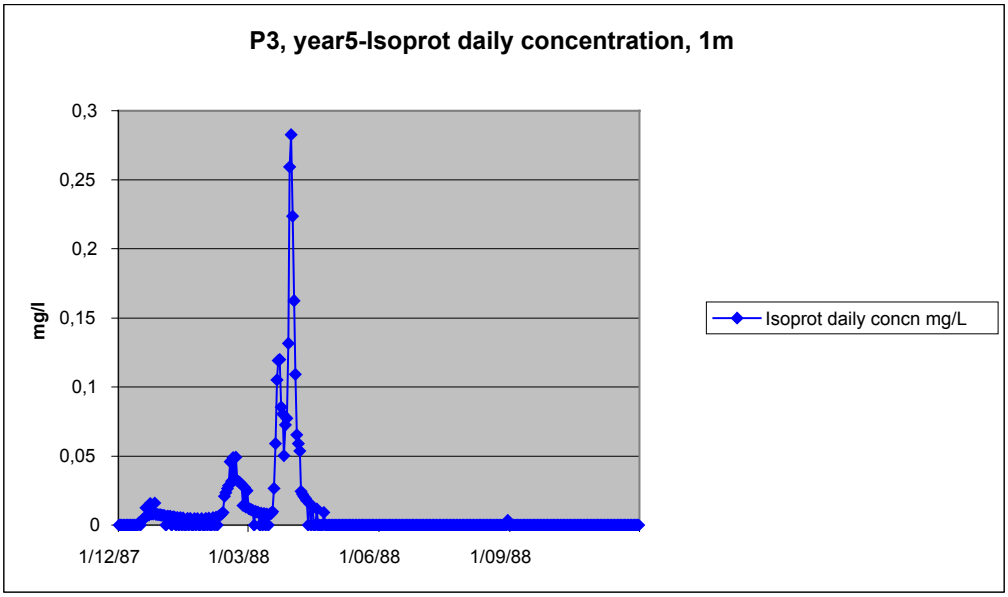


Fig. 135 - Predicted pesticide concentrations at 1-m depth.

Figure 136 presents the daily values of downwards flow (drainage) and isoproturon mass flow (leaching) at 1-m depth (below the root zone) together with values for daily evapotranspiration above the canopy. The same variables, but in terms of annual cumulative mass flow, are reported in Figure 137.

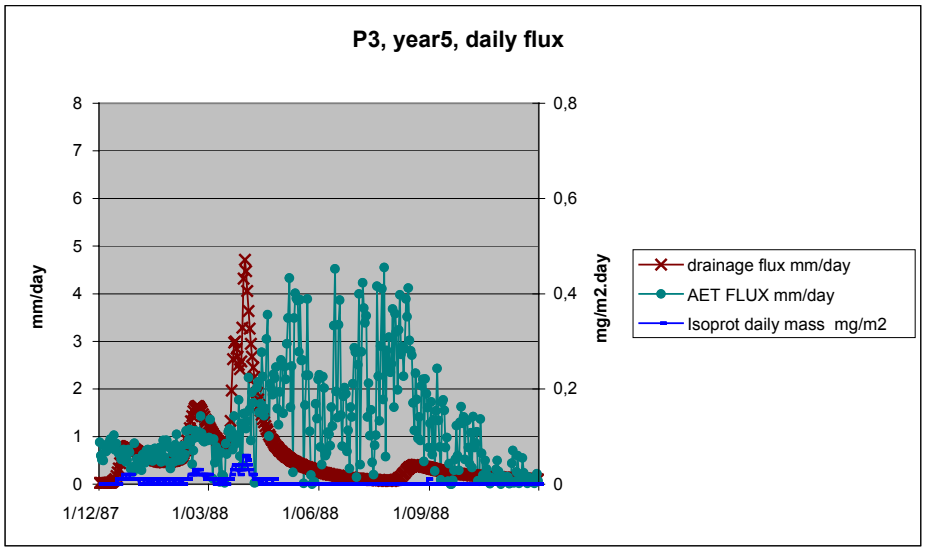


Fig. 136 - Predicted daily fluxes for drainage, evapotranspiration and pesticide leaching at 1-m depth.

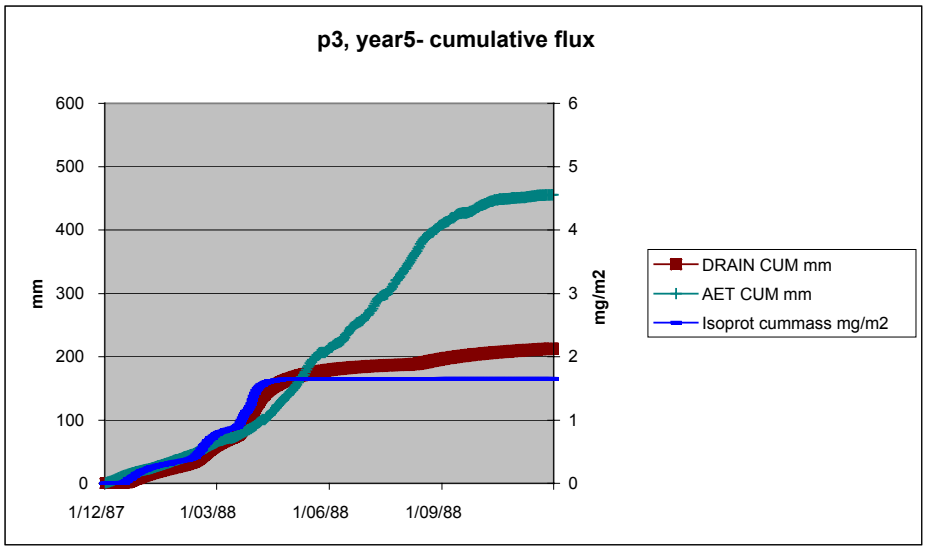


Fig. 137 - Predicted annual cumulative mass flow.

- ***Aquifer level***

A comparison between predicted levels of aquifer and measured values for the five piezometers for which information was available for the period of simulation is provided on Figure 138. These data are the only information in the simulation period which could be used for model evaluation.

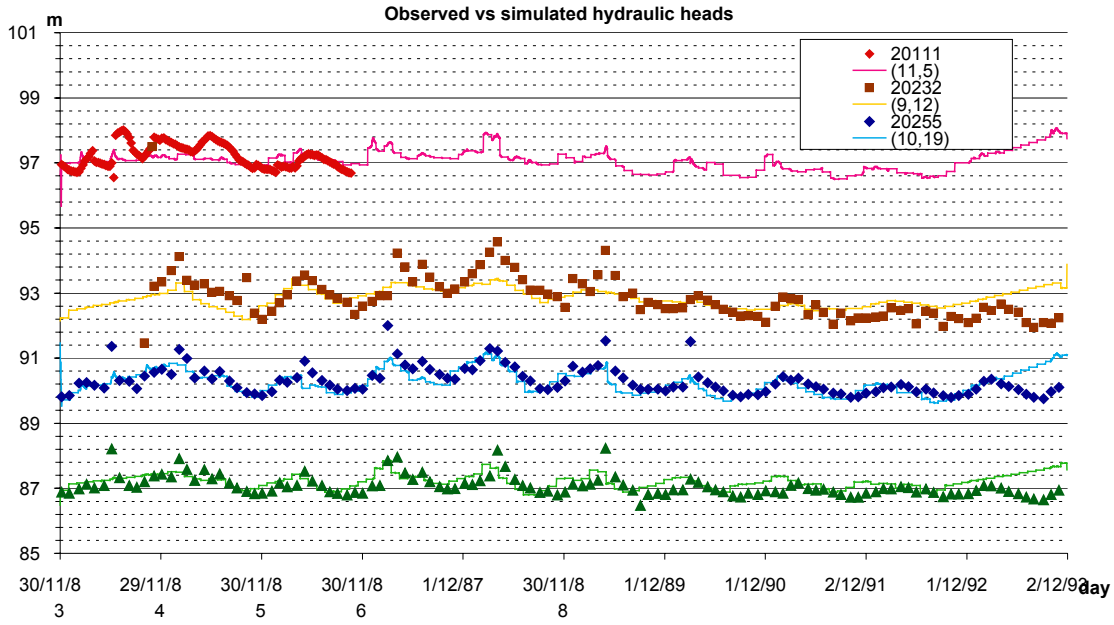


Fig. 138 - Comparison between predicted (line) and measured (dots) groundwater levels.

3.3.2. 2D simulations

The second set of simulations was carried out at the scale of the catchment. For each of the 10 years of simulation, the spatial distribution of the following variables was simulated:

- crop distribution over the period of simulation;
- cumulative amount of water loss by gravity flow (drainage) below the root zone (1 m below the soil surface);
- cumulative amount of pesticide leaching (isoproturon) at the same depth;
- and, cumulative amount of evapotranspiration above the canopy.

A typical example of simulation results is given in Figure 139 for the year 1990.

In absence of experimental data to compare against, it was not possible to infer any judgement concerning the representativeness of these observations. Comparison against simulations by other models revealed that the groundwater was always replenished by percolation from the soil using our model whereas a strong depletion from groundwater and from the soil, with important upwards flow to the atmosphere, were predicted by MARTHE or TRACE at certain times during the simulation.

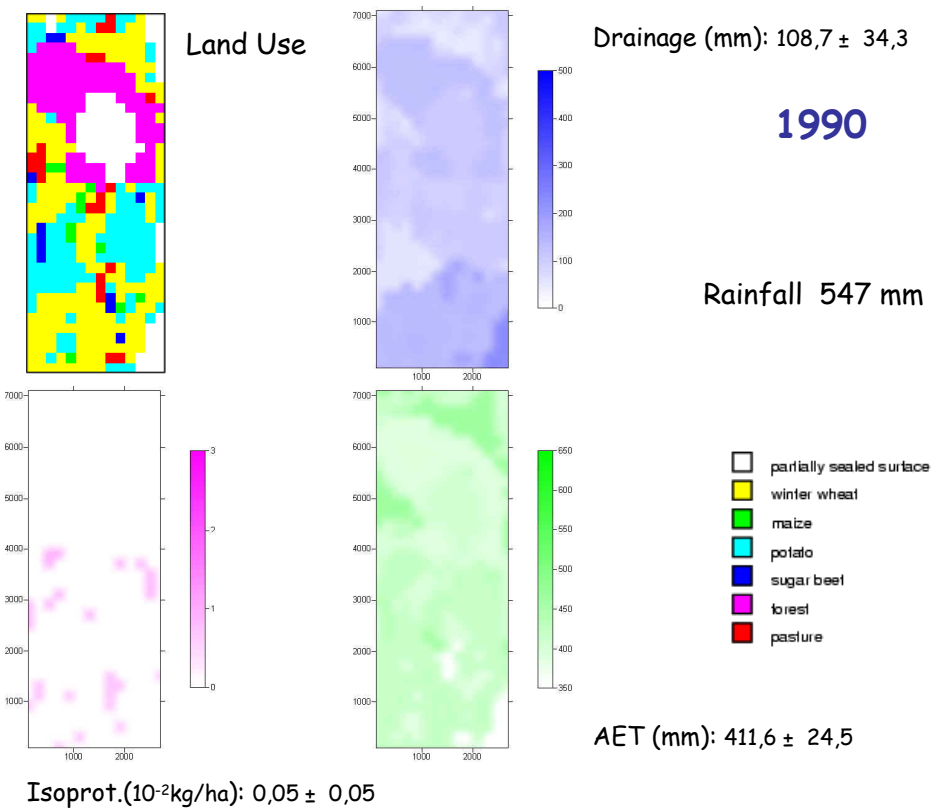


Fig. 139 - Simulations of water and pesticide fluxes at Zwischenscholle.

3.3.3. Summary

The revised ANSWERS model which integrated new subroutines for pesticide fate was used to simulate the transport of water and isoproturon in the unsaturated zone of the Zwischenscholle catchment over a period of 10 years. The only experimental data which could be used for the evaluation of the model were those concerning changes in groundwater level in four wells. An adequate fit to these data was noted. Concentrations and fluxes of isoproturon, changes in water content, drainage and evapotranspiration fluxes were also simulated although no validation against monitoring data was possible.

3.4. Modelling using MACRO and MODFLOW [SAPROV]

The system enabling the coupling of the root zone model MACRO with the groundwater flow model MODFLOWT (section 2.3. in chapter 2) was used to simulate the behaviour of water and isoproturon in the Zwischenscholle catchment. Predictions from the MACRO model at the boundary unsaturated/saturated zone were fed to MODFLOWT in order to simulate the evolution of groundwater level and the fate of isoproturon. Information on the spatial distribution of soils, crops and pesticide applications were integrated in the modelling.

3.4.1. Material and methods

- ***Models and coupling tool***

A description of MACRO and MODFLOWT as well as their coupling is provided in section 2.3. in chapter 2.

- ***Site***

The description of the characteristics of the site and of the inputs for the simulations have been reported elsewhere (Ciocanaru *et al.,* 2002; section 3 in chapter 1). The Zwischenscholle area is characterized by forest and agricultural land use. A grid covering the simulation area using cells of 200 m x 200 m was built, resulting in a total of 14 columns and 36 rows. The soil profile was a variable horizon of Pseudogley over alternate layers of gravel and sand. A subdivision of the area using the four soil types is presented in Figure 140.

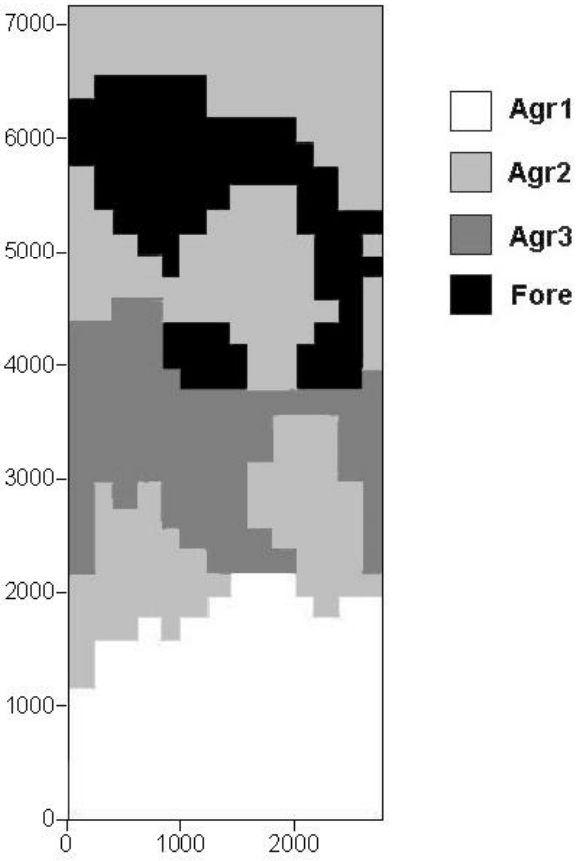


Fig. 140 - Division of the landscape into the four representative soil profiles.

The main crop was sugar beet and, to a lesser extent, winter wheat, winter barley and winter rye. Estimates of the distribution of crops in the catchment were used to generate a random spatial distribution of these crops for each year of simulation.

- ***Simulations***

The coupling tool was used to simulate the behaviour of water and isoproturon (IPU) at the Zwischenscholle site. Hydrological fluxes were simulated with MACRO across the catchment for 10 years and for each crop-soil combination. The behaviour of isoproturon in different meshes of the grid was simulated to assess the variability of the transfer of IPU in the soil profile for the different soil-crop combinations. Simulations were performed for the first 5 m of the soil profile. Outputs of MACRO (water flow and pesticide concentration) at the boundary unsaturated/saturated zone were used as inputs to MODFLOWT in order to simulate the fate of pesticide in the aquifer.

3.4.2. Results and discussion

- ***Unsaturated zone***

Table 38 presents the randomised scheme of crops in the soils treated with IPU at least on one occasion. Figure 141 reports the water balance simulated for the three combinations Agr1, Agr2 and Agr3.

Table 38 - Crop rotation in the three soils.

Year	Agr1	Agr2	Agr3
1984	WW	WW	WW
1985	WW	WW	PA
1986	SB	WW	PA
1987	SB	SB	MZ
1988	SB	SB	WW
1989	SB	PA	SB
1990	WW	SB	PA
1991	WW	WW	PA
1992	WW	SB	SB
1993	WW	SB	WW

WW = Winter Wheat, MZ = Maize, PA = Pasture, SB = Sugar beet.

The three crop rotations in the three soils (the forest soil was not simulated) did not induce much difference in the predicted water balance. Cumulative actual evapotranspiration (AET) was predicted to be 4,205 mm for Agr1, 4,535 mm for Agr2 and 4,153 mm for Agr3, while water volumes predicted to leach below 5 m were 3,084 mm for Agr1, 2,588 mm for Agr2 and 3,027 mm for Agr3. The spatialized MACRO model worked properly, but the running still involved some manual actions to be taken during the modelling. Improvements to the system are needed to completely automate the simulation procedure. Predictions for concentrations of IPU at 0.5-m depth are reported in Figure 142. Large loads of isoproturon were simulated by the system and contamination of the groundwater cannot be excluded on the basis of these results.

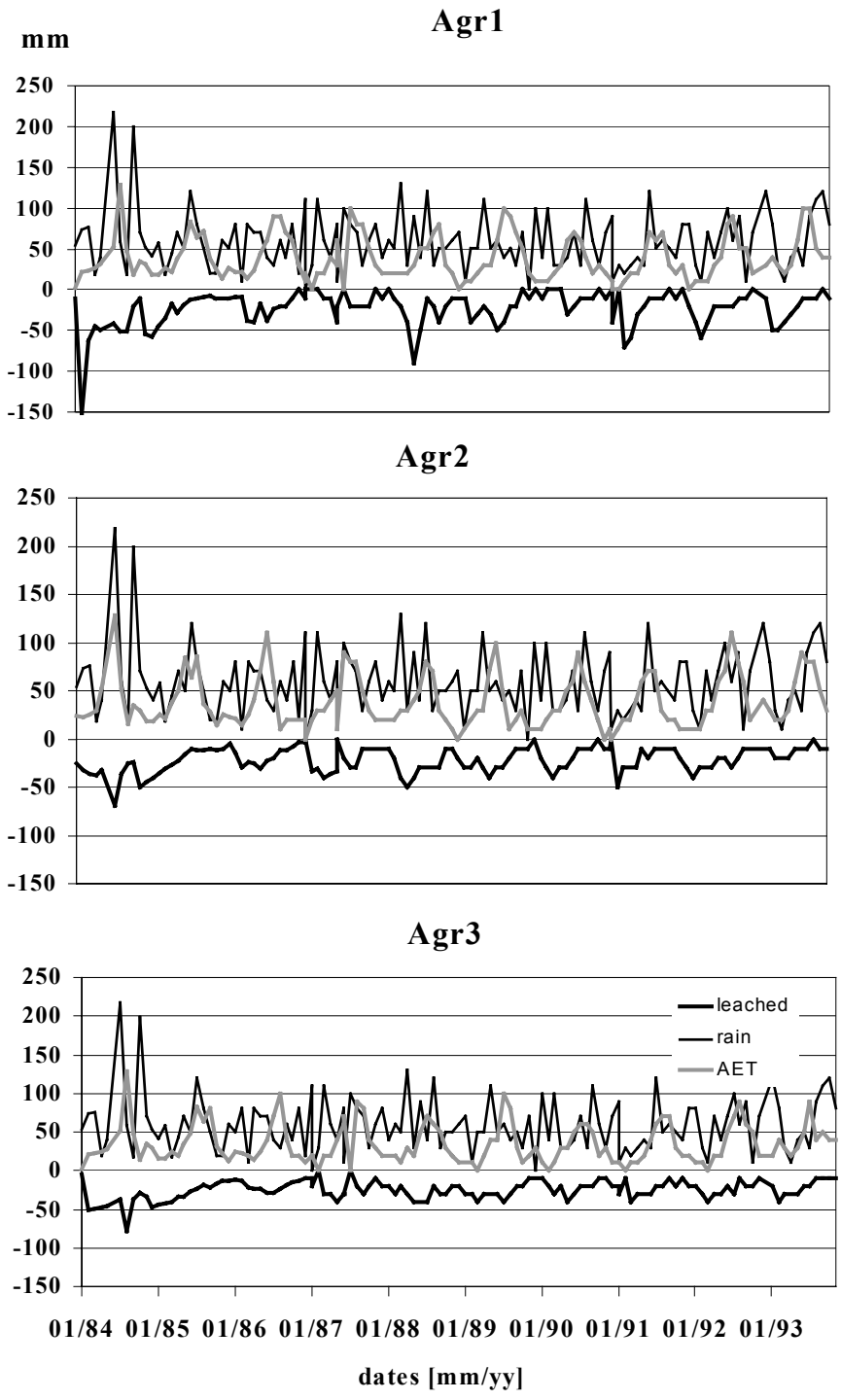


Fig. 141 - Predicted water balance for the three combinations soil/crop rotation.

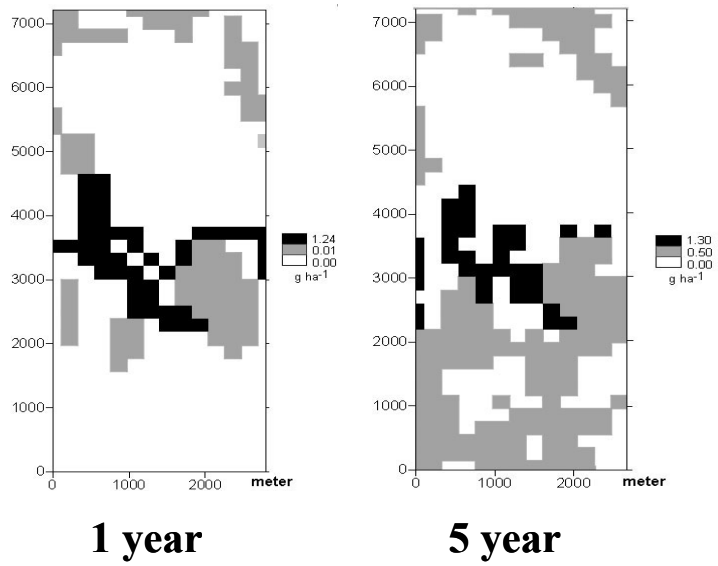


Fig. 142 - Distribution of isoproturon at 0.5 m depth after 1 year (1985) and 5 years (1989) of the simulation. Results for a total of 504 cells (2,800x7,200m) are shown.

- ***Saturated zone***

The transfer of water and pesticide to and in the aquifer was simulated with the groundwater flow model MODFLOWT. MACRO results (10-day cumulated means) for water flux and pesticide concentrations were fed to MODFLOWT and used to run the model over a ten-year period. Other inputs used in the modelling are presented in Figure 143.

BASIC PACKAGE ⟹ IUNIT ARRAY
[*.BAS] Option packages
Definition of hydrologic model

Number of layer and types
" of columns and rows
Boundary conditions
Initially heads for each cells
Time discretizations

1 Block-Centered Flow [*.BCF]
2 Wells [*.WEL]
3 Drains [*.DRN]
4 Rivers [*.RIV]
5 Evapotranspiration [*.EVT]
7 General Head Boundary [*.GHB]
8 **Recharge [*.RCH]**
9 Strongly Implicit Procedure [*.SIP]
10 ORTHOMIN for Flow [*.OMN]
12 Output Control for Flow [*.OC]
.....
N others options

Fig. 143 - MODFLOWT input structure.

Simulation results for water table levels are reported in Figure 144.

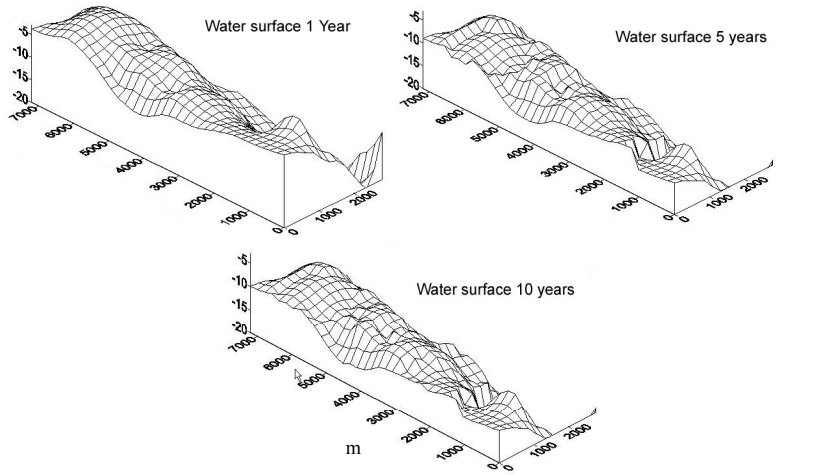


Fig. 144 - Water table depth after 1, 5 and 10 years of simulation.

Data on pesticide concentrations in groundwater are not reported in the present section as model results were still being processed at the time this report was put together. Problems were encountered in the management of the input/output structure of MODFLOWT and are being resolved. Further work is required to evaluate the tool against measured data.

3.4.3. Summary

The coupled tool MACRO/MODFLOWT was used to simulate the behaviour of water and isoproturon in the unsaturated/saturated zones of the Zwischenscholle test site for a period of 10 years and for different soil-crop combinations. Predictions from the MACRO model for the bottom layer were used as inputs to the groundwater flow model MODFLOWT. Further work is needed to resolve remaining problems in the management of the input/output structure of MODFLOWT and to evaluate the tool against measured data for water fluxes and pesticide concentrations.

4. APPLICATION OF MODELLING TOOLS FOR THE ZWISCHENSCHOLLE LYSIMETER DATASET

A ring test was undertaken by three of the modelling teams involved in PEGASE to evaluate the capabilities of the models with regard to the simulation of water and pesticide fluxes. This involved the simulation of the fate of a pesticide in a 1-m^2 undisturbed lysimeter over a two-year period. Selected characteristics of the dataset were as follows: i) upper boundary condition: open to atmosphere (natural climatic conditions); ii) cropping: winter wheat, then winter barley and oat; and iii) pesticide application: 248.11 mg/m^2 methabenzthiazuron (MBT). The dataset was provided by FZJ.

4.1. Modelling using TRACE and 3DLEWASTE [FZJ]

The TRACE/3DLEWASTE model was evaluated using lysimeter data (Pütz, 1993) provided by FZ Jülich. The lysimeters contained an Orthic Luvisol, sampled a few kilometers northwestern of Zwischenscholle. This soil type approximates some of the soil types found at the test site 'Zwischenscholle'. The lysimeter station was located at the test site in the Research Centre Jülich, providing relevant meteorological data for the test site. The lysimeter experiment covered a period of 627 days after the application of the herbicide methabenzthiazuron. The modelling had three main objectives: i) to check the applicability of the plant database (Van Heemst, 1988) to the test site 'Zwischenscholle', and to identify the crucial parameters by calibration; ii) to test the performance of the tool concerning the prediction of pesticide transport in the unsaturated zone at local scale; and iii) to check that all relevant processes were correctly implemented in TRACE/3DLEWASTE.

4.1.1. Data and model parameterisation

Five undisturbed soil cores (free draining lysimeters) containing an Orthic Luvisol were monitored for water and pesticide transport. The cores were 1.1 m long and had a surface area of 1.0 m^2. Three pedogenetic soil horizons were distinguished (Table 39). One of the lysimeters was treated on 25 November 1988 with TRIBUNIL at a field-rate of 2.8 kg/ha equivalent to an application of the active ingredient methabenzthiazuron (MBT) at 248.11 mg m^{-2}. The winter wheat was harvested and soil samples were taken on 3 August 1989 (252 days after application). In the following vegetation period, winter barley was cropped and harvested on 11 May 1990. The next vegetation cover was oat, which was harvested on 13 August 1990, when a last soil sampling was carried out 627 days after the application.

Precipitation, humidity, air temperature, wind speed and radiation were monitored on a daily basis from 25 November 1988 to 13 August 1990. Soil moisture was measured every three days at depths of 25 cm and 85 cm using a neutron probe. Leachate was collected every three weeks. The amount of drainage was measured directly while the actual evapotranspiration (Et_a) was calculated from the soil water balance.

Table 39 - Physical and chemical properties of the Orthic Luvisol used in the lysimeter experiment.

Soil horizon	clay [%]	silt [%]	sand [%]	ρ_b [kg m^{-3}]	f_{oc} [%]	pH [$CaCl_2$]
A_p 0-0.4 m	15.4	78.2	6.4	$1.57 \cdot 10^3$	1.0	7.2
A_l 0.4-0.6 m	21.9	77.1	1.0	$1.59 \cdot 10^3$	0.4	6.9
B_t 0.6-1.1 m	26.1	73.4	0.5	$1.67 \cdot 10^3$	0.3	6.6

ρ_b = bulk density, f_{oc}=organic matter content.

The soil water retention function was described using the van Genuchten (1980) model with parameter m=1:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{1 + (\alpha|h|)^n}$$

where θ denotes the water content ($cm^3\ cm^{-3}$), h is the pressure head (cm), θ_r is the residual water content ($cm^3\ cm^{-3}$), θ_s is the water content at saturation ($cm^3\ cm^{-3}$), α is the inverse of the bubbling pressure (cm^{-1}) and n is a dimensionless shape parameter (-).

The unsaturated hydraulic conductivity function was described by the Gardner model (1958):

$$K(h) = \frac{K_s}{1 + (b|h|)^c}$$

where K is the unsaturated hydraulic conductivity (cm d^{-1}), K_s is the saturated hydraulic conductivity (cm d^{-1}), and b (cm^{-1}) and c (-) are empirical parameters. The soil hydraulic properties listed in Table 40 have already been used by Vereecken and Kaiser (1999). They derived the soil hydraulic properties from the soil properties listed in Table 40 with the pedotransfer functions of Vereecken *et al.* (1989 and 1990) and fitted the θ_r and α values.

Table 40 - Retention parameters, hydraulic conductivity parameters, dispersivity λ and distribution coefficient K_d for the soil horizons of the Orthic Luvisol.

depth [m]	θ_s [$cm^3\ cm^{-3}$]	θ_r [$cm^3\ cm^{-3}$]	α [cm^{-1}]	n [-]	K_s [cm d^{-1}]	B [cm^{-1}]	c [-]	λ [cm]	K_d [$cm^3\ g^{-1}$]
0-0.4	0.39	0.01	0.0036	0.82	84.09	1.044	1.55	1.7	5.27
0.4-0.6	0.40	0.07	0.0037	0.79	126.63	1.688	1.45	1.7	2.11
0.6-1.1	0.38	0.10	0.0015	0.75	39.80	1.854	1.41	1.7	1.58

The sorption of MBT was described with a linear sorption isotherm. The values of the distribution coefficient K_d ($m^3\ kg^{-1}$) given in Table 40 were calculated from a partition coefficient K_{oc} of 527 $cm^3\ g^{-1}$, found in the Agritox database (http://www.inra.fr/agritox) and the organic matter content assuming $K_d = K_{oc}\ f_{oc}$. The retardation factor for the top horizon at water saturation was calculated to be 21.2, indicating a high sorption of MBT. 3DLEWASTE does not account for temperature or soil moisture dependent degradation. A first order kinetic decay with a half-life of 200 days was assumed. The degradation rate for sorbed and dissolved MBT was supposed to be the same.

The potential reference evapotranspiration Et_p was calculated according to the approach of Penman/Monteith (Monteith, 1975). Potential evapotranspiration and precipitation a were applied as the upper boundary condition, while a seepage face was applied to the lower boundary at the bottom of the lysimeter. The seepage face boundary was characterized by a no-flow boundary for unsaturated conditions:

$$q(z,t) = 0 \qquad \text{for} \qquad h < 0$$

If the seepage face became saturated, the boundary turned into a prescribed head boundary with h(z,t)=0. The vertical lysimeter wall was set as a no-flow boundary condition. The spatial discretization in vertical direction was 1 cm resulting in 110 finite elements.

In order to evaluate the model performance, a total of three criteria were calculated. A commonly used criterion for model validation is the *root mean square error* (RMSE), where the root of the mean squared residuals is calculated. The RMSE has the unit of

the considered variable. The squared residuals are also used for the second criterion applied, which is the *Coefficient of Model Efficiency* (CME, Nash and Sutcliffe, 1970). These two criteria are used to determine the proportion of the deviation from the observed mean, which can be explained by the model:

$$CME = \frac{\sum_{i=1}^{n} (x_o(t) - x_{omean})^2{}_i - \sum_{i=1}^{n} (x_o(t) - x_s(t))^2{}_i}{\sum_{i=1}^{n} (x_o(t) - x_{omean})^2{}_i}$$

where x_o is the observed value, x_s is the simulation result at time t and x_{omean} is the arithmetic mean of the observed values. The CME is a dimensionless criterion that can take negative values. The highest value possible is 1, indicating that observation and model are in complete agreement. The *Index of Agreement* can have values between 0 and 1 (IA, Willmott, 1981):

$$IA = 1 - \frac{\sum_{i=1}^{n} (x_o(t) - x_s(t))^2{}_i}{\sum_{i=1}^{n} (|x_o(t) - x_{omean}| + |x_s(t) - x_{omean}|)^2{}_i}$$

Because they are dimensionless, the CME and the IA can be used to compare the performance of the model for different variables, while the RMSE gives an idea about the model error in the units of the variable under consideration.

4.1.2. Results

Figure 145 shows a comparison between observed and modelled cumulative actual evapotranspiration. In general the model matched the measurements, which showed only small standard deviations, except for the two drying periods with high evapotranspiration demands. During the first spring period (1989) TRACE slightly underestimated the amount of actual evapotranspiration. The calculation of selected model performance criteria with the mean of the measured actual evapotranspiration and the corresponding model results (Table 41) confirmed that TRACE reproduced the temporal course of evapotranspiration quite well. The only parameters that were calibrated were the maximum rooting depth and the crop conversion factor (Doorenbos and Pruitt, 1977, see section 2.1. in chapter 2). For winter wheat, the initial root depth of 85 cm was changed to 108 cm and the initial scaling factor for the potential evapotranspiration of 1.2 was changed to 1.3. The rooting depth of winter barley was changed from 100 cm to 90 cm and the crop conversion factor was reduced from 1.1 to 0.65. For oat, the initial rooting depth of 80 cm was changed to 100 cm and the initial crop conversion factor of 1.0 was increased to 1.3.

Predicted values are in solid lines whilst the observed data appear in error-bars indicating the mean and the standard deviation of the measurements in the five lysimeters.

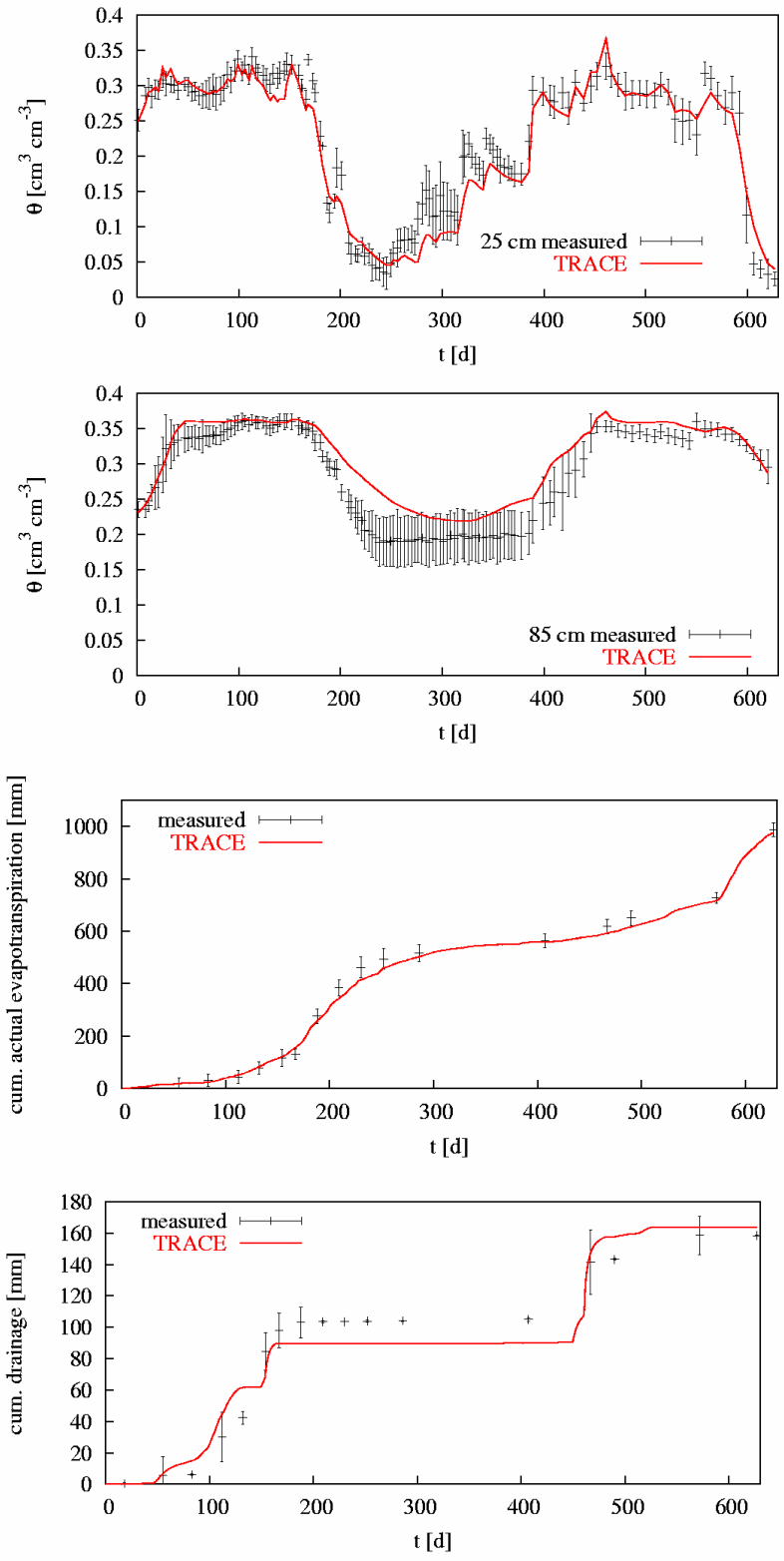


Fig. 145 - Comparison between predicted and measured soil moisture, actual evapotranspiration and drainage.

Table 41 - Quantification of the prediction performance concerning water flow.

Variable	RMSE[a]	CME[b]	IA[c]
drain [mm]	10.2	0.58	0.89
Et_a [mm]	17.1	0.96	0.99
θ_{25cm} [-]	0.025	0.93	0.98
θ_{85cm} [-]	0.031	0.79	0.94

[a] Root mean square error, [b] Coefficient of model efficiency, [c] Index of Agreement.

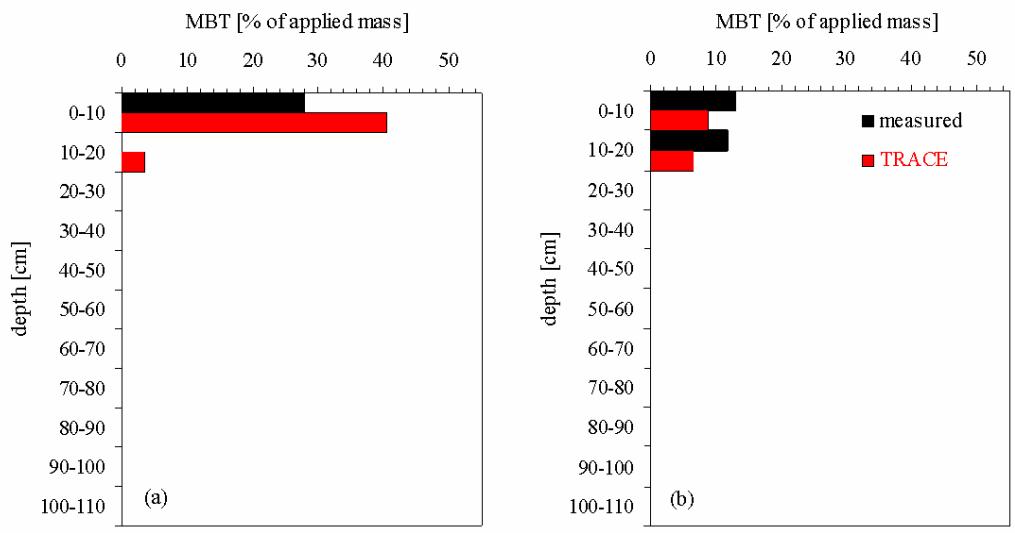
A comparison of the calculated and observed volumetric soil moisture at two depths is shown in Figure 145. At a depth of 25 cm, TRACE was able to reproduce the drying quite accurately during the drying period of the spring 1989. During the following wetting period (autumn and winter 1989), TRACE slightly underestimated the re-wetting. In general, for the depth of 25 cm, the model was in accordance with the measurements. The good fit was supported by the CME of 0.93.

TRACE over-estimated soil water contents at 85-cm depth during the spring and the summer of 1989 (Fig. 145). The measurements exhibited a large standard deviation during the summer of 1989 when the soil was very dry. In the following vegetation period (spring and summer of 1990), TRACE results matched the measurements. The effect of drying was much less pronounced during this second period.

Figure 145 also shows the comparison between modelled and measured cumulative drainage. The largest amount of drainage was measured during the winter of 1988/1989. TRACE under-estimated this amount slightly. In relation to the mean, the standard deviation of the measured drainage was higher than the standard deviation of the measured evapotranspiration. During the second period of drainage (winter of 1989/1990), TRACE over-estimated the amount of drainage.

The overall water balance was well reproduced by TRACE. The measured actual evapotranspiration for the whole modelling period was 990 mm, whereas TRACE predicted an amount of 977 mm. The deviation between the measured drainage amount of 158 mm and the amount predicted with TRACE (163 mm) was equal to an error of 3.4 %. The measured precipitation was 1067 mm and the change in soil moisture was thus slightly underestimated by TRACE. The measured change in soil moisture was -82 mm while TRACE calculated an amount of -73 mm.

For TRACE/3DLEWASTE, the degradation of MBT was calculated with a first order approach. Figure 146a reveals that all of the remaining total MBT mass was found in the upper 10 cm of the soil 252 days after application. This observation was generally reproduced by TRACE/3DLEWASTE although the model predicted a small amount of MBT in the soil layer between 10 and 20 cm depth. TRACE/3DLEWASTE over-estimated the residual mass of MBT by 53 %. After 627 days, the measurements showed that the total mass that remained in the profile was slightly lower than the mass remaining after 252 days and that the mass was distributed in the two uppermost layers (0-10 and 10-20 cm). The agreement between measurements and predicted values is shown in Figure 146b.



Depth is given in cm below soil surface, Figure (a) is 252 days after application and Figure (b) is 627 days after application.

Fig. 146 - Comparison between predicted and measured MBT residues.

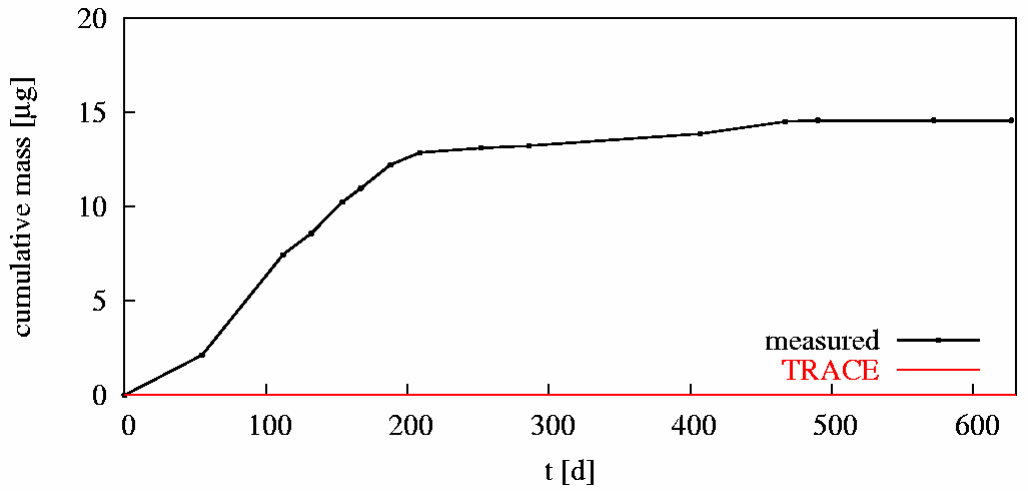


Fig. 147 - Comparison between predicted and measured MBT leaching.

According to Figure 147, the measured concentrations of MBT in the drainage water showed a small peak roughly 100 days after application. The total mass of MBT lost by leaching during the experimental period was 14.58 µg, equivalent to 0.0059 % of the total applied mass of MBT. In contrast to these observations, TRACE/3DLEWASTE did not predict any leaching at all.

4.1.3. Discussion and conclusions

Water flow measurements were well reproduced by TRACE and the estimated overall water balance was very close to the measurements. The actual evapotranspiration was slightly underestimated, while the amount of drainage was slightly overestimated. Still,

the calculated model performance indices indicate that all relevant processes and state variables (evapotranspiration, drainage and soil moisture) were well described. Calibration of the rooting depth and the crop conversion factor significantly improved the model results. Compared to the crop conversion factor, the calibration of the rooting depth was of minor importance. The crop conversion factor was increased during the calibration procedure, except for the winter barley. The decrease of the crop conversion factor for winter barley during calibration can be explained by the fact, that during the experiment, the winter barley suffered from a plant disease resulting most likely in a reduction of transpiration. The increase of the crop conversion factor for winter wheat and oat was necessary to reproduce the drying of the soil during the spring periods. This was done successfully for the soil moisture at 25 cm depth, but the decrease in the soil moisture at 85 cm depth during the first spring was not that well reproduced, which might be attributed to a compensation mechanism. The plant may have adapted to the low soil moisture near the surface by extracting more water from deeper soil layers. This process is yet not considered in TRACE. In general we conclude that the plant database (Van Heemst, 1988) provides useful estimates for plant parameters. However, care should be taken not to under-estimate transpiration by using crop conversion factors that are too small. The unability of the model to correctly calculate the soil water uptake might also be due to incorrect estimates of the potential evapotranspiration for the reference vegetation. If this method is not well adapted, changing the crop conversion factor is only a re-calibration of the errors made during the calculation of the potential evapotranspiration.

The degradation of MBT was described using the simple first-order kinetics implemented in 3DLEWASTE. For the first date (Fig. 146a), the residual mass estimated with 3DLEWASTE was 53 % too high, and part of the mass was simulated deeper (10-20 cm) than observed (0-10 cm). For the second date, the simulated residual mass was located at the right depths (0-10 and 10-20 cm), but again overestimated by 50 %. No leaching was predicted with the model, although a very small amount of MBT (< 0.01 % of the applied mass) was measured in the drainage water. This leaching was probably due to macropore flow, a process not accounted for in the model. At present, a macropore flow approach can hardly be applied at the regional scale test site ‘Zwischenscholle’ because relevant parameters necessary to drive such a model cannot be obtained from the available soil maps.

The application of a conservative tracer would have been useful to validate the transport modelling.

4.1.4. Summary

The coupled model TRACE/3DLEWASTE was applied in a 1-dimensional mode to a lysimeter data set covering a 627-day period. Three crops were grown during this period and measurements were available for soil moisture, actual evapotranspiration, drainage, residual concentrations of methabenzthiazuron (MBT) and leaching.

The lysimeter measurements were used to evaluate the model performance concerning water flow. For this purpose the performance indices root mean square error, Coefficient of Model Efficiency and Index of Agreement were calculated. The modelling exercise demonstrated that relevant processes such as soil water movement, evapotranspiration and drainage were well reproduced by TRACE. The calibration of plant parameters showed that the plant database (Van Heemst, 1988) is

applicable to the test site 'Zwischenscholle'. Calibration of the crop conversion factors and the rooting depth significantly improved the model calculations. Profiles of MBT concentrations in the soil were rather well reproduced with 3DLEWASTE, while the residual concentrations were overestimated by about 50 %. The very small amount of MBT leached was probably the result of macropore flow, which cannot be simulated by TRACE/3DLEWASTE.

4.2. Modelling using MARTHE [BRGM]

The MARTHE model was developed in the 1990s (Thiéry, 1993, 1994) to simulate water, heat and solute transfer in unsaturated/saturated zones. As part of the PEGASE project, MARTHE was upgraded to simulate processes related to pesticide fate (section 3.1. in chapter 2). The following section reports on the evaluation of the new version of the model against results from a lysimeter leaching study which involved the herbicide MBT.

4.2.1. Material and methods

The modelling was based on the results of a leaching experiment conducted in Forschungszentrum Jülich (FZJ) on a lysimeter containing an undisturbed core of 1.1 m length and 1.0 m^2 of surface (Ortihic Luvisol soil). This type of soil is quite common in the Zwischenscholle area. Three soil horizons were observed in the lysimeter with thicknesses of 40, 20 and 50 cm. Their physical and chemical characteristics are presented in Table 42.

Table 42 - Physical and chemical properties of the soil.

Depth	clay [%]	silt [%]	sand [%]	ρ_b [kg/m³]	f_{oc} [%]	pH
0-40 cm	14.5	79.1	6.4	1570	1	7.2
40-60 cm	21.8	76.7	1.5	1590	0.4	6.9
60-110 cm	24.4	74.5	1.1	1670	0.3	6.8

ρ_b = bulk density, f_{oc} = organic matter content.

At the beginning of the experiment, the soil moisture profile was measured using a neutron probe. During the experiment which started 25/11/1988 and ended 13/08/1999 (627 days), daily measurements of precipitation, minimum and maximum air temperature, humidity, wind speed and radiation were recorded. Based on these data, potential evapotranspiration was calculated using the Penman/Montheith equation (1975). The amount of drainage was measured every 38 days on average throughout the experimental period and actual evapotranspiration (AET) was calculated from the mass balance of the soil:

$$\mathrm{AET} = \mathrm{prec.} - \mathrm{drain.} - \Delta\Theta \qquad [\mathrm{mm}]$$

where prec. is the precipitation [mm], drain. is the drainage at the bottom of the lysimeter [mm] and $\Delta\Theta$ is the change in soil moisture content [mm] over the whole soil monolith during a specific period of time. In addition, soil moisture was measured with a neutron probe at two depths (25 cm and 85 cm) every 4.5 days on average.

Three crops were cultivated according to agricultural practice during the study period. Metabenzthiazuron (MBT) was applied at 248.1 mg/m^2 on 25 November 1988 before emergence of the winter wheat. The crop was harvested on 3 August 1989 (252 days after application) and soil samples were taken. Winter barley was cropped during the next vegetation period and harvest took place on 11 May 1990. The next crop was oat, which was harvested on 13 August 1990, when a last soil sampling was carried out (627 days after the initial application in November 1988).

For the modelling exercise, the soil column was subdivided in 110-cm thick cells of unit surface. Recharge flow on the surface was calculated on the basis of daily precipitation and potential evapotranspiration. At the bottom, a seepage face condition was set. For the time step 0, the initial condition of water content in all cells was set to the measured soil moisture profile. The hydrodynamic parameters were chosen to match the characteristics of water retention and hydraulic conductivity curves derived from pedotransfer functions (Vereecken *et al.,* 1989, 1990) (Table 43).

Table 43 - Parameters of the water retention and hydraulic conductivity laws used in MARTHE.

Depth	Brutsaert WRC				Gardner HCC		
[cm]	θ_s [%]	θ_r [%]	h_t [cm]	b [-]	K_s [cm/d]	h_k [cm]	b_k [-]
0-40	39	0	277.78	1.2195	84.09	0.9578	1.554
40-60	40	7	270.27	1.2642	162.63	0.5924	1.452
60-110	38	10	666.67	1.3298	39.80	0.5394	1.408

The effect of vegetation was introduced in the computation by accounting for transpiration of crops, water uptake by roots and restriction of uptake according to hydric stress state of vegetation. The parameters used to describe the vegetation were obtained by trial-and-error calibration from initial values selected from the literature (Feddes *et al*., 1978; FOCUS, 2000) and suggestions by the model developer (Thiéry, 2002). Calibration aimed at minimising the discrepancy between measured and predicted values for actual evapotranspiration, drainage at the bottom of the lysimeter and soil moisture contents at two depths. Two different approaches were tested with vegetation schemes similar to those implemented in the MACRO and LEACHP models.

Solute transport was solved using the TVD numerical scheme. Sorption was modelled assuming instantaneous equilibrium and a linear isotherm. Distribution coefficient $K_d = K_{oc} \cdot f_{oc}$ used in simulation were selected on the basis of a Koc value of 527 cm^3/g of MBT (AGRITOX, 2001).

Degradation was assumed to follow first-order reaction kinetics. Two approaches describing the effects of temperature and soil moisture on degradation were tested. The first approach related the half life of the herbicide with soil moisture contents according to the Walker equation (1987):

$$DT_{50}(\theta) = A \cdot \theta_g^{-B}$$

where DT_{50} is the half life [d], θ_g is gravimetric soil moisture content in % [kg/kg], A is the half life (for θ_g = 1 %) = 213 [d] and B is a shape parameter = 0.31 [-]. The relation between temperature and half life was described using the following equation:

$$DT_{50}(T) = Q^{\frac{(T-T_0)}{10}} \cdot DT_{50}(T_0)$$

where Q is a constant ≈ 2, T is the actual temperature [°C] and T_0 is the temperature at which the reference DT50 was measured.

In the second approach, it was assumed that the temperature and soil moisture influenced degradation according to the equation of Graham-Bryce *et al.* (1982):

$$k(T,M)=\exp[a+b*\ln(M)+(g*1/T)]$$

where k is degradation rate [d^{-1}], T is temperature [°K], M is gravimetric soil moisture [%] and a, b, g are empirical parameters [-],[-],[°K]. Wüstemeyer (2000) found the following parameter values for MBT:

$$\ln(k)=7.0+1.343*\ln(M)-4476*1/T$$

Longitudinal dispersivity was assumed to be uniform and equal to 1.7 cm.

In order to take into account the effect of temperature on degradation of MBT, a temperature field was computed for every time step by solving the equation of heat diffusion and convection.

4.2.2. Results and discussion

Two sets of results obtained with MARTHE are presented below. The first set was related to the effect of vegetation on the water balance and on the degradation of MBT, while the second set addressed the effect of temperature and soil moisture on degradation of MBT.

Changes in the vegetation parameters were found to improve the simulation of actual evaporation (Fig. 148), without drastically changing the drainage at the bottom of lysimeter (Fig. 149), which was adequately simulated by the model. Almost the same amount of drainage was observed for all simulations after the soil dried up (days 220 to 380) because actual evapotranspiration was lower than for the bare soil. The largest influence of vegetation on model predictions was observed for the simulation of soil moisture contents (Figs 150 and 151). The largest discrepancies between the data and the model were observed during the long periods of high evaporation and little precipitation. Vegetation parameters were found to improve the overall quality of the modelling considerably.

The influence of vegetation (uptake by roots) on residuals of MBT in the soil profile was also significant and generally resulted in an increase in MBT leaching compared to simulations where no crops were considered (Fig. 152). This effect was most noticeable over long time periods (Fig. 153).

Crops which were simulated using the MACRO scheme were found to extract less pesticides (7.7 % after 252 days and 12.7 % after 627 days) than those which were modelled using the LEACHP scheme (11.1 % and 19.2 % respectively). The model predicted that no MBT would leach at the bottom of the lysimeter (Fig. 154).

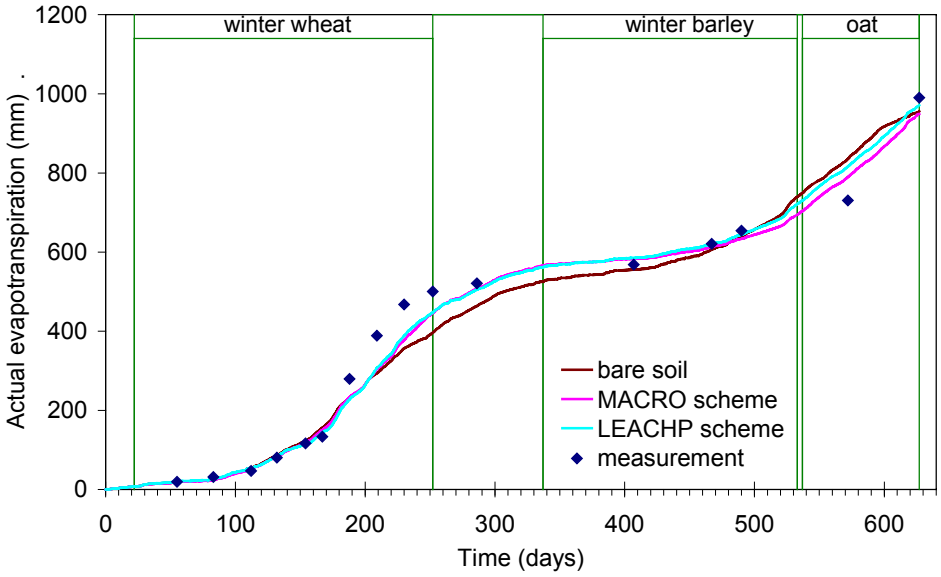


Fig. 148 - Measured and simulated cumulative actual evapotranspiration.

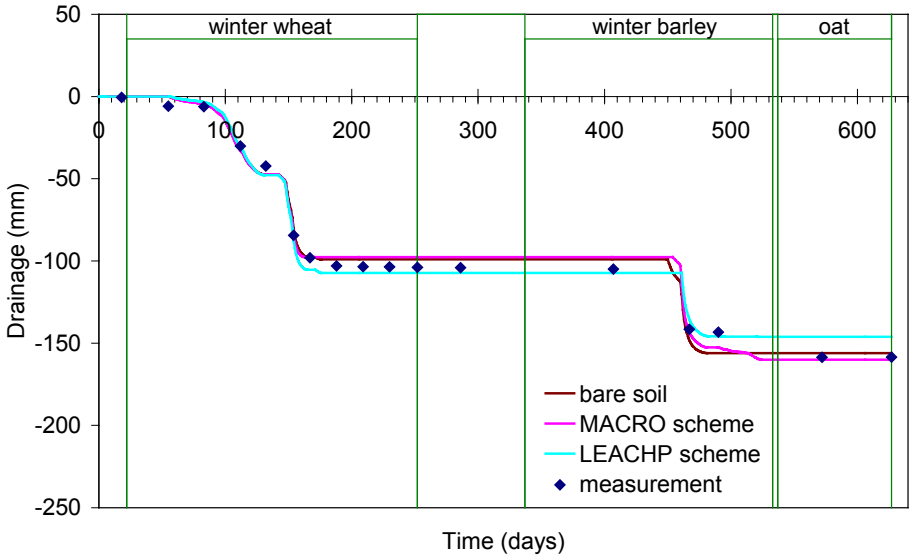


Fig. 149 - Measured and simulated cumulative drainage flux.

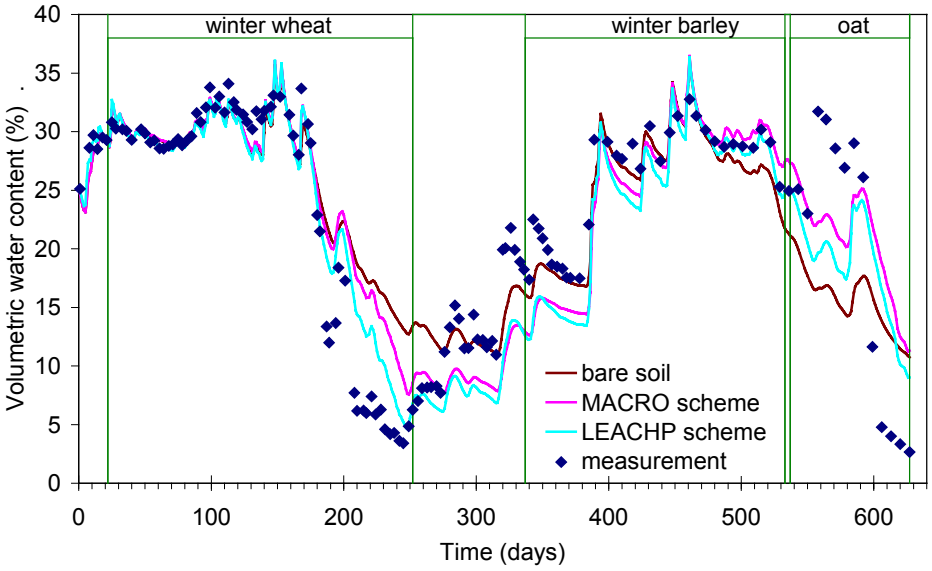


Fig. 150 - Measured and simulated soil moisture content at 25 cm depth.

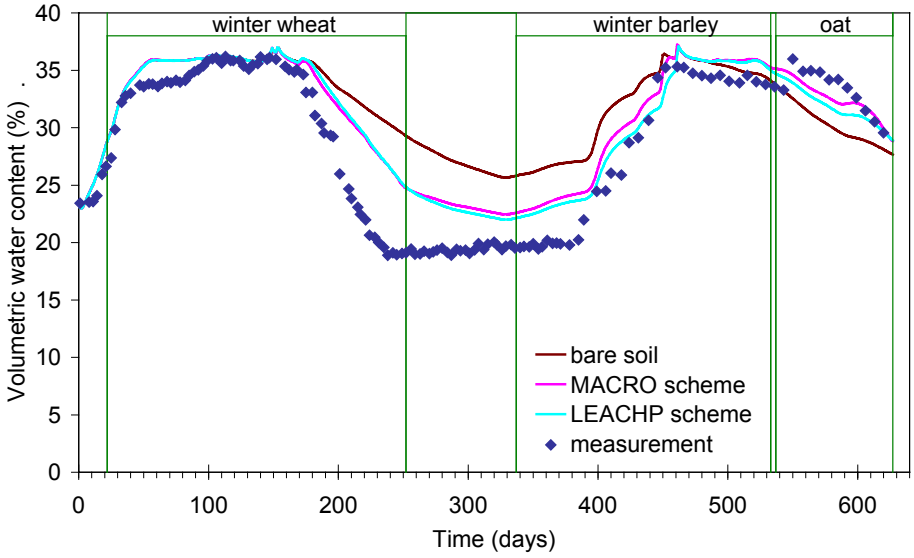


Fig. 151 - Measured and simulated soil moisture content at 85 cm depth.

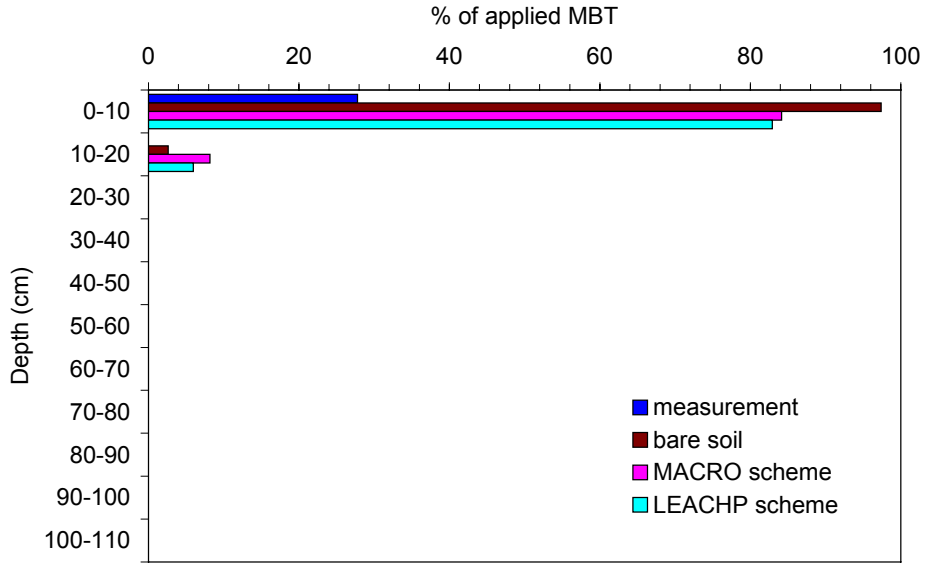


Fig. 152 - Residual MBT in the soil profile 252 days after application (no degradation).

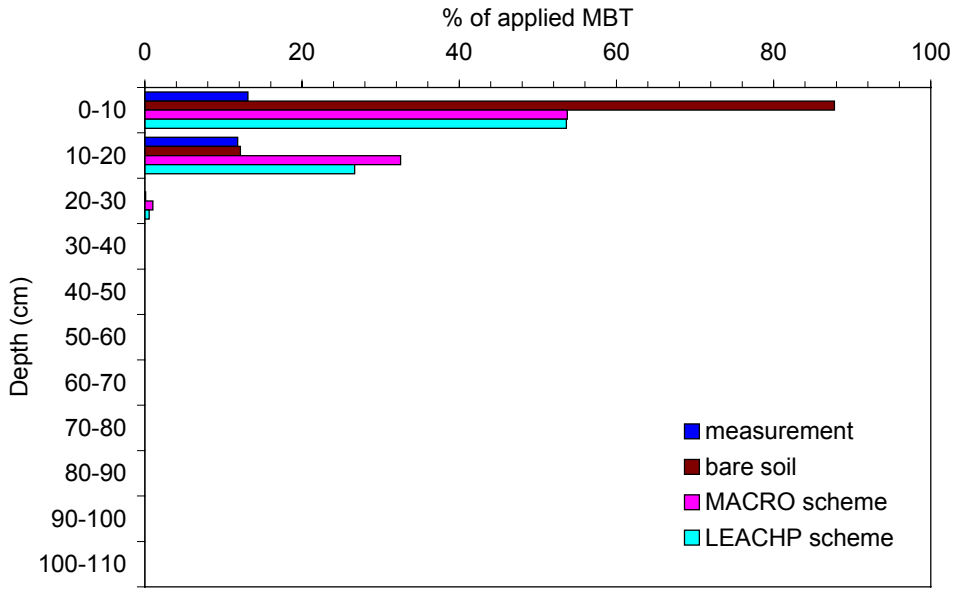


Fig. 153 - Residual MBT in the soil profile 627 days after application (no degradation).

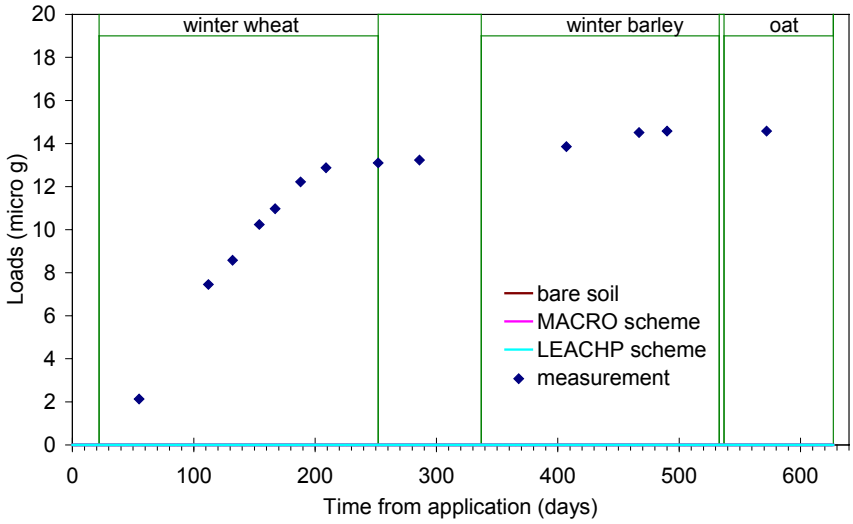


Fig. 154 - Accumulated amount of MBT in the leachate (no degradation).

Accounting for temperature effect on degradation according to the first approach (section 3.1.2. in chapter 2) was found to result in a considerable increase in MBT residuals in the soil profile (Fig. 155). In contrast, saturation was negatively correlated to the amount of MBT residues in soil. This was particular obvious from after 627 days of simulation (Fig. 156). The combined effect of temperature and saturation provided a good agreement to the data for a shorter period of time (Fig. 156) with a small overestimation of residuals.

When the second approach was used (*i.e.* combined effects of temperature and saturation on degradation), MBT residuals were larger by factors of 1.66 after 252 days when the temperature correction was activated in isolation (Fig. 157), 3.06 when corrections for soil humidity were made and 4.15 when both effects were considered compared to simulations which did not include any correction on degradation.

A comparison between measured and predicted total amounts of residuals demonstrated that the best fits to the data were obtained for the second approach with corrections for temperature and saturation on degradation (Table 44).

Table 44 - Total MBT residues in the soil profile (figures are expressed in in % of the MBT applied).

Total residual of MBT	After 252 days	After 627 days
Measured	27.8	24.9
First approach	34.0	6.1
Second approach	25.4	5.8

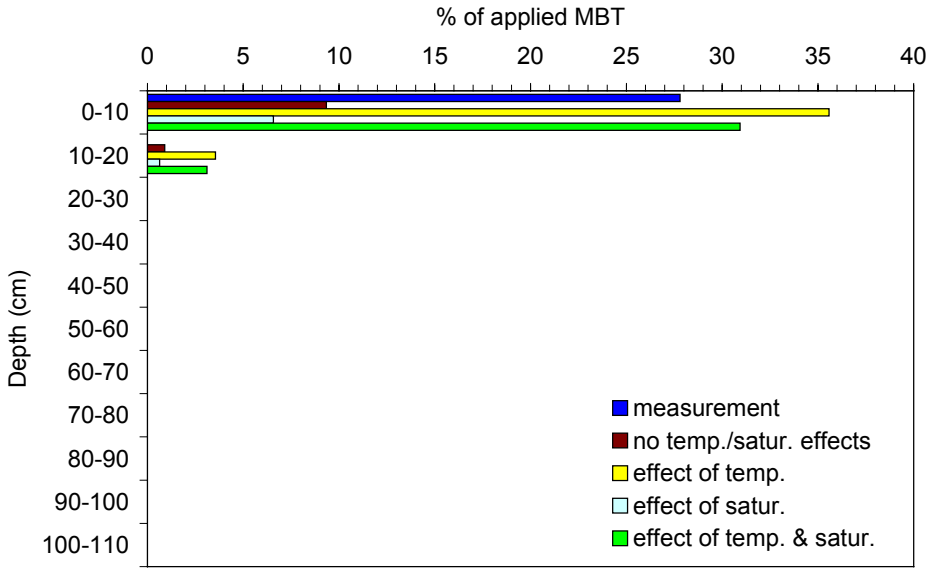


Fig. 155 - Residues of MBT in the soil profile 252 days after application (first approach).

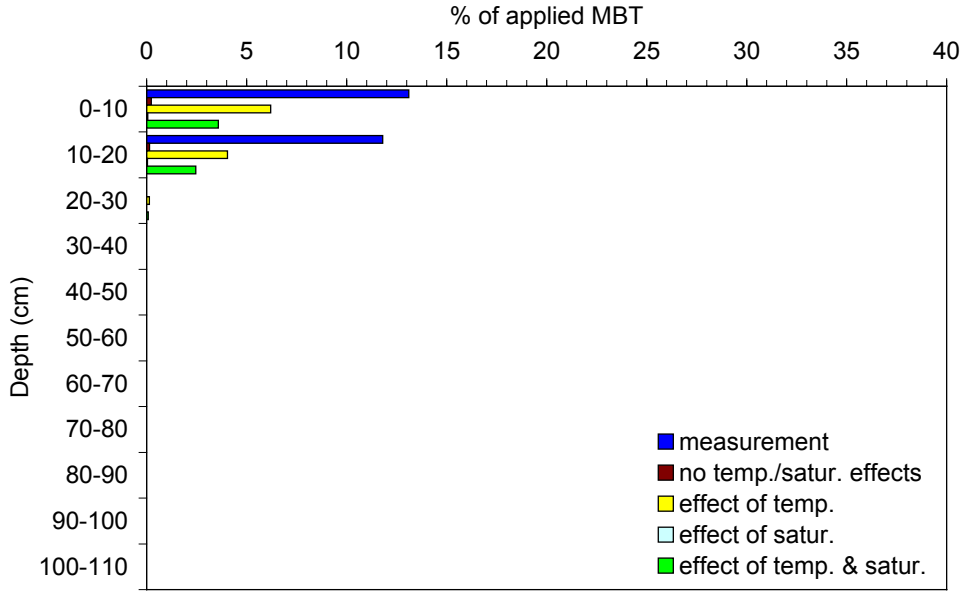


Fig. 156 - Residues of MBT in the soil profile 627 days after application (first approach).

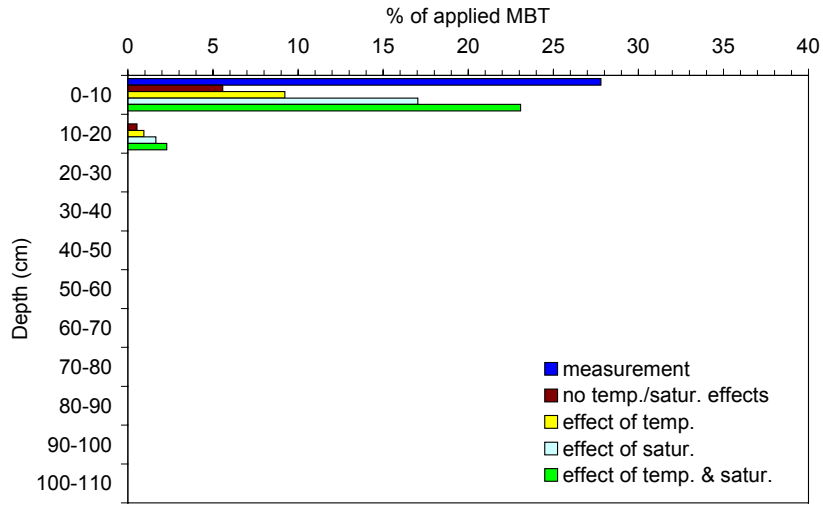


Fig. 157 - Residues of MBT in the soil profile 252 days after application (second approach).

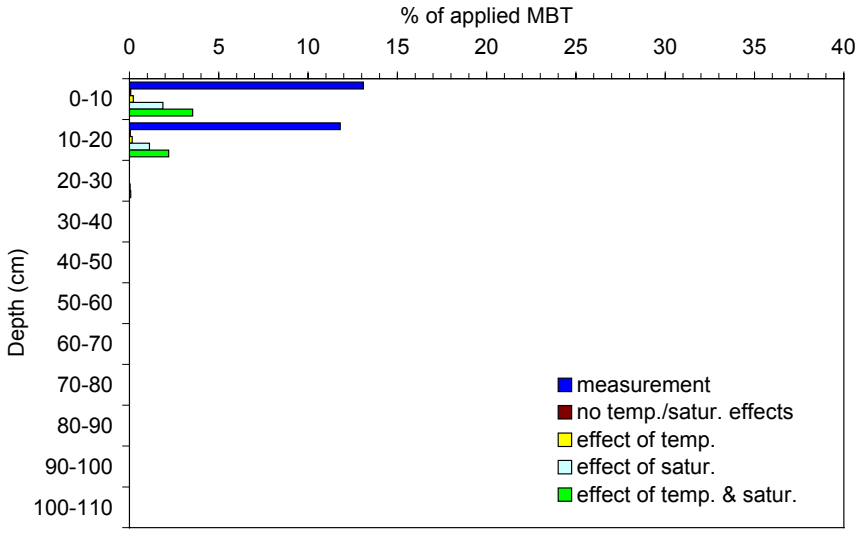


Fig. 158 - Residues of MBT in the soil profile 627 days after application (second approach).

4.2.3. Conclusions

Accounting for the effects of vegetation in the simulation of water flow improved the goodness-of-fit between model predictions and experimental data. The investigations showed that different approaches can lead to similar results with regard to the distribution of soil moisture in the profile.

The model did not predict the presence of MBT in leaching although the compound was detected in leachates collected in the field. This was attributed to the fact that preferential flow is not accounted for in MARTHE.

The overall performance of MARTHE in the simulation of one-dimensional vertical flow and pesticide fate in lysimeters may be considered satisfactory. However, the model would benefit from the implementation of a preferential flow subroutine.

4.2.4. Summary

Different tests were conducted with MARTHE to evaluate the influence on water transfer and pesticide fate of vegetation and corrections for temperature/soil moisture on degradation. Predicted results were compared to measurements of water flow, soil moisture distribution and MBT residuals in soil and leaching collected during a lysimeter experiment. Vegetation was found to have a crucial effect on the distribution of soil moisture in the soil profile. Similarly, the distribution of MBT residues in soil was found to be significantly affected by subroutines for the corrections of degradation according to soil moisture and temperature. The leaching of MBT through the lysimeter could not be replicated with MARTHE. This was attributed to the absence of preferential flow subroutines in MARTHE.

4.3. Modelling using ANSWERS [LTHE]

4.3.1. Supporting data

Input data provided by FZJ included:

- climatic time series of precipitation, PET, minimum and maximum temperatures, and global radiation;
- dates of emergence and harvest for crops;
- soil profile defined by grain size, density, organic C, pH, dispersivity;
- initial profiles of soil moisture or pressure heads;
- MBT application rate and date;
- sorption and degradation parameters and their dependence upon temperature and soil moisture.

Data for model verification consisted of:

- time series soil moisture content at two depths;
- time series of drainage flux at the bottom of the lysimeter;
- time series of actual evapotranspiration (obtained by mass balance between rainfall, drainage output and internal change of soil water storage);
- MBT concentration profiles at two dates;
- time series of MBT in drainage water;
- time series of soil temperature at 10 cm depth;
- crop yield.

4.3.2. Parameter estimation

A set of Model Parameter Estimation Routines (MPER) were used in the modelling:

- MPER 1 with the parameters describing the hydraulic properties of the soil. These were obtained through the use of statistical correlations (pedotranfer functions) from a database of 2,000 types of soils (Rawls and Brakensiek, 1985). Parameters included: Ks the saturated hydraulic conductivity (cm/h); Ψ_f, the wetting front capillary pressure head (cm); n, the available porosity (cm^3/cm^3), (Green and Ampt (1911) equation); η the conductivity shape parameter (Brooks and Corey (1964) equation), and θ_S (cm^3/cm^3), the water content at natural saturation were determined from soil texture, organic matter content (OM) and cation exchange capacity (CEC);
- MPER 2 with the parameters describing the plant behaviour in terms of water uptake and actual evapotranspiration. These were obtained from a database containing 78 different types of crop which integrates information at different phenological stages (from sowing to harvest) on time course values of the Leaf Area Index and root depth (Knisel, 1980). It should be noted that the correlation used to determine the crop parameters was not error free since the data in plant database mixes different soil types and croppig practices (*e.g.* irrigation, fertilisation);
- MPER 3 with the parameters describing pesticide fate processes. The most important variables are the soil organic matter, the Koc, and the half life. Koc and half life were taken from the Agritox database and were 520 cm^3/g and 125 days, respectively. Two important assumptions were made. First, it was assumed that degradation was only affected by temperature (no degradation at or below 0°C and maximum degradation at 25°C). Secondly, pesticide uptake was assumed to be 10 % of water uptake.

Two simulations were carried out: i) a blind simulation with the parameters determined only from the database; and ii) a simulation where crop parameters (Leaf Area Index and Root Depth) were adjusted to obtain a better fit between measured and simulated values for cumulative drainage out of the lysimeter.

4.3.3. Modelling results

- ***Soil temperature***

A good description of soil temperature is essential to simulate pesticide degradation. Figure 159 shows that temperatures were adequately simulated by ANSWERS.

- ***Soil water content***

Predictions of soil water contents at two different depths (Figs 160 and 161) revealed a poor fit in some periods of the simulation, which was attributed to an inadequate calibration of crop parameters.

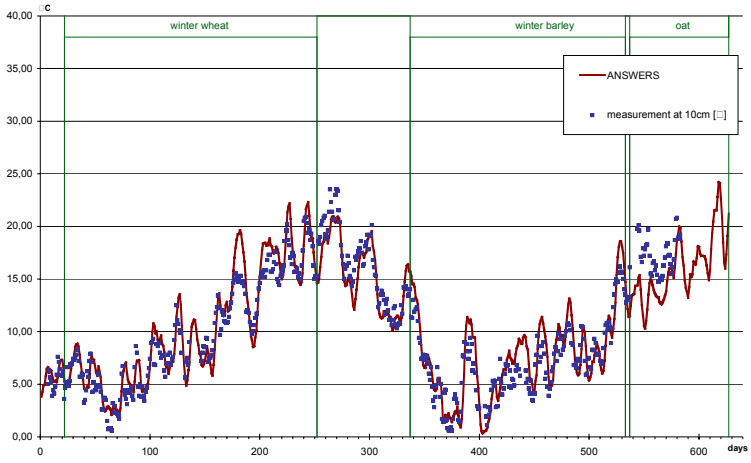


Fig. 159 - Comparison between measured and simulated soil temperatures at 10 cm.

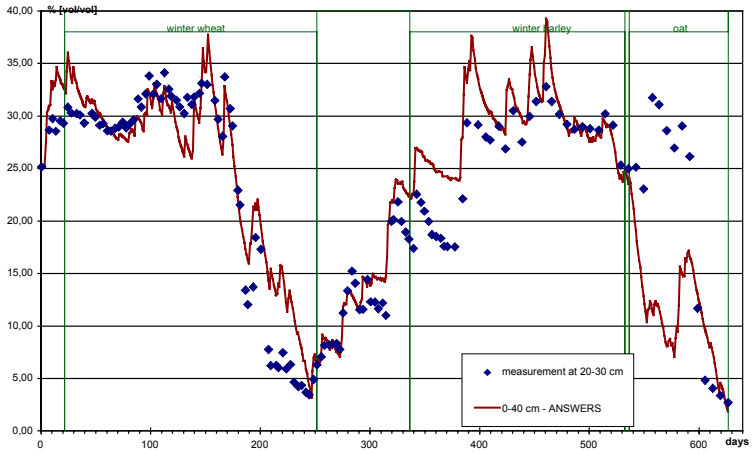


Fig. 160 - Comparison between measured and simulated soil water contents at 10 cm.

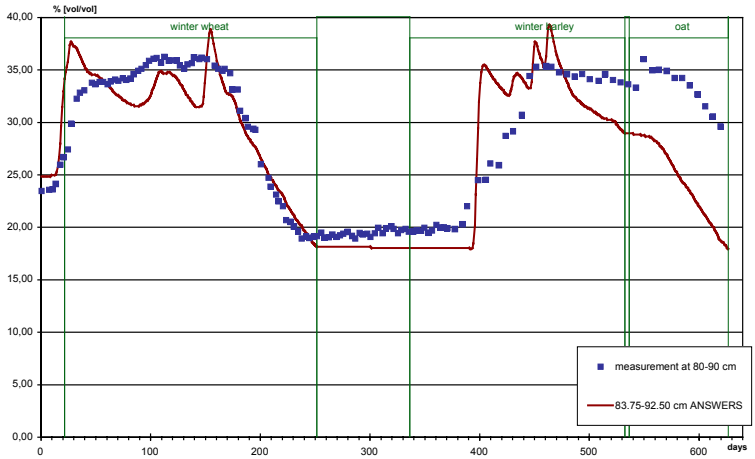


Fig. 161 - Comparison between measured and simulated soil temperatures at 90 cm.

- ***Soil water balance***

The comparison between simulation and measurements was performed on two variables: i) the cumulative amount of water draining from the lysimeter (direct measurement); and ii) the cumulative actual evapotranspiration, estimated from changes in soil moisture within the lysimeter. The performance of the model was satisfactory even when no calibration was undertaken (Figs 162 and 163).

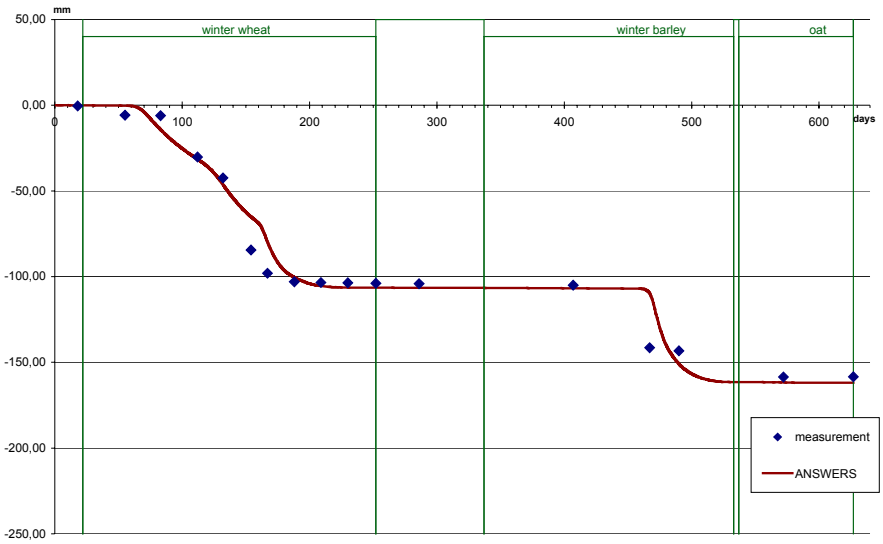


Fig. 162 - Comparison between measured and simulated cumulative drainage.

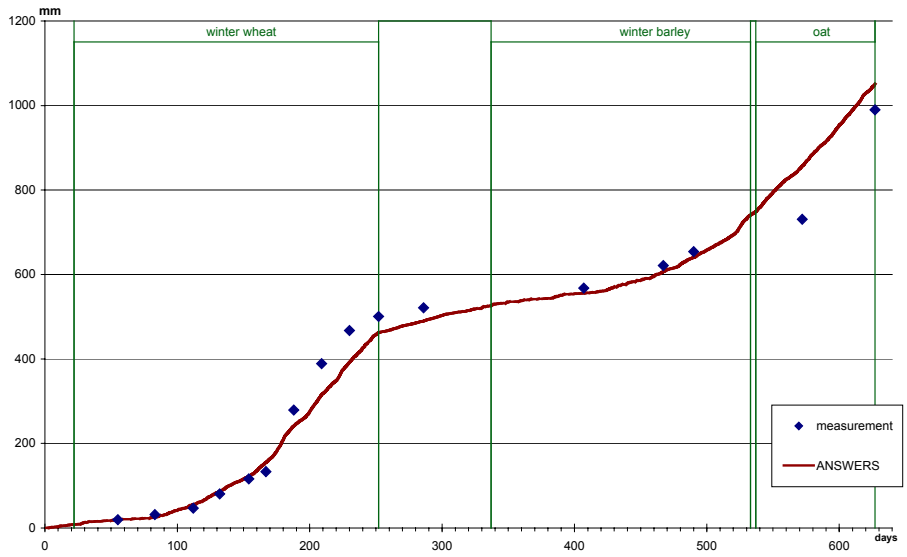


Fig. 163 - Comparison between measured and simulated cumulative evapotranspiration.

- ***Pesticide transport***

Two different methods were used to account for the degradation of MBT in soil.

- the first approach adopted was that used in GLEAMS (Knisel, 1993). It assumes than the degradation is a function of temperature only (no degradation at or below 0 °C, maximum degradation at 25 °C);
- the second approach was based on experimental values provided by FZJ to characterise the coupled effect of soil temperature and soil water content on the degradation of MBT. Experimental results are provided in Figure 164. For each temperature, the decrease in Half Life can be related to soil moisture using the following equation:

$$DT50 = A(\text{soil moisture})^{-1,343}$$

where A is related to temperature T by A = -255,9 LnT + 10395.

The temperature and water contents were taken in the middle of the first layer for both approaches.

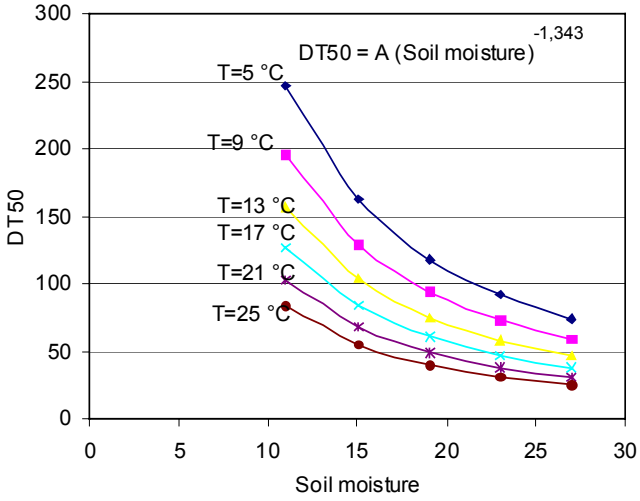


Fig. 164 - Half life (DT50, days) versus water content for a range of temperatures.

Figure 165 shows profiles of pesticide (expressed as % mass by soil layer with respect to the total mass of MBT applied) at 245 and 624 days predicted by ANSWERS using the two approaches for degradation. ANSWERS could not simulate the leaching data in such a short column since the model considers a first layer of about 40 cm. Figure 166 shows that the parameterisation of degradation with effects of temperature and water content induced a too important decrease in pesticide concentrations. This was already noted in a previous modelling study by FZJ with the Wave model.

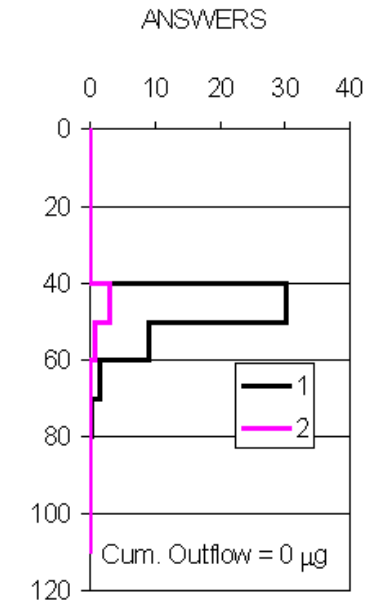


Fig. 165 - Profile of pesticide (expressed as % mass by soil layer with respect to the total mass of MBT applied) at 245 days. The modelling was undertaken assuming degradation to depend only of temperature (option 1) or temperature and water content (option 2).

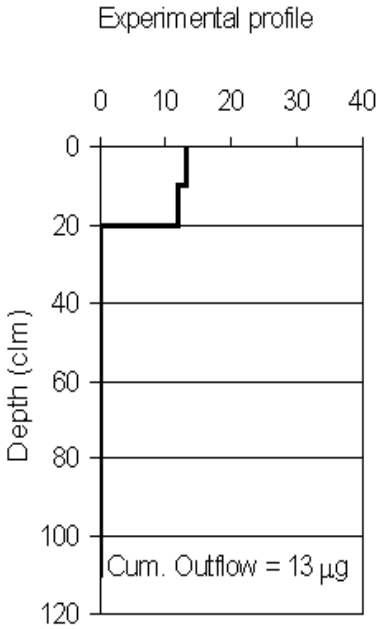


Fig. 166 - Profile of pesticide (expressed as % mass by soil layer with respect to the total mass of MBT applied) at 245 days. The modelling was undertaken assuming degradation to depend only of temperature (option 1) or temperature and water content (option 2).

Figure 167 provides a comparison between measured and predicted total cumulative leaching of MBT out of the lysimeter. At the end of the two-year period, the total amount of MBT flowing out of the lysimeter was measured to be 15 μg (0.0059 % of the applied mass). No leaching was simulated with ANSWERS although it should be noted that the very small amount of leaching measured may be considered to be non significant.

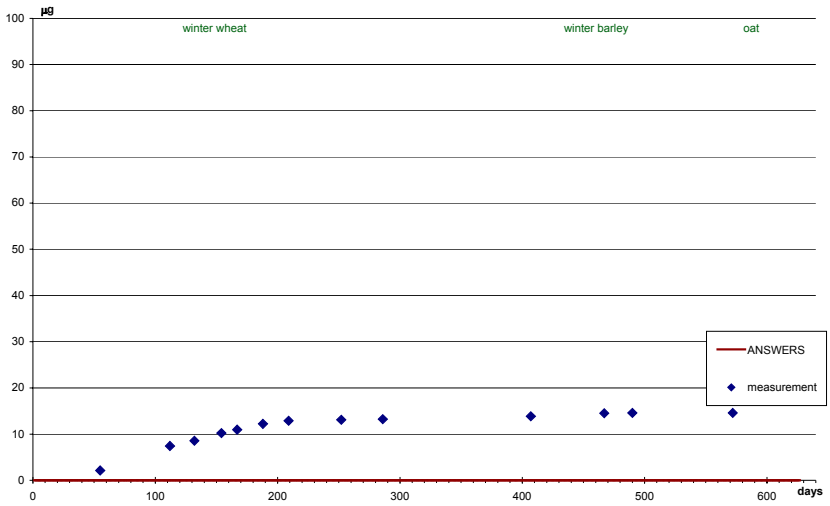


Fig. 167 - Comparison between measured and simulated cumulative leaching of MBT.

4.3.4. Summary

ANSWERS, with its new pesticide routine, was used to simulate the transport of water and MBT in the Zwischenscholle lysimeter over a two-year period. Predicted soil temperature, soil water content and soil storage were close to measured data although no calibration was undertaken. In contrast, the simulation of pesticide concentration (detected in the upper 20 cm of the soil profile only) was not satisfactory. This is essentially due to the structure of the model in which the upper horizon of soil is represented by a single reservoir.

5. APPLICATION OF MODELLING TOOLS TO THE MARTIGNY DATASET

5.1. 3D modelling of the Martigny large scale dataset using MARTHE [University of Neuchâtel, via EPFL]

Within the frame of the PEGASE Project, the Centre of Hydrogeology at the University of Neuchâtel, was involved in the study of the Swiss experimental site in Martigny, where pesticide concentrations were monitored on a limited area (4 km^2, see Fig. 168). To simulate pesticide transport in this area in a way as realistic as possible, the flow domain had first to be described and the watertable behaviour simulated on a much larger scale (Fig. 168). The Centre's contribution aimed thus at characterizing the main

features of the aquifer upstream of Martigny and at simulating the behaviour of the aquifer on a larger area (12 km^2) using the MARTHE 6.2 model.

The understanding of the aquifer behaviour resulting from an hydrogeological study allowed to model the system in a reasonable way, and then to provide the flow domain characteristics and boundary conditions to be used to simulate pesticide fate in the smaller area.

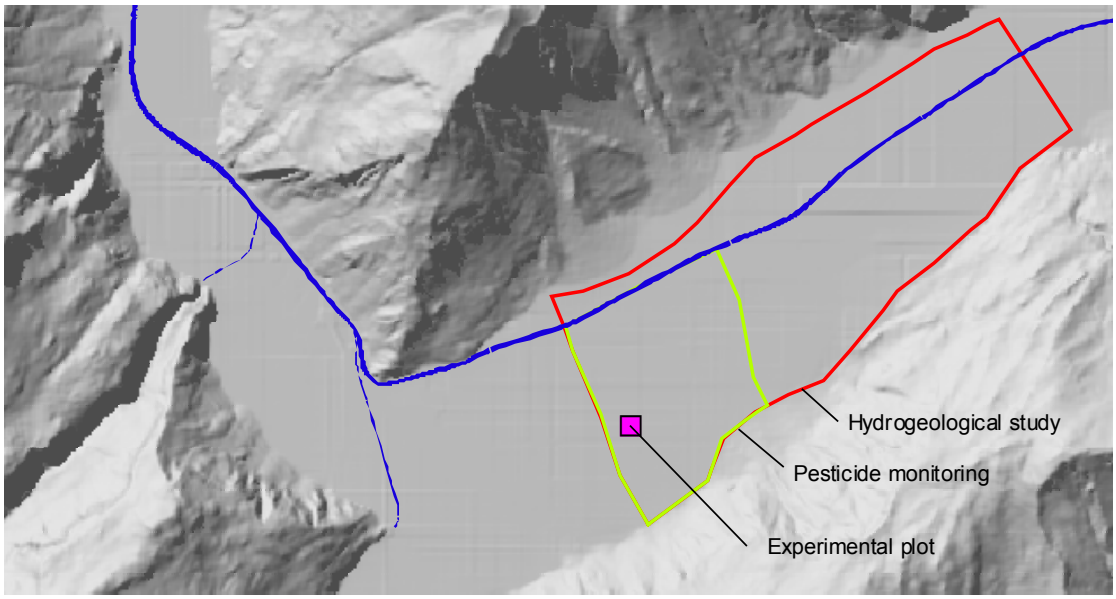


Fig. 168 - Study areas for the pesticide monitoring and the hydrogeological study.

5.1.1. Modelling approach

The piezometric surveys carried out twice a year (high and low waters) on the whole river plain by the research centre on alpine environment (CREALP) were used to draw seasonal piezometric maps from 1994 to 2001, along with two maps of electrical conductivity for 2001 and 2002. These maps and the data provided by nine automatic limnigraphs measuring the piezometric head of the water table and the Rhône river were used to analyse the effects of the river on the groundwater levels.

In a second stage, 91 boreholes descriptions were used to assign an equivalent hydraulic permeability and thus define the hydrodynamic characteristics of the various layers of the aquifer according to the TNO method REGIS (http://www.nitg.tno.nl/ned/projects/regis/data/REGIS_litho_k_code.shtml). Similar soil layers could then be grouped into more important structural units.

Finally a numerical model of the aquifer was elaborated using the MARTHE model. This model was then used to simulate under various assumptions the groundwater behaviour over the 1994-2001 period. Checking the simulation results against the observed piezometric heads helped to select the most adequate boundary conditions. The various tested boundary conditions include depth constant heads on the upper and lower boundaries (A), lateral inflow on a small part of the southern boundary (C) and a

no flow condition on the rest of the lateral boundaries (B), flux conditions on two water wells (D, E) and transfer conditions to account for the exchanges between the Rhone and the main canal and the groundwater. This large scale water flow model was then used to define realistic boundary conditions (on a monthly basis) on the edges of the smaller pesticide monitoring area. Since there is only little variation from one year to the other, the simulated boundary conditions on the year 2001 are considered valid for 2002 also.

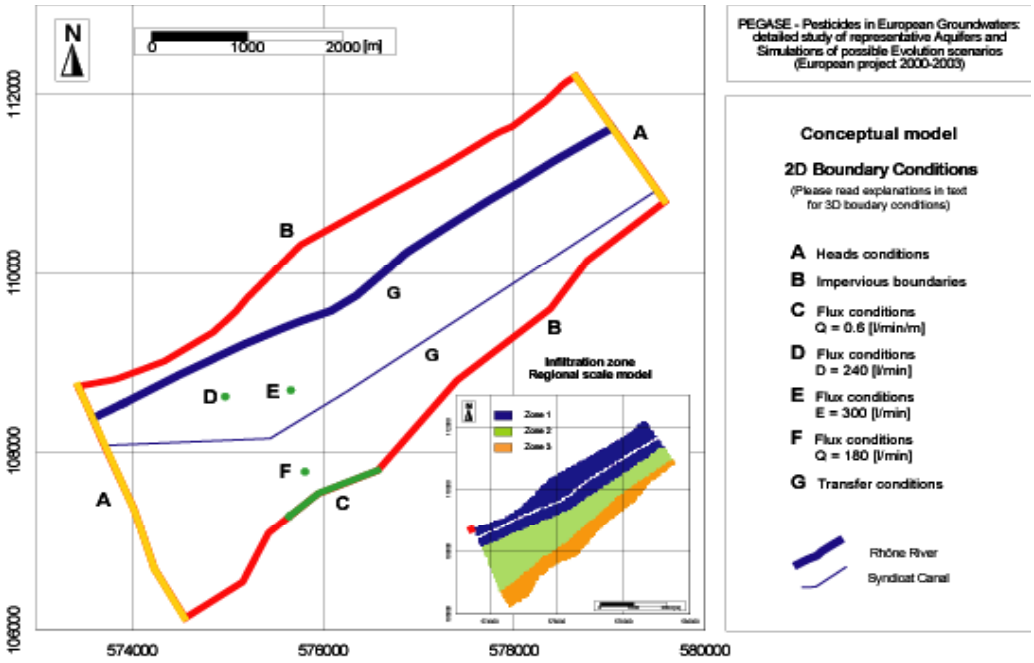


Fig. 169 - Conceptual model used in the MARTHE modelling of the Martigny dataset.

The piezometric maps, the electrical conductivity maps and the monitoring of some wells show that groundwater behaviour is strongly influenced by the Rhone river inflow, especially in the Branson area. There is also evidence of lateral inflows on the southern edge of the valley, in the Charrat area.

The flow domain could be simplified down to four principal structural units including from top to bottom: surface silts, surface gravels, intermediate silts and bottom gravels. Their hydrodynamic characteristics have been estimated.

The fitted numerical model reproduced quite well the observed heads on the 1994 to 2001 period, thus confirming the important effect of the Rhone river in supplying water to the groundwater (70 % of the aquifer recharge according to the simulated hydrological balances).

The simulations also allowed to get a rough estimate of parameters that are difficult to measure, such as the thickness and permeability of the Rhone river bed.

5.1.2. Discussion

The hydrogeological analysis and the aquifer simulations on the larger area, using the Marthe model, provided the information that is requested to simulate pesticide fate in a meaningful way on the smaller area. This information includes the geometry and hydrodynamic characteristics of the aquifer (*i.e.* surface elevation and for each of the four layers, bottom boundary, hydraulic conductivity, storage coefficient), the observed heads on the 1994-2001 period (high and low waters) and on the simulated heads (monthly basis).

Thus the soil and pesticide data that had been obtained from the experimental plot on one hand and from the spatial groundwater survey on the other hand is completed to form a complete and quite exhaustive dataset.

5.1.3. Summary

Seasonal piezometric maps (high and low waters for the 1994-2001 period), electrical conductivity maps (2001-2002) and automatic head records, along with 91 borehole logs were used to analyse the hydrogeological features of the Rhone river plain on a 12 km^2 area upstream of Martigny. Four main structural units of the aquifer were identified and their hydrodynamic properties estimated. Subsequently, all those data were used to calibrate the 3D groundwater flow model MARTHE, which includes river recharge to the aquifer, lateral inflow, canal-groundwater in- and outflows, etc.

This model was then used to derive the relevant aquifer properties (including geometry, hydrodynamic properties, and initial and boundary conditions) of a smaller flow domain (4 km^2) were pesticide fate had been monitored.

With these additional data, the Martigny dataset contains all the information requested to simulate pesticide fate from the unsaturated zone into the aquifer and fate in the aquifer in a meaningful way.

5.2. Modelling of the local scale Martigny dataset using ANSWERS [LTHE]

Modelling was undertaken with the ANSWERS model (section 1.2. in chapter 2) for the Martigny 1.5-m^2 experimental plots (section 1.2. in chapter 2). The field data which were collected from 20 April to 31 October 2001 (*i.e.* soil particle size distribution, bulk density, climatic data, suction, humidity, concentration profiles for bromide and selected pesticides) were analysed in relation to the evaluation of the values for model parameters and to the driving data required for modelling at the local scale. The revised version of the ANSWERS model (section 1.2. in chapter 2) allows to account for water capillary rise. The system simulated was a 1D soil column bounded by water at a depth defined using daily monitoring data for water table depths. This allowed both the unsaturated and saturated zones to be accounted for.

5.2.1. Data analysis and parameter estimation

- ***Meteorological data***

Available data from the station at Saxon were (at a 30-minute time step) air temperatures (°C), air humidity (%), air pressure (hPa), wind speed (m s^{-1}) and incoming solar radiation (W m^{-2}). These data were used to calculate the reference evapotranspiration ET_0 on the basis of the FAO-56 Penman-Monteith equation (Allen *et al.*, 1998). During the study period (20 April to 31 October 2001), the cumulative ET_0 reached 776 mm, whereas only 435 mm of rainfall were measured on the site (Fig. 170). The climatic demand was therefore very high.

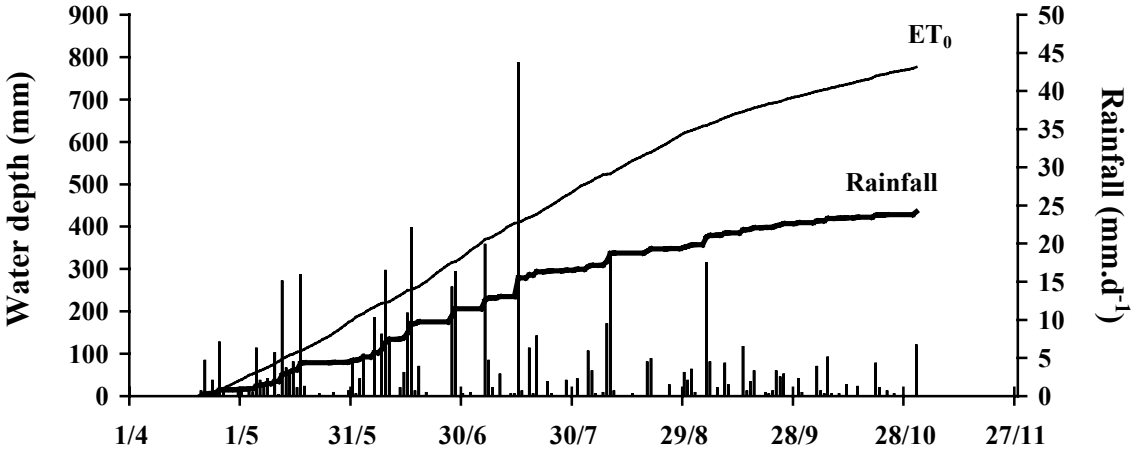


Fig. 170 - Rainfall and Penman-Monteith reference evapotranspiration. Cumulative values on the left y-axis (mm) and daily rainfall on the right y-axis (mm.d^{-1}).

- ***Groundwater data and soil moisture contents***

The groundwater depth fluctuated between 1.30 and 1.96 m bgl (below ground level) during the study period. The shallow position of the water table combined with a high climatic demand significantly influenced soil humidity values. Soil moisture TDR measurements revealed that the time variation of the soil water storage was very low (difference between maximum and minimum = 31 mm) compared to the 495 mm stored in the 120-cm unsaturated soil profile (Fig. 171).

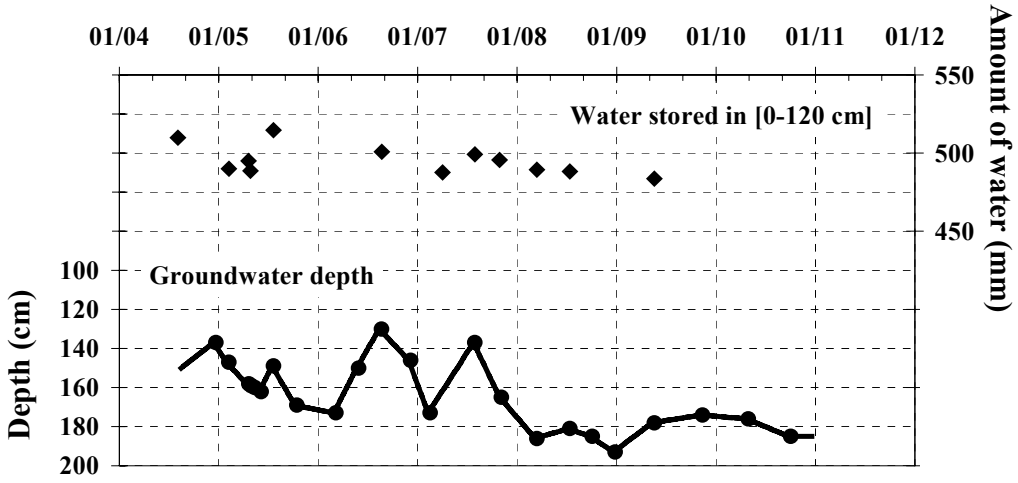


Fig. 171 - Measured groundwater depth and linear interpolation (left y-axis) and amount of water stored in the [0-120 cm] soil profile (right y-axis).

- ***Soil data***

On plots P1 and P4, disturbed soil samples collected at 10, 30, 50, 70 and 100 cm-depth were analysed to determine the particle size distribution curve using seven fractions (clay [<2 µm], fine silt [2-20 µm], coarse silt [20-50 µm], sand I [0.05-0.1 mm], sand II [0.1-0.316 mm], sand III [0.316-1 mm] and sand IV [1-2 mm]). Similarly, 59 values of soil dry bulk density ρ_d (g cm^{-3}) were measured at 10, 30, 50, 70 and 95-100 cm depth. A total of 3 horizons were considered in the modelling: [0-30 cm] with a bulk density of 1.49 g cm^{-3}, [30-75 cm] with a bulk density of 1.47 g cm^{-3}, and [75-200 cm] with a bulk density of 1.40 g cm^{-3}.

- ***Hydrological properties***

Parameters of the retention and hydraulic conductivity curves were calculated according to Rawls and Brakensiek's (1985) pedotransfer functions. The characteristics induced were very different from on-site measurements (sets of measured suction and soil humidity at the same time and the same depth) (Fig. 172). In particular, the air entry value obtained with pedotransfer functions appeared to be very small compared to the measured value. This is probably due the fact that pedotransfer functions were inaccurate given the high silt content (from 57 to 78 %), with an important range of particles close to clay. Measured values defining the retention curves were thus used in the modelling.

The Green & Ampt wetting front suction parameter, h_f, was assumed to be equivalent to the effective capillary drive and it deduced from Brooks and Corey's parameters as proposed by Morel-Seytoux *et al.* (1996). Saturated hydraulic conductivity K_s was measured on soil samples as well as in situ (auger hole method) throughout the plain (Soutter, 1996).

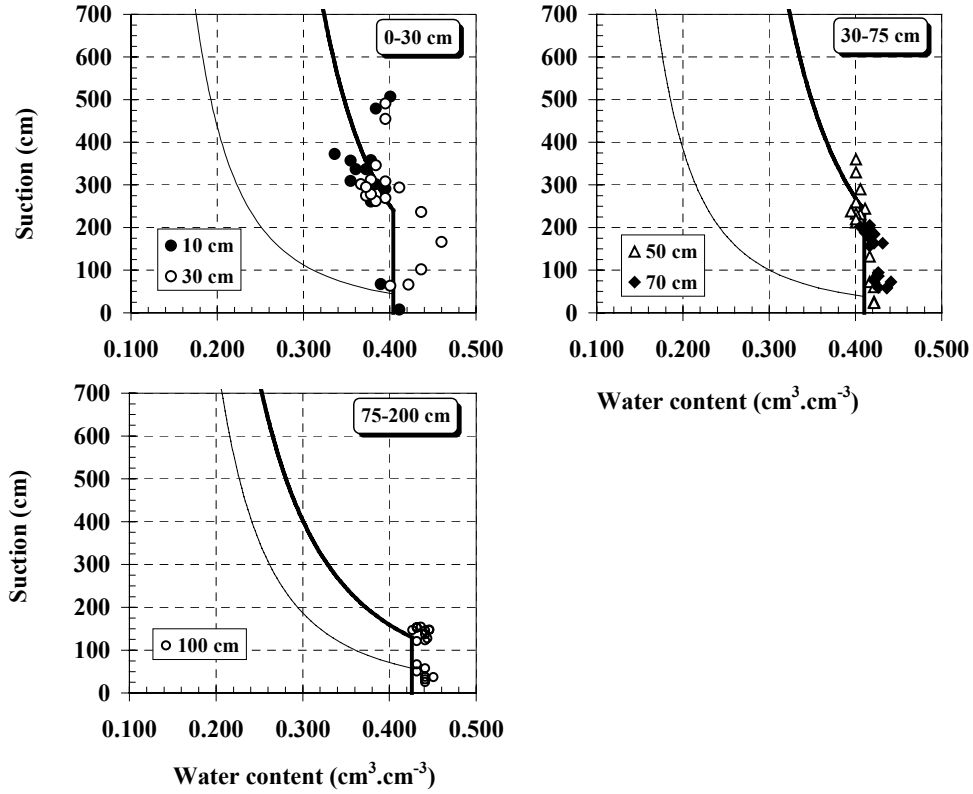


Fig. 172 - Plot P1. Comparison between Brooks and Corey retention curves i) derived using Rawls and Brakensiek's pedotransfer functions (thin line) and ii) with h_b-values calibrated (thick line) to go through measurements (symbols).

5.2.2. Modelling with ANSWERS

The modified version of ANSWERS, which allows water table-bounded conditions (defined as inputs with daily water table depths) and capillary rise to be simulated (section 1.2. in chapter 2), was used to undertake preliminary 1D modelling of the water balance at Martigny. Table 45 summarizes the required parameters obtained either from the Rawls Brakensiek pedotransfer functions or from direct calibration to site measurements (plot P1). The parameters L_1 and L_2 used to compute the evapotranspiration dependent upon the groundwater depth were set to h_B- (the height of the capillary fringe) and 3 m, respectively. Figures 173 and 174 present a comparison of the two different approaches on simulated water contents and cumulative actual evapotranspiration, respectively. The length of the capillary fringe was found to have a strong influence on soil water contents and on water balance terms at the boundary of the system.

The modelling exercise was discontinued for the following reasons: i) the hydraulic characteristics could not be predicted with the use of pedotransfer function; ii) the arbitrary selection of values for L_1 and L_2, two parameters used in the calculation of evapotranspiration, was judged to be problematic; and iii) there was evidence of preferential flow phenomena in the field, which cannot be simulated by ANSWERS.

Table 45 - Parameters of the Brooks & Corey retention and hydraulic conductivity curves, and of the Green & Ampt model.

Plot P1	θ_r ($cm^3.cm^{-3}$)	θ_s ($cm^3.cm^{-3}$)	λ (-)	h_B (cm)	K_s ($cm.h^{-1}$)	η (-)	h_f (cm)
Rawls & Brakensiek (1985)							
[0-30 cm]	0.046	0.404	0.369	44.3	0.27	8.4	42.3
[30-75 cm]	0.046	0.410	0.372	38.1	0.38	8.4	36.4
[75-200 cm]	0.045	0.426	0.343	58.0	0.18	8.8	54.4
Derivation of shape parameters from calibration							
[0-30 cm]	0.0	0.404	0.206	240.0	0.27	12.7	388.2
[30-75 cm]	0.0	0.410	0.220	240.0	0.38	12.1	384.5
[75-200 cm]	0.0	0.426	0.310	130.0	0.18	9.5	197.4

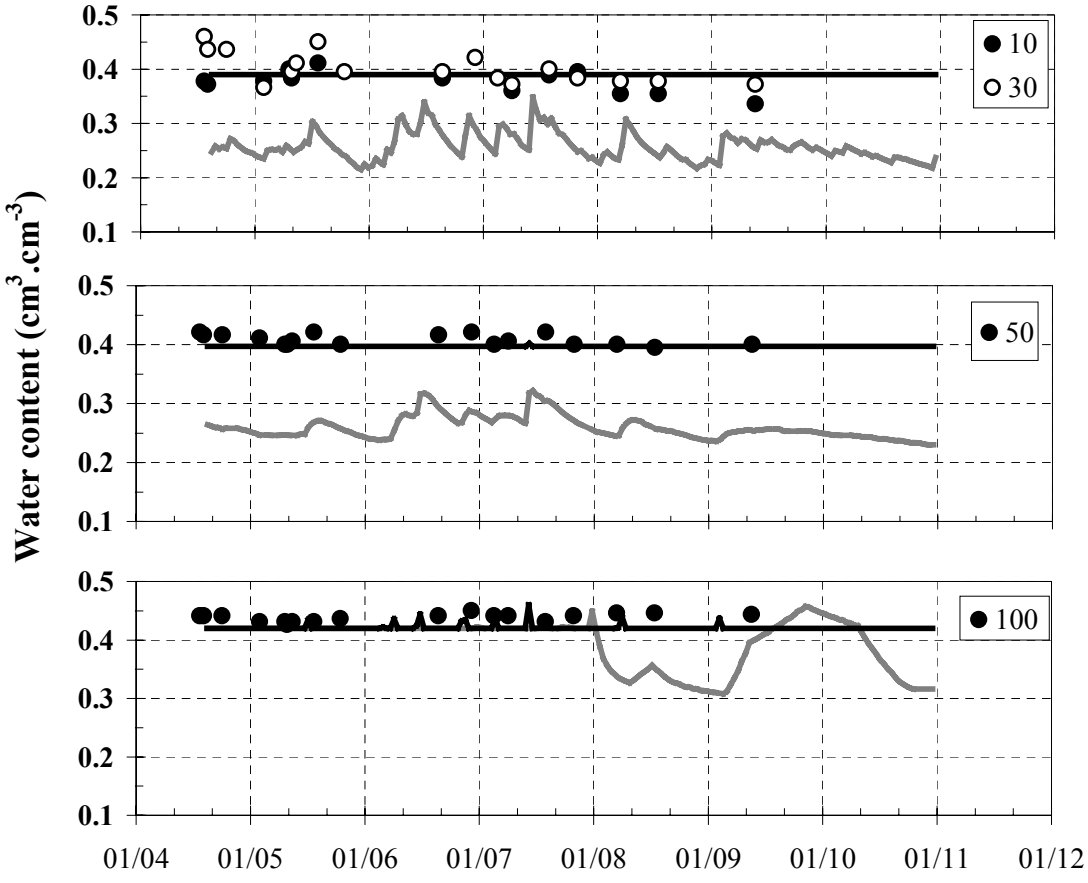


Fig. 173 - Comparison between measured water content at various depths (10, 30, 50, 100 cm), and simulation: i) grey thick line, using Rawls & Brakensiek's (1985) pedotransfer functions, and ii) black thick line, deducing shape parameters calibrating h_B-values.

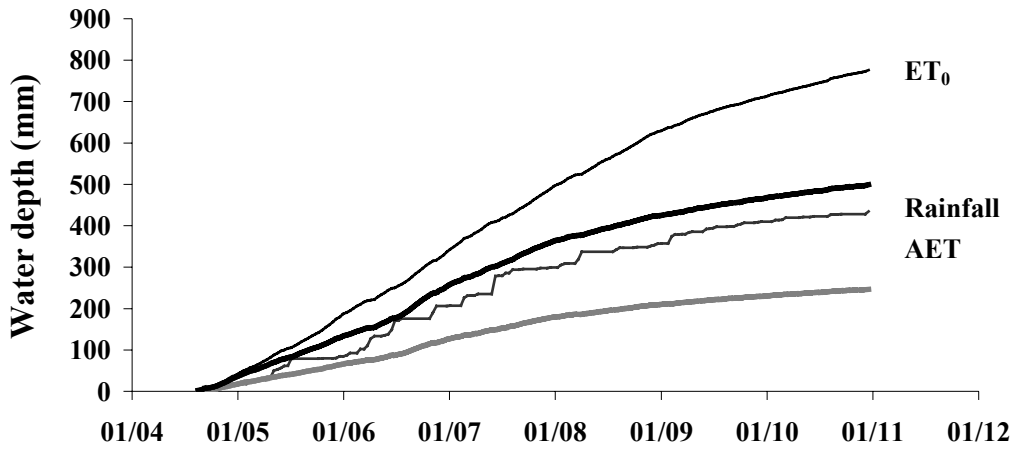


Fig. 174 - Cumulative rainfall, reference evapotranspiration, ET_0, and calculated actual evapotranspiration: i) grey thick line, using Rawls & Brakensiek's (1985) pedotransfer functions, and ii) black thick line, deducing shape parameters from calibrating h_B-.

5.2.3. Summary

ANSWERS was intended to be used to simulate water movement and pesticide transport in the Martigny experimental plots. The modelling exercise was discontinued for the following reasons: i) the hydraulic characteristics could not be predicted with the use of pedotransfer function; ii) the arbitrary selection of values for L_1 and L_2, two parameters used in the calculation of evapotranspiration, was judged to be problematic; and iii) there was evidence of preferential flow phenomena, which cannot be simulated by ANSWERS.

5.3. Modelling using MACRO [SAPROV]

Water movement and transport of isopoturon (IPU) in the Martigny field leaching experiment (section 5 in chapter 1) was simulated in 1D using the MACRO model (Jarvis *et al.,* 2001). Modelling results were compared with field leaching data and with simulation results obtained using ANSWERS (section 5.2. in the present chapter). The aim of the work was to undertake a preliminary calibration of the two models.

5.3.1. Modelling approach

- ***Model***

MACRO is a physically-based preferential flow model that can be used to describe water and solute transport in a range of soil types. The total soil porosity is divided into two flow domains (macropores and micropores), each of them characterised by a flow rate and solute concentration. Crop development is based on a simple model that accounts for emergence, maximum leaf area and harvest dates. Pesticide degradation is modelled using first-order kinetics. Degradation half-lives need to be specified for the

solid and liquid phase in the macropores and micropores, and may be adjusted for temperature and moisture effects. Sorption is assumed to be at instantaneous equilibrium and to be described by a Freundlich isotherm. MACRO version 4.3 (Jarvis *et al.,* 2001) was used in the current work.

- ***Calibration data***

The data used in the calibration were those generated during a field leaching in Martigny for a 1.2-m deep bare soil. The dimensions of the experimental plot were 2.5 x 1.6 m (length x width) and water and pesticide fluxes were monitored from 20 April to 31 October 2001 through suction cups. IPU was applied on 11 May at an application rate of 351 mg/m^2. Detailed information on the field experiment and on the input derived for simulations are described in section 5 in chapter 1 and section 5.2. in present chapter.

- ***Calibration of MACRO***

Table 46 presents some of the values attributed to MACRO parameters. The values of K_s and ET_0 were suggested by LTHE & EPFL and were used in the modelling. Values for sorption and degradation were taken from the literature (Nicholls, 1994). The model was first calibrated against measured soil water contents. Calibration of the pesticide component of the model was carried out by varying sorption coefficients and degradation rates.

Table 46 - Input data used in the simulation exercise.

WATER COMPONENT				PESTICIDE COMPONENT (isoproturon)			
Dataset		MACRO		Dataset		MACRO [c]	
ET_0	K_s (m s^{-1})	BGRAD[a]	1/h (mm^{-1})[b]	K_{oc} (L kg^{-1})	$t_{1/2}$ (days)	K_d (1th layer)	K_{deg} (d^{-1})
Calculated FAO-56	2.78 10^{-7} calibrated	Medium	7 10^{-5} ([c])	130	20	1.04	0.034

[a] = permeability factor; three options (low, medium, high).
[b] = variable groundwater depth.
[c] = calibrated value by attempts.

5.3.2. Modelling results

- ***Water component***

Figure 175 reports simulation results for ANSWERS and MACRO against measured values for water contents in the experimental plot P1. The use of the data proposed by EPFL and LTHE provided a good calibration of the water component, although slight differences at depth were noted. Differences in the simulation of the cumulative water balance between the two models were found (Fig. 176). The cumulative actual evapotranspiration (AET) and the cumulative drained water (DRAIN) simulated by ANSWERS were larger than those predicted by MACRO. These differences did not have significant influence on the predictions for the distribution of water in the profile.

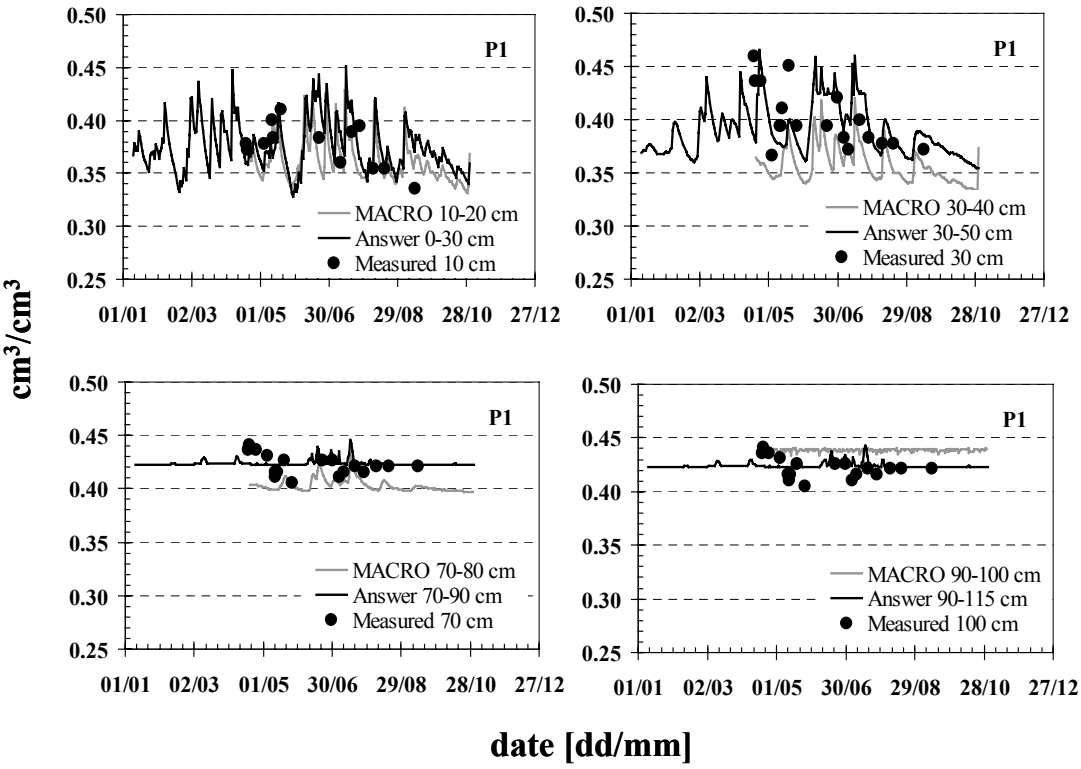


Fig. 175 - Soil moisture measured and simulated with MACRO and ANSWERS.

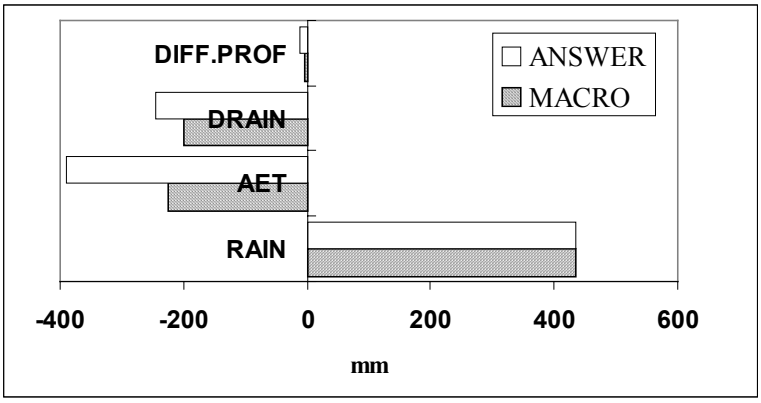


Fig. 176 - Cumulative water balance simulated with the two models.

- ***Pesticide component***

The simulation exercise was performed for isoproturon (IPU) and with input data reported in Table 46. Results are reported in Figures 177 (IPU concentrations in the soil solution) and 178 (IPU concentrations in the soil solution + sorbed IPU).

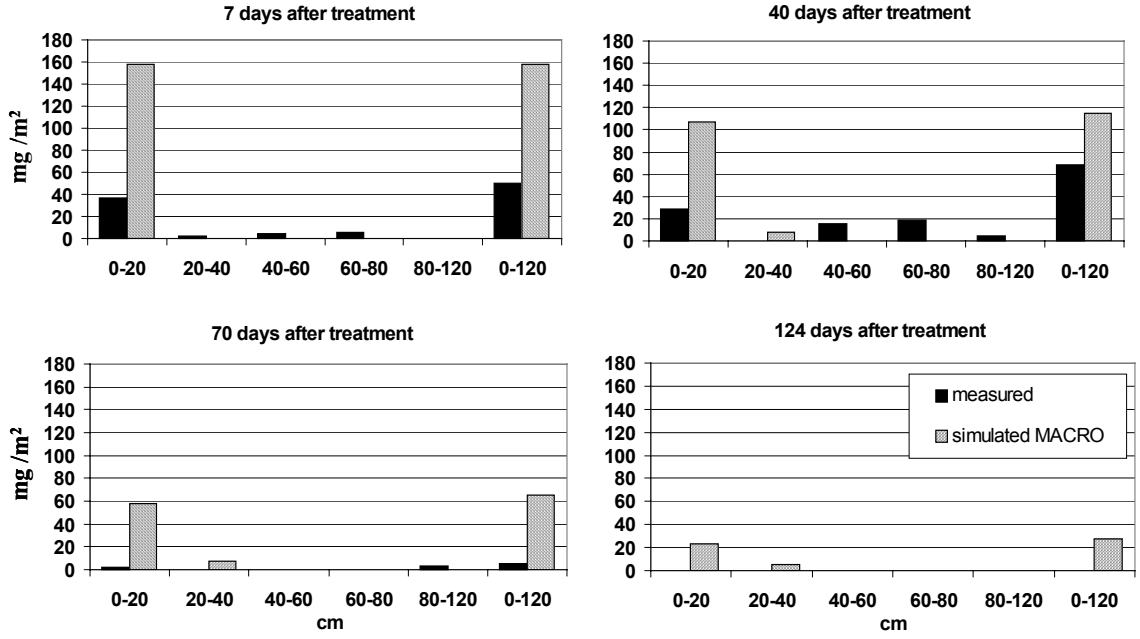


Fig. 177 - Isoproturon in the soil solution along the 120 cm of soil profile, measured and simulated with MACRO.

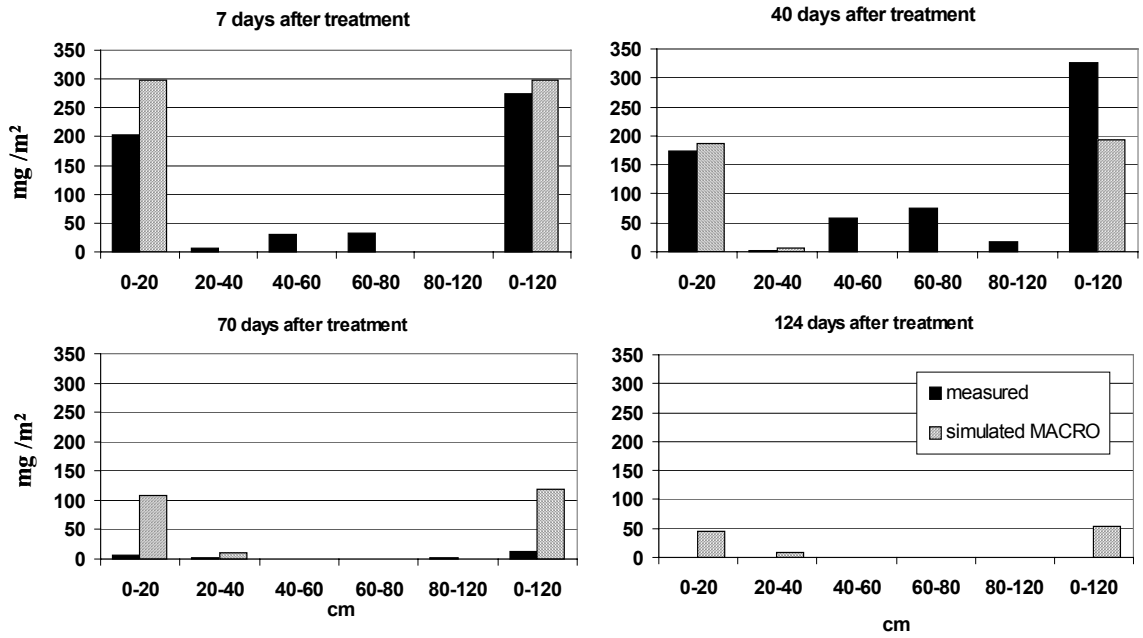


Fig. 178 - Isoproturon along the 120 cm of soil profile (concentrations in the soil solution + adsorbed), measured and simulated with MACRO.

MACRO appeared to underestimate pesticide movement in the soil profile. IPU measured in the soil solution moved quickly along soil profile: only 14.3 % of applied remained in the first 120 cm 7 days after treatment (DAT) and IPU had almost disappeared at 70 DAT. In contrast, MACRO simulated a slow downwards movement of IPU and IPU was predicted to be still present in the first 40 cm (about 9 % of applied) at 124 DAT. Discrepancies between measured and simulated IPU concentrations in the soil solution in the first 120 cm soil profile may be due to suction cups not sampling the totality of water moving down the profile, in particular that moving along preferential flow pathways. The comparison between IPU concentration in the whole soil (solution + adsorbed) showed a better agreement between measured and simulated data (Fig. 178), but discrepancies were still noted. Total measured and simulated IPU concentrations were comparable at 7 DAT and 40 DAT, even if MACRO simulated a slower movement to depth and IPU remained in the first 40 cm of the soil profile. IPU could not be measured in the profile at 70 DAT while MACRO simulated its presence until 124 DAT (14.3 % of applied). Differences between measured and simulated data in the total pesticide concentration at 70 and 124 DAT may be ascribed to the choice of degradation and sorption parameters. Attempts to calibrate the model through an increase in DT50 by 50 % and a 60 % decrease in K_{oc} failed (data not shown).

5.3.3. Summary

The MACRO model was used to simulate results of the Martigny field leaching experiment. MACRO predictions were compared to measured data and predictions by the ANSWERS model. Results for the distribution of soil moisture at four depths in the profile were adequately simulated by the two models in the shallow horizons. Concerning pesticide behaviour, the parameterisation of MACRO was found to underestimate pesticide movement in the soil profile, but this might be due to the lack of suitability of concentration data generated using suction cups. Differences between measured and simulated data in the total pesticide concentration were attributed to the choice of degradation and sorption parameters although a simple attempt to improve the fit to the data by varying these parameters failed.

5.4. Modelling using PESTGW [WRc]

5.4.1. Evaluation of PESTGW against Martigny data

The screening tool PESTGW was tested against data from the Martigny experimental site. Data were available for unsaturated zone porewater concentrations and groundwater concentrations of bromide and atrazine. Site data from Martigny were used to select input parameters for PESTGW where possible and results were compared to real data (Figs 179 and 180).

Measured atrazine concentrations in the unsaturated zone below the soil base were under-predicted by PESTGW by a factor of five (5.0×10^5 ng/l predicted vs. 2.5×10^6 ng/l measured). Plot 3 was irrigated with 15 mm of water immediately after the application of atrazine and bromide on 11 May 2001. Although this recharge has been added to the recharge in the PESTGW input file, the predicted atrazine peak shows some delay when compared to the measured data. This is likely to be a product between the monthly recharge (coarse compared to daily) used in PESTGW and the

fact that fissures in the soil zone are not considered in PESTGW. Fissures in the soil would be likely to increase pesticide transport from the ground surface to just below the base of the soil zone through preferential flow processes.

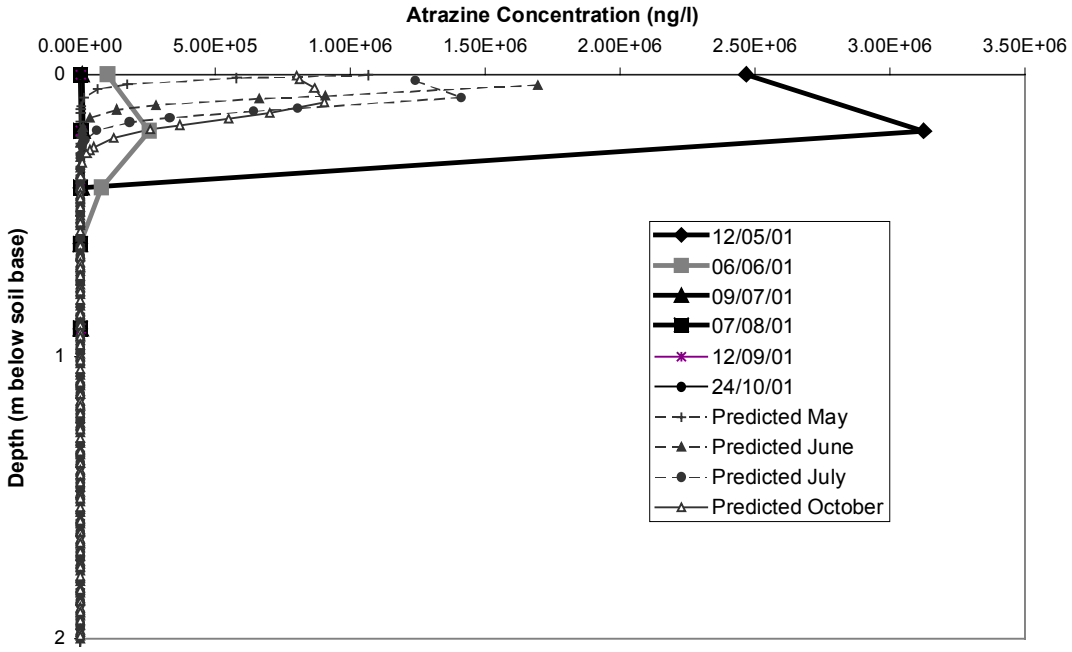


Fig. 179 - Comparison between predicted and measured atrazine concentrations for Plot 3 at Martigny.

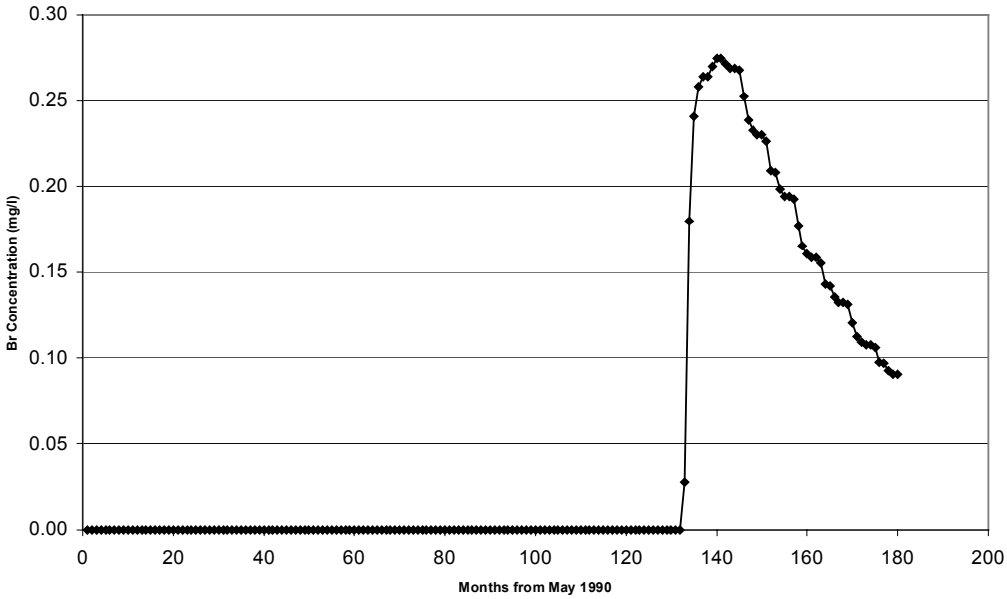


Fig. 180 - PESTGW output for Plot 3 at Martigny (up to 18 mg/l Br were measured).

The groundwater predictions from PESTGW for Plot 3 show a significant under-estimation of the pesticide impact by up to two orders of magnitude. Sensitivity trials conducted with the Plot 3 input file showed that groundwater concentrations similar to measured bromide concentrations were predicted if the recharge was increased threefold. Measured bromide concentrations were shown to decrease from 18 mg/l to 6 mg/l within 2 months (mid May – mid July 2001), but the predicted impact lasted for 20-40 months. It is therefore likely that the peaks measured in the field were the result of rapid daily spikes of bromide via a fissure pathway being diluted in daily volumes of groundwater. The fact that the predicted bromide concentrations were much lower than those measured is attributed to dilution in monthly volumes of groundwater.

5.4.2. Evaluation of PESTGW against other groundwater data

PESTGW was also evaluated against data from Compton in the UK. Porewater atrazine concentrations analysed from cores taken from a borehole constructed at Compton (southern England; chalk subsoil) in October 1994 (BH 1) were used to calibrate the output from PESTGW at month 130 (Oct. 1994) (Fig. 181).

The preferred calibration profile is given by 'Calib D=0.0003'. As dispersion in this profile has reduced the distinctive peaks, it is necessary to reduce the dispersivity (D) in order to appreciate profile chronology. 'Calib D=0.000003' is only included to appreciate how the depth of the predicted peaks match up with the measured peaks. The chronology of the peaks shown for the real data (BH 1, 1994) can only be presumed as the peaks may be the result of inherent variability caused by the sampling and testing procedures. The immunoassay (IA) test kit which was used for the analysis of atrazine, is considered to have a RSD (Relative Standard Deviation) of less than 20 % at low concentrations (Clark *et al.,* 1996). This means that if the average atrazine concentration of a sample is 0.8 µg/l, an RSD of 20 % would return an expected standard deviation of $\pm$ 0.16 µg/l. A site-specific RSD test of the IA kit was carried out on samples from another borehole at Compton (BH 2, 1994) and this test indicated that a lower RSD can be expected when using IA kits for chalk cores (Table 47).

Table 47 indicates that RSD values of $\leq$5 % can be relied upon when determining atrazine at concentrations above 0.35 µg/l when using the IA kits. The error bars shown in Figure 181 refer to an RSD of 5 %, and therefore indicate that the trends determined by the IA results are genuine. The parameters used to achieve the predicted profile shown for 'Calib(D=0.0001)' is given in Table 48.

The predicted concentration at BH 1 shows a reasonable correlation to the measured atrazine profile. The 'Calib + D=0.000001' profile does indicate however that there is some discrepancy between the presumed and predicted atrazine peaks for the 1990 and 1991 application. This may be due to local variations in porosity in the region between 4 m bgl and 7 m bgl, and/or the effect of the variable moisture content within the capillary zone. Solutes within the capillary zone may have enhanced dispersivity due to the zone's high moisture content, especially when fluctuations in the groundwater level are encountered.

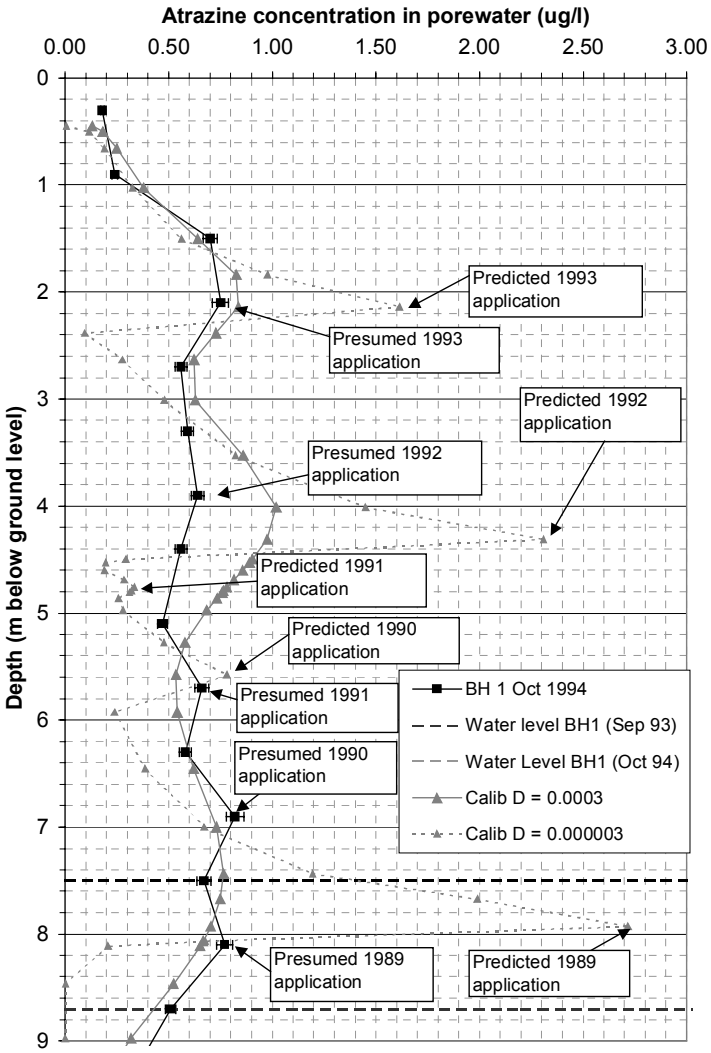


Fig. 181 - Calibration of PESTGW against Compton data.

Table 47 - RSD values obtained from IA tests on Compton cores (BH 2, 1994).

Depth (m bgl)	Atrazine concentration from initial sample (μg/l)	Atrazine concentration from duplicate sample (μg/l)	Mean (μg/l)	SD (μg/l)	RSD (%)
0.3	0.58	0.52	0.55	0.03	5
1.9	0.41	0.43	0.42	0.01	2
3.9	0.35	0.33	0.34	0.01	3
5.1	0.08	0.07	0.08	0.01	13
5.7	0.08	0.03	0.06	0.03	50
6.9	0.43	0.44	0.44	0.01	2
11.1	1.21	1.15	1.18	0.03	3
15.3	0.62	0.58	0.60	0.02	3

Table 48 - Calibration parameters (UK Chalk) for the predicted profile presented in Figure 181.

Parameter	Value	Units
Koc	100	litres/kg
λ soil	40	days
λ chalk	2000	day
BFI	0.94	-
Soil Top Level	0	cm bgl
Soil Base Level	40	cm bgl
foc soil	4	%
Pb soil	1.50	Mg/m3
n soil	46	%
%age Fissuring	1	%
Unsaturated zone base level	7.7	m bgl
n chalk	8	%
foc chalk	0.05	%
Pb chalk	1.65	Mg/m3
Dispersivity	0.0003	m2/d

5.4.3. Summary

The screening tool PESTGW was evaluated against data for atrazine concentrations from Martigny. The tool was found to underestimate atrazine concentrations in porewater and groundwater by factors of 5 and ca. 100, respectively. This was attributed to a rapid transport of water and pesticides in the field through preferential flow phenomena and to the fact that PESTGW accounts for a dilution of any concentrations in a groundwater volume. Additional tests of the tool were undertaken against UK data.

6. APPLICATION OF A MODELLING TOOL TO LES TROIS FONTAINES DATASET

6.1. 3D modelling using MARTHE [BRGM]

Detection of pesticide residues in the water at the spring of Les Trois Fontaines (section 2 in chapter 1) confirmed the high vulnerability of karstic systems to pesticide contamination. Understanding mechanisms of groundwater recharge in a karstic system and pesticide dynamics at the catchment scale is therefore critical for any effective management and prevention strategy. The aim of the present modelling was to verify the usefulness of the deterministic model MARTHE for describing pesticide behaviour in a complex groundwater system at a large scale. MARTHE predictions were compared to measured data for concentrations of atrazine and isoproturon at the spring of karstic catchment.

6.1.1. Material and methods

The karstic system of Les Trois Fontaines is situated in the eastern part of the Loiret department (France) between two tributaries of le Loing river: l'Ouanne and la Cléry. The groundwater system was characterised based on results from a piezometric campaign (about 200 points) in 1990. Comparison with previous campaigns (1981, 1982, 1983, 1988) enabled the definition of the hydrogeological limits of the system through a zero flux boundary. These limits were validated using an additional compaign of 2003.

The studied area was divided into a grid with 50 columns, 46 rows with a horizontal resolution of 250 m. The domain of the model in the horizontal plane consisted of 729 active cells which gave an area of 45.56 km^2. At the top boundary of the model, averaged topographic altitudes were calculated from a Digital Terrain Model with a 50 m resolution (DEM IGN). The bottom boundary was fixed at the constant altitude of 70 m. In the vertical direction, three horizons were distinguished based on the examination of the Infoterre database and geological maps:

- a loamy soil (depth 0-1.5 m);
- a layer of clay (depth 0-25 m);
- an underlying chalk formation where the aquifer is located.

The modelling was undertaken with the improved version of the MARTHE model (section 3.1. in chapter 2). The model domain was divided in vertical into 6 layers with variable thickness (Table 49).

Table 49 - Scheme of vertical subdivision.

Layer	Thickness	Soil types
1	0.3 m	washed out and degraded loam, sediments, outcropping chalk
2	0.3 m	washed out and degraded loam, sediments, outcropping chalk
3	1.0 m	degraded loam, clay, chalk
4	10.0 m	clay, chalk
5	14.0 m	chalk with a central drain system
6	14.0 to 84.1 m	chalk with a central drain system

The landscape consisted of a large loamy plateau (about 1.5 m depth) located upstream of the basin and some small ones downstream, valleys of temporary brooks where chalk is outcropping (can be seen as zones of preferential infiltration) and a thin loamy soil (about 0.5 m depth) with the flint clay underneath on the rest of the area.

A central drainage system was implemented at the bottom layer of the model on the basis of the piezometric maps available. The existence of a very permeable zone in the centre of the system was confirmed by two tracing tests (Lasne, 1992). The model calculated recharge based on precipitation and potential evapotranspiration. The overflow of groundwater was allowed in the northern part of the model where a small river flows and natural sources are present (Moulin de Loince, 3 Fontaines). The simulation was set up for the period extending from 1/1/1989 to 31/12/2002 (14 years). Annual precipitation over the period ranged between 507.2 mm and 976.5 mm with a mean of 731.4 mm. Daily time series of potential evapotranspiration (PET) were obtained from a meteorological station at Orléans Bricy (about 100 km from the basin)

while precipitation data were sourced from the station Les Plets (Chuelles) located in the basin. Precipitation and PET were applied uniformly over the whole area.

The simulation of hydrodynamics was performed with a daily time step using time series of precipitation and potential evapotranspiration. The influence of crop coverage was not taken into account. For each type of soil, van Genuchten's relationships were used to describe the water retention curve and hydraulic conductivity curve in the following form:

$$\Theta_{(h)} = \Theta_r + (\Theta_s - \Theta_r) \cdot \left[1 + \left(\frac{h}{h_t} \right)^{1/b_t} \right]^{b_t - 1} \qquad K_{(h)} = K_s \sqrt{\frac{\theta - \theta_r}{\theta_s - \theta_r}} \cdot \left\{ 1 - \left[1 - \left(\frac{\theta - \theta_r}{\theta_s - \theta_r} \right)^{\frac{1}{1-b_t}} \right]^{1-b_t} \right\}^2$$

with $h_t = \frac{1}{\alpha}$ [L] the suction for half saturation and $b_t = \frac{1}{n}$ [-].

A manual calibration was performed to determine soil parameters (Table 50). It was observed that the selection of the distribution of initial hydraulic heads were crucial to the final modelling results. This can be explained by the presence of a low permeable and thick (10 m) clay layer overlaying the whole chalk formation. New initial conditions for each calibration run (after changing the parameters) were thus calculated assuming constant infiltration rate of 0.379 mm/d. This infiltration rate was derived from the assumption that the flow rate at the spring of Les Trois Fontaines (at the beginning of simulation about 100 l/s) is approximately equal to 50 % of the whole basin. Equilibrium (constant outflow at the spring and constant hydraulic heads in 2 observation points) was achieved after running a pseudo steady state simulation for 48 years. Only two parameters were tested during calibration: θ_{sat} and K_{sat}. It should be noted that results presented can probably be improved further as the system was very sensitive to both initial conditions and hydrodynamic parameters, and calibration was found to be very time consuming and was thus somewhat limited.

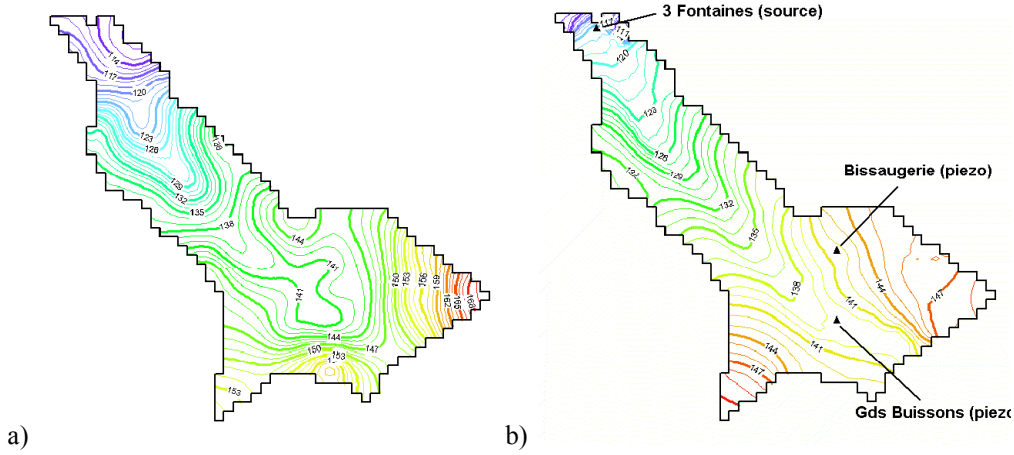
Table 50 - Values of the parameters of the water retention law and hydraulic conductivity law resulting from the calibration.

Soil type	Code	θ_{sat} %	θ_{res} %	h_t m	b_t -	K_{sat} m/s
Degraded loam	1,12	50	8	0.28	0.642	1.0e-5
Washed out loam	11	50	8	0.28	0.642	1.0e-5
Sediments	13	40	5	0.28	0.384	1.0e-4
Flint clay	2,20	38	7	1.25	0.917	5.0e-7
Chalk matrix	3	30	3	0.50	0.714	1.0e-5
	30	30	3	0.50	0.714	2.2e-5
	31	30	3	0.50	0.714	3.4e-5
	32	30	3	0.50	0.714	1.5e-5
	33	30	3	0.50	0.714	3.0e-5
Chalk drain	40	2	1	0.50	0.714	3.1e-4
	41	2	1	0.50	0.714	6.1e-3
	42	2	1	0.50	0.714	6.1e-3
	43	2	1	0.50	0.714	1.2e-2
	44	2	1	0.50	0.714	9.0e-4

The fate of isoproturon (herbicide used in cereal cultivation) and atrazine (herbicide used in maize cultivation) were simulated as these two herbicides have been used in the catchment of Les Trois Fontaines. It is estimated that 10 % of the area is occupied by maize and 50 % by wheat. The application of atrazine usually takes place at the end of April - beginning of May, when the maize is sown, with an average dose of 1,000 g/ha. However, application rates in excess of 2,000 g/ha were common before 1987. The application of isoproturon usually takes place at the turn of November and December but sometimes also in mid March depending on the climatic conditions. The application rate of isoproturon at the site was taken as 1,800 g/ha (Baran, 1999). The longitudinal dispersivity (αL) for the aquifer was assumed to be equal to 1,000 m for the unsaturated zone and the transversal dispersivity was taken as αT = αL/10.

6.1.2. Results and discussion

The maps of water table elevation observed in spring 2003 and simulated at the end of 2002 were very similar (in terms of the shape of the contours and the range of values) close to the spring (Fig. 182). The simulated shapes of the water table in the vicinity of the two observation piezometers were slightly different from the observed. Simulated elevation was lower than that observed. This demonstrates that there is a large difference between those two parts of the model and that further work on the modelling is required. This is also confirmed through the analysis of time series of outflow at the spring (Fig. 183) and of piezometric levels in the two observation wells. A satisfactory response of the system compared to the measurements in terms of period of the year when peaks were observed and trend of peak discharges was observed in the spring although the values were slightly underestimated at the beginning of the simulation. The same can be said about piezometric levels in the two observation wells. Good agreement was achieved for Les Grands Buissons (Fig. 184) while at Bissaugerie (Fig. 185), which is close to Les Grands Buissons, a poor fit to the data was obtained. The measured variations in water levels were much larger that those reproduced by the model.



a) observed in spring 2003; b) simulated at the end of 2002.

Fig. 182 - Contours of water table elevation.

Several simulations were performed to assess the role of sorption and degradation on the presence of atrazine and isoproturon in the spring water of Les Trois Fontaines and to test different application scenarios.

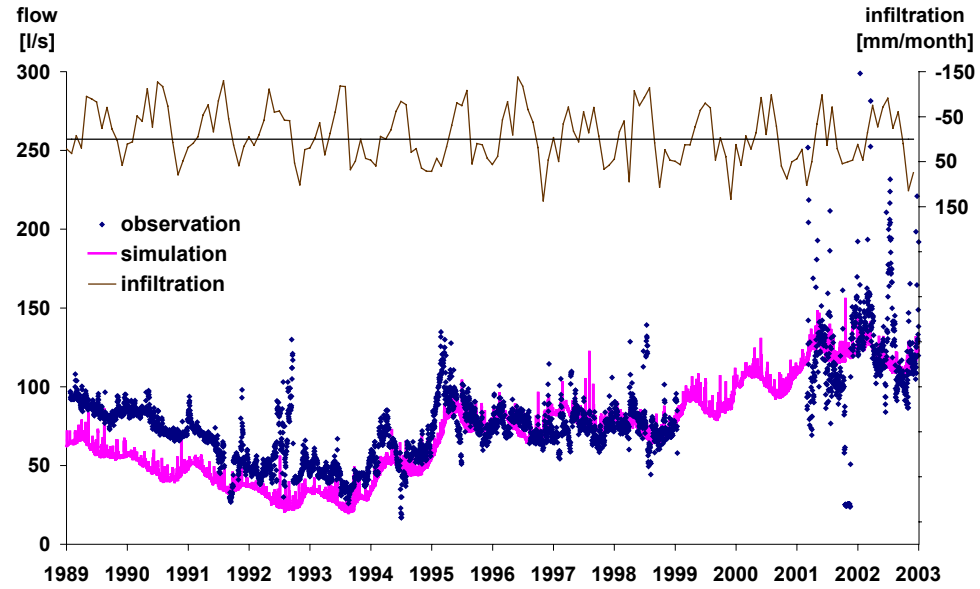


Fig. 183 - Time series of the outflow at the spring of Les Trois Fontaines.

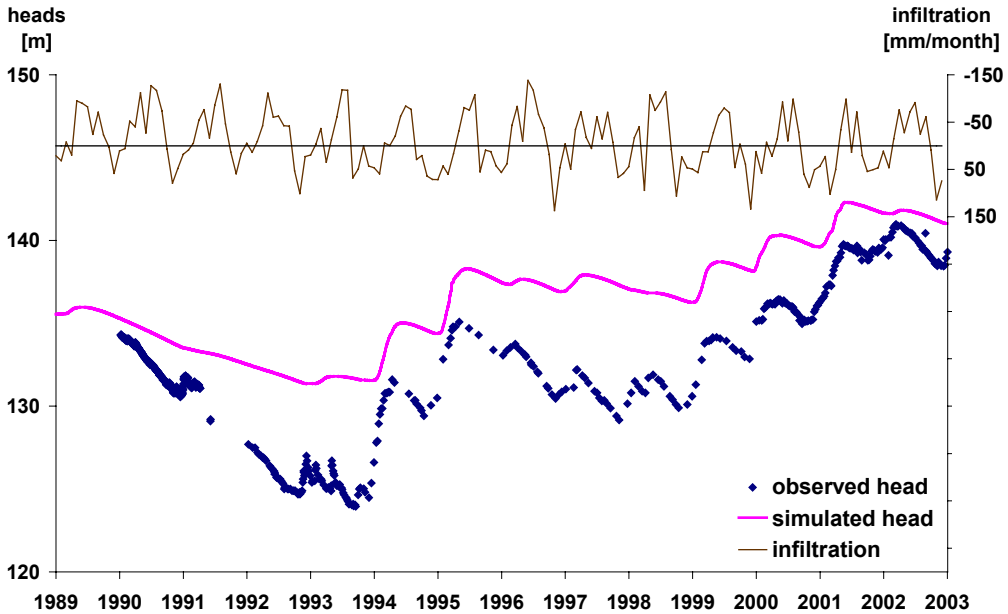


Fig. 184 - Time series of piezometric level at Bissaugerie.

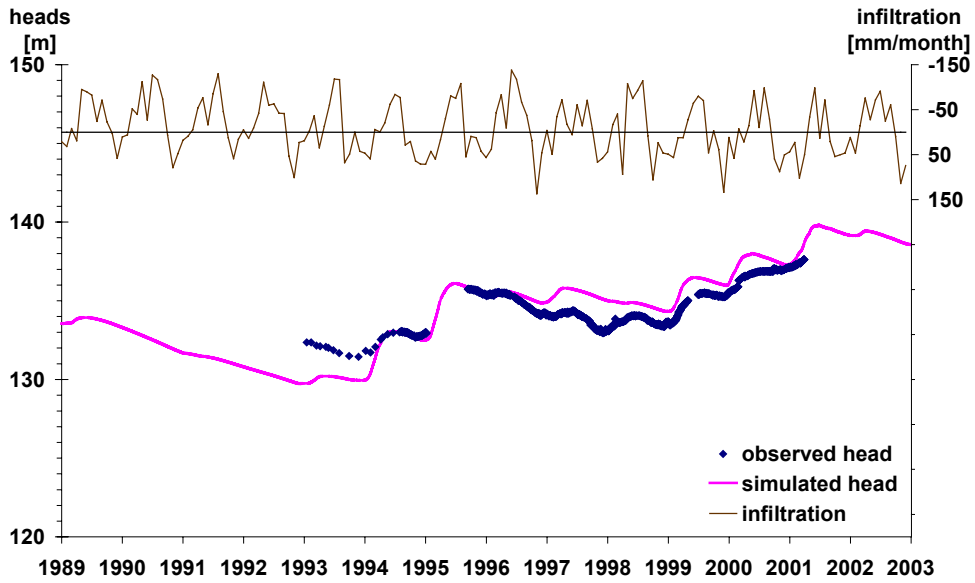


Fig. 185 - Time series of piezometric level at Grands Buissons.

- ***Simulations for atrazine***

Given that there was no information on the exact location of the plots where pesticides have been applied during the last 15 years, the first set of simulations assumed applications of atrazine every 1 May uniformly on the total area excluding one cell where the spring was located. The estimated application rate of 0.01g/m^2 was equivalent to the real application of 1,000 g/ha over 10 % of the total area. Sorption and degradation were initially assumed to occur in the first three top layers only (depth from 0 to 1.6 m) with values of RhoKd = 1.29 and DT50 = 60 days. The model predicted that concentrations of atrazine would progressively increase, thereby overestimating measured concentrations in the spring by up to two orders of magnitude. The same trend was observed when sorption was accounted for although the overestimation was much less. Satisfactory fits to the data (within one order of magnitude) were obtained when degradation in the subsoil was considered. Except for the last three years, the period of the year when peaks were observed and the range of values obtained were rather satisfactory. Simulating both processes at the same time resulted in an under-estimation of measured concentrations in the spring. A second scenario was considered where atrazine was assumed to be applied to 10 % of the total area with an application rate of 1,000 g/ha. The dates of application were not changed, but the distribution coefficient was decreased to RhoKd = 0.7 and the half life was increased to DT50 = 90 days. It was also assumed that sorption and degradation were the same in all layers of the model, including in the saturated zone. When atrazine was applied in the vicinity of the spring (Fig. 186), simulated peak concentrations were within the lower range of measured values. Calculated concentrations were however drastically reduced when atrazine was assumed to be applied to a neighbouring cell of the spring (shift of the application zone).

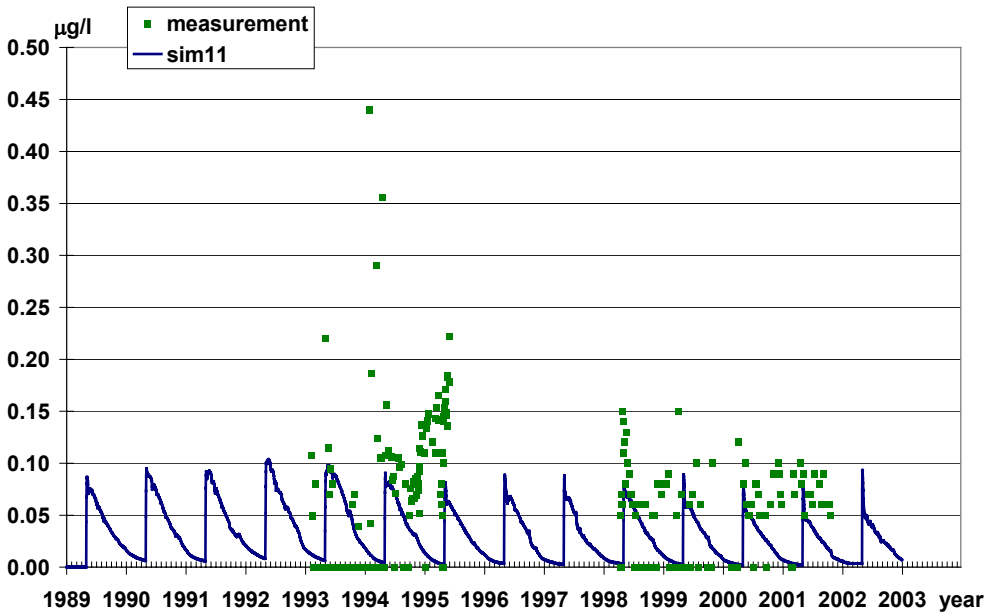


Fig. 186 - Concentration of atrazine – application on 10 % of the watershed in the area surrounding the spring.

- ***Simulation of isoproturon***

Application of isoproturon (IPU) was assumed to occur on 1 March every year. The first set of simulations assumed uniform application of IPU on the whole area of the basin excluding again the cell where the spring is located. The application rate was set to 0.09 g/m^2 which is equivalent to an application of 1,800 g/ha over 50 % of the total area. It was also assumed that sorption with RhoKd = 1.13 and degradation with a half life DT50 = 20 days take place in the first 3 top layers only (depth from 0 to 1.6 m). Simulated maximum values of IPU concentration in the spring were much smaller compared to measured values. A small increase in background concentrations at the end of simulation also occurred. This was assumed to represent the effect of the vertical IPU penetration through the zone of no degradation (below 1.6 m) and its horizontal travelling in the saturated zone which conducts water to the spring area. Assuming that IPU was applied on 50 % of the total area only was not sufficient to improve the simulation. Sorption and degradation parameters were therefore altered in an effort to improve the fit to the data. The smallest values reported in the AGRITOX database (Agritox, 2001) was then chosen (*i.e.* Koc = 80 ml/g and DT50 = 32 d). Both sorption and degradation were still assumed to occur in the first 1.6 m of soil only (top 3 layers). The simulation results were significantly improved when the spring was assumed to be surrounded by the area where IPU was applied at a rate of 1,800 g/ha (Fig. 187) although the two very large peaks were not reproduced. Shifting the application area away from the spring resulted in low and more uniform concentrations (lack of local peaks) in the spring. The considerable increase in concentration at the end of simulation confirms the increase in the importance of IPU transfer within the saturated zone as time goes by.

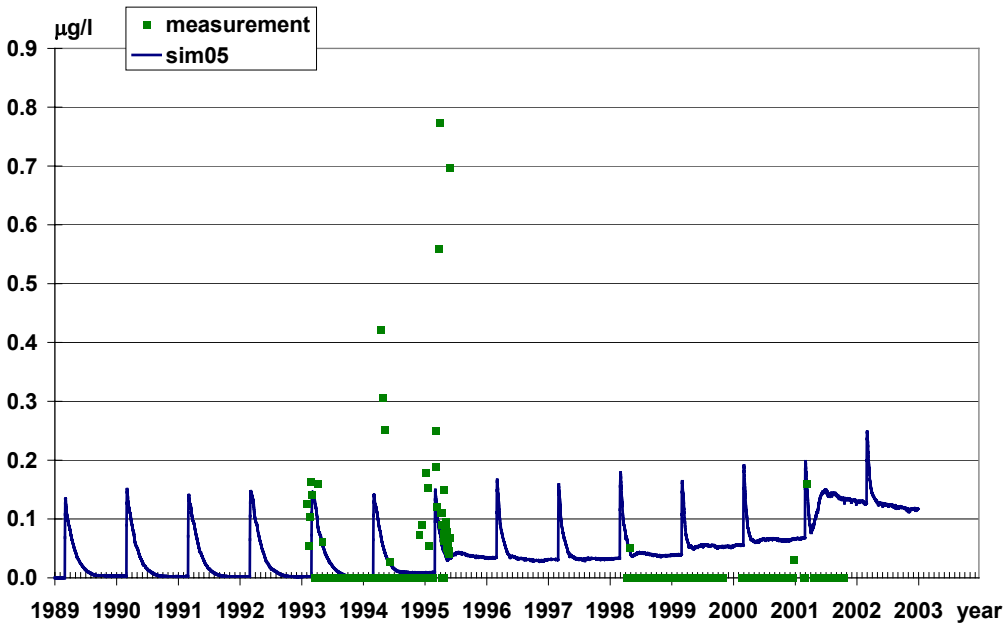


Fig. 187 - Concentration of isoproturon – application on 50 % of the watershed in the area surrounding the spring.

6.1.3. Discussion and conclusions

The comparison between predicted and measured data for water flow demonstrated the ability of the MARTHE model to reproduce measured discharge of the Les Trois Fontaines spring. However, it should be noted that the agreement was not satisfactory in specific periods (notably in 1989-1992) and locations (*e.g*. Bissaugerie). This suggests that additional work should be done on the conceptualisation and/or calibration of the model for a better fit to measured data to be obtained. The fact that peaks of pesticide concentration were observed in specific years and not in others could not be reproduced by the model. This suggests that additional information such as a more precise location of the plots where atrazine and isoproturon were applied and the dates of their application should be included in the model.

6.1.4. Summary

The karstic system of Les Trois Fontaines was simulated for a 14-year period using the 3D model MARTHE. The comparison between predicted and measured data for water flow demonstrated the ability of the MARTHE model to reproduce measured discharge of the Les Trois Fontaines spring. However, it should be noted that the agreement was not satisfactory in specific periods and locations. Two different assumptions were made with regard to the distribution of pesticide applications in the catchment. The fact that peaks of pesticide concentration were observed in specific years and not in others could not be reproduced by the model. This suggests that additional information such as a more precise location of the plots where atrazine and isoproturon were applied and the dates of their application should be included in the model.

7. APPLICATION OF MODELLING TOOLS AT THE HAVDRUP SITE [E&R DTU]

The work performed at Havdrup in terms of monitoring and modelling has been or is in the process of being published in the refereed literature (Jørgensen *et al.,* 2002, 2003, 2004a, 2004b). The reader is referred to these publications for further information. A brief summary of each of the papers is presented below.

7.1. Summaries

- ***Monitoring and modeling of flow and transport of bromide and pesticides (MCPP, metsulfuron, and prochloraz) in till and local aquifer from field injection of pesticides (Jørgensen* et al., *2002)***

The study provides data of flow and pesticide transport along fractures in unoxidized clayey till and includes 1) hydraulic apertures and spacing of fractures and fracture channels, 2) flow in fracture channels as percentage of total flow in fractures and bulk till, 3) flow rates in fractures and fracture channels, and 4) migration rates of non-reactive tracer (bromide) and pesticides (mecoprop (MCPP), metsulfuron-methyl and prochloraz) along fracture channels into an under laying local aquifer under a natural hydraulic gradient. The study moreover provides lab to field scale calibration of a Discrete Fracture Matrix Diffusion (DFMD) groundwater model, which is shown to be suitable for simulation of the flow and pesticide transport observed in the field experiment. In two experimental fields 96 % and 98 %, respectively, of total flow was conducted along fractures in the till, while the remaining few percent of flow occurred in the clay matrix. Distribution of flow along the fractures was investigated by conducting a dye tracer experiment followed by laboratory tests using large undisturbed columns (LUC), collected along dyed and non-dyed fracture sections. The dye was only found in vertical primary fractures and it was channelled along only 10-26 % of the total fracture width (measured in horizontal sections of 40 m^2). The dye tracer was not found along secondary vertical fractures or the few horizontal fractures in the experimental fields. Two LUC, collected along the non-dyed sections of the primary fractures revealed fracture apertures of 12 μm and 14 μm, which are equivalent to flow rates of 9-22 m/day for natural hydraulic gradients at the site (0.8-2.3). On the basis of these aperture values it was estimated that 94 % of flow in the fractures was conducted along the fracture channels, while only 6 % of flow in the fractures was conducted along the non-dyed fractures. Cubic law calculated mean aperture for the dyed fracture sections was 49 μm, while a local measurement obtained from a LUC, collected along a dyed fracture channel (root channel), revealed an hydraulic aperture of 124 μm. The latter fracture aperture value is equivalent to a flow rate of 0.8-2 km/day for the natural range of hydraulic gradients at the site. For infiltrated bromide (non-reactive tracer) and mobile pesticides mecoprop (MCPP) and metsulfuron, very rapid migration (0.28-0.5 m/day) and high relative breakthrough concentrations (30-60 %) into the aquifer was observed to occur along the dyed fracture root channels. Only traces were measured from infiltration of the strongly sorbed pesticide prochloraz. A 3D Discrete Fracture Matrix Diffusion (DFMD) model (FRAC3DVS) was used to simulate the flow and tracer transport observed in the experiment. Prior to the simulations the model description of sorption and solute exchange between fractures and matrix domains had been calibrated on the basis of LUC transport data. Using this calibration, the DFMD model could be fitted to the observed field transport data using parallel wall fracture

transport apertures of 40 and 60 μm. These transport apertures are in reasonable agreement with the mean hydraulic aperture value of 49 μm calculated for the fracture channels. This show that LUC calibrated DFMD model is suitable for field scale simulations of bulk discharge, preferential flow and pesticide transport from the clay-rich till into the local aquifer of the field site.

- ***Evaluation and implication of conventional pesticide monitoring techniques in clayey till (Jørgensen* et al., *2003)***

The investigation estimates the probability of conventional vertical monitoring well screens (10 cm in diameter) intersecting with vertical fracture traces in clayey tills. The estimate was based on fracture spacing measured from 13 Danish field sites, including the PEGASE Havdrup site. The investigation furthermore estimates the probability of sampling mobile pore water from the wells due to intersection of the well screens with fractures that are hydraulically conductive and thereby represents the mobile pore water of the till material. A simple calculation scheme and diagrams is provided and permits for evaluation of the probability of planned monitoring wells collecting mobile pore water on the basis of specified fracture spacing and well dimensions.

The investigation finds that for commonly used vertical and 10 cm in diameter monitoring well screens, the probability for intersection between well screens and hydraulically conductive fractures is generally less than 50 % from 2 to 7 m depth in Danish clayey till.

Simulations carried out for the mobile pesticide metabolite BAM using the discrete fracture/matrix diffusion numerical model FRAC3Dvs, reveals that well screens, that are situated 0.25 m and 2 m away from a hydraulically conductive fracture from the Havdrup site, will delay observations of BAM concentration 2 years and 18 years, respectively, relative to the break through of BAM into the local aquifer immediately underlying the screens in the till. Based on a field experiment carried out at the Havdrup site, the probability for this monitoring result to occur was 85 %, while it was only 15 % for sampling mobile water from the hydraulically conductive fractures in the till. On the basis of these results it is concluded that there is a significant risk that water samples collected from conventional vertical monitoring wells may systematically delay observations and underrate concentrations of downward progressing contamination in the mobile pore water of clayey till aquitards.

The investigation moreover concludes that the probability of sampling the mobile pore water from fractures can be enhanced by using large diameter screens, angled or horizontal wells, and by using wells, which are constructed in commonly occurring thin sand layers or sand lenses in the till aquitard.

- ***Evaluation and comparison of suitability of equivalent porous (EPM), dual porosity (DP (CXTFIT, MODFLOW/MT3D)) and discrete fracture matrix diffusion (DFMD (FRAC3Dvs)) modeling approaches to predict solute transport during variable flow rate and time (Jørgensen* et al., *2004a)***

The previous investigation revealed that fractures and biopores can act as preferential flow paths in clay aquitards, and may rapidly transmit contaminants into underlying aquifers. Reliable numerical models for assessment of groundwater contamination from such aquitards are needed for planning, regulatory and remediation purposes. In this

study high resolution preferential water saturated flow and bromide transport data were used to evaluate the suitability of equivalent porous medium (EPM), dual porosity (DP) and discrete fracture/matrix diffusion (DFMD) numerical modeling approaches for assessment of flow and non-reactive solute transport in clayey till. The experimental data were obtained from four large undisturbed soil columns (taken from 1.5 to 3.5 m depth) taken from a site similar to the Havdrup site, in which biopores and channels along fractures controlled 96 % to 99 % of water-saturated flow. Simulating the transport data with the EPM effective porosity model (FRACTRAN in EPM mode) was not successful because calibrated effective porosity for the same column had to be varied up to 1 order of magnitude in order to simulate solute breakthrough for the applied flow rates between 11 mm/day and 49 mm/day. Attempts to simulate the same data with the DP models CXTFIT and MODFLOW/MT3D were also unsuccessful because fitted values for dispersion, mobile zone porosity, and mass transfer coefficient between mobile and immobile zones varied several orders of magnitude for the different flow rates, and because dispersion values were furthermore not physically realistic. Only the DFMD modeling approach (FRACTRAN in DFMD mode) was capable to consistently simulate the observed changes in solute transport behavior during alternating flow rate and time without changing values of calibrated fracture spacing and fracture aperture to represent the macropores. This result is of crucial importance to groundwater managers in order to ensure selection of models suitable for simulation of pesticide transport in clayey till at field condition, which naturally includes both time-variable flow rate and a time-variable perspective.

- ***Evaluation of key-parameters (geological, hydrological, pesticide properties) evaluation of aquifer vulnerability under clay-rich till aquitards (Jørgensen* et al., *2004b)***

The study investigates the influence of key factors, mainly recharge rate and degradation half-life, on downward migration of a widely used pesticide (mecoprop or MCPP) through the clayey till aquitard at the Havdrup site. The study uses the numerical model FRAC3Dvs, which is a 3D discrete fracture/matrix diffusion (DFMD) numerical transport model. The model was calibrated with laboratory and field data from the Havdrup site, but the overall findings are expected to be relevant to many other sites in similar settings. Fracture flow and solute transport parameters for the model were obtained through calibration using well-characterized laboratory experiments with large (0.5 m diameter by 0.5 m high) undisturbed columns of fractured till, which were described in a previous paper (Jørgensen *et al.,* 1998). A second level of calibration and sensitivity analysis was then carried out using hydraulic head, MCPP transport data, and fracture spacing data from the field site. The simulations of downward migration of MCPP revealed that the contaminant concentration and flux across the lower aquitard boundary at 16 m depth (and into the underlying aquifer) is strongly influenced by the recharge rate at the base of the aquitard and by the rate of degradation of MCPP, both of which were varied over ranges measured or estimated for the field setting (recharge of 20 to 120 mm/y and no degradation to DT50 = 0.5 year). The simulated transport rates and concentrations were significantly less sensitive to variations in fracture spacing (1 to 10 m). Increasing the recharge rate from 20 to 120 mm/y causes the simulated flux of MCPP entering the aquifer 20 years after its introduction to increase by a factor 102. For the same range of recharge rates, but with a degradation half-life of 0.5 years, MCPP concentrations entering the aquifer after 20 years increased by a factor of 8,400. The minimum biodegradation half-life of 0.5 years is approximately the rate measured in the

laboratory for MCPP in the aerobic oxidized zone (upper 3 m) of the till from this site. Biodegradation half-lives for MCPP in the deeper, unoxidized tills are expected to be greater than 5 years, but even at these lower rates they can have a significant influence on simulated MCPP concentrations entering the aquifer. The results indicate that for aquifers overlain by fractured clayey tills, the vulnerability to contamination with pesticides and other wide-spread agricultural contaminants is going to vary strongly in the watershed as a function of the distribution of recharge rate and aquitard redox environment. Overall the simulations indicate that a calibrated DFMD groundwater flow and contaminant transport model can be a very useful tool for evaluating downward migration of pesticides in this type of setting. Hence, calibrated DFMD models may prove very useful for assisting in land management decisions and policy.

7.2. Discussion and conclusions

The study indicates that the Havdrup aquitard is typical for clayey till aquitards in the Danish area. The results obtained are therefore considered to be generally representative to similar geological sittings with the same application of pesticides. Thereby the results have wide implications for understanding, monitoring and modelling of pesticide fate and evolution in groundwater especially in the northern hemisphere countries.

More than 95 % of total flow in the aquitard was conducted along fractures in the till, while the remaining few percent of flow occurred in the clay matrix at very slow flow rate. It was moreover found that 94 % of flow in the fractures was conducted along fracture root channels, while only 6 % of flow in the fractures was conducted along fractures without root channels. Estimated flow rates in the fracture root channels were 0.8-2 km/day for the natural range of hydraulic gradients at the site. The 3D Discrete Fracture Matrix Diffusion (DFMD) model (FRAC3DVS) was used to simulate bromide, MCPP and metsulfuron transport observed in an earlier experiment. Prior to the simulations the model description of sorption and solute exchange between fractures and matrix domains had been calibrated on the basis of LUC transport data. Using this calibration, the DFMD model could be fitted to the observed field transport data when using parallel wall fracture transport apertures of 40 and 60 μm. These transport apertures are in reasonable agreement with the mean hydraulic aperture value of 49 μm calculated for the fracture channels. This show that LUC calibrated DFMD model is suitable for field scale simulations of bulk discharge, preferential flow and pesticide transport from the clay-rich till into the local aquifer of the field site.

Extended simulations taking into account the full aquitard show that MCPP concentration and mass flux into the underlying aquifer are mainly dependent on the degradation rate of the pesticide and on the groundwater recharge rate into the underlying aquifer. The influence of flow rate and degradation rate are intertwined, resulting in 1 to 4 orders of magnitude higher MCPP flux into the aquifer from aquifer recharge rates of 20 mm/y and 120 mm/y, respectively, for no degradation and MCPP half life of 0.5 y. It is found that the range of MCPP flux into the aquifer varied less than one order of magnitude due to changing fracture spacing from 1 to 10 m or due to preferential flow in thin sand layers, representing common conditions observed at the current and other study sites in Denmark.

One implication of the study is that the vulnerability of an aquifer overlain by till to contamination is likely to vary substantially across a watershed, due to variations in

recharge rate and geochemical conditions (which can affect contaminant degradation rate) in the till. Since recharge rate can vary as a function of both material properties of the till and position within the flow system (*i.e.,* recharge area versus discharge area), vulnerability to contamination may vary substantially, even if the thickness of the till is relatively constant. The linear relationship between root zone concentrations and the concentrations entering an underlying aquifer, suggest that measuring pesticide residues and flow proportional monitoring of pesticide concentration in the root zone should also be a high priority, especially for mobile pesticides with long half-lives in the sub-soil environment.

It was found that residual MCPP concentrations in the aquifer recharge will evolve very differently depending on the rate of aquitard flow and pesticide degradation. The simulations indicate that for aerobic aquitard conditions (T½ <1 y), MCPP residual concentrations above the drinking water standard should not be expected in most recharge water 10 years after even very high concentration point or non-point MCPP sources have terminated. For the case with no degradation of MCPP the simulations indicate that concentrations entering the aquifer may still exceed the drinking water standards more than 50 years after relative low source concentrations have been terminated. However, the simulations also show a very important influence of even low degradation rates (DT50 = 5y) to reduce even high initial contaminant concentrations in the longer perspective. Overall the simulations indicate that the degree of protection provided by a fractured till confining layer can vary substantially, and that a calibrated DFMD groundwater flow and contaminant transport model can be a very useful tool for evaluating downward migration of pesticides in this type of setting. Hence, calibrated DFMD models may prove very useful for assisting in land management decisions and policy.

With respect to monitoring of downward migration of pesticides it was found that when using conventional monitoring wells for investigation of contaminant sources in clayey till there is a high risk that fractures may cause mobile contaminants to by-pass the monitoring wells. The probability of interception between monitoring wells and hydraulic conductive fractures is often significantly less than 50 %. For well screens situated 0.25 m and 2 m away from a conductive fracture the first concentrations of the pesticide would be measured 2 years and 18 years, respectively, after the contaminant had been transported into an underlying aquifer, and observed concentrations would be greatly underrated. Underlying aquifers may be subjected to contamination by downward moving contamination without being observed in monitoring wells in the till.

8. DISCUSSION OF MODEL EVALUATION ACTIVITIES

In a first step, new subroutines implemented in a number of modelling tools considered within PEGASE (chapter 2) were subjected to a verification process. This involved simulating reference datasets from the literature or comparing model results to analytical solutions. A particularly thorough analysis was undertaken for MARTHE where new subroutines for crop development, water and pesticide uptake, sorption, degradation, effects of temperature and humidity on degradation were evaluated using a range of 1D and 2D modelling exercises. Numerical and theoretical investigations have demonstrated that new subroutines have been correctly implemented in the models and that the new functionalities of the model can be used in confidence. In a

second step, the models which were developed or refined within the scope of the project (chapter 2) were used to simulate water transport and pesticide fate either at the scale of the soil profile or the aquifer (regional scale) based on the data collected during monitoring studies (chapter 1). A stepped approach was used for the more comprehensive codes (MARTHE and TRACE/3DLEWASTE) where 1D modelling exercises were carried out to evaluate the models, but also to support the more comprehensive subsequent modelling activities in 2D or 3D. In a number of instances, the modelling tools were calibrated against the measured water fluxes, groundwater levels and pesticide concentrations in the groundwater to estimate the capabilities of the models.

One of the interesting aspect of the present evaluation exercise was that the diversity of datasets available for model testing enabled the evaluation of models and specific subroutines against data which were not used in their development or refinement of the models. This provided the basis for an independent evaluation of the modelling tools developed within PEGASE.

Modelling of the Brévilles dataset proved a challenge to the modellers involved despite the facts that the site was initially selected for his alleged simplicity and that very comprehensive data acquisition and system characterisation activities were deployed at the site. This highlights the true challenging nature represented by the simulation of water and pesticide fluxes in the combined root, unsaturated and saturated zones and the need for model calibration. The relative stability in groundwater heads observed in the Brévilles aquifer could not be reproduced by the models.

Groundwater levels were relatively well predicted by the models which were used to simulate water flow and pesticide fluxes at the Zwischenscholle site (TRACE+3DLEWASTE, MARTHE, ANSWERS, MACRO+MODFLOWT). Activities related to the evaluation of pesticide fate subroutines were somewhat limited at Zwischenscholle given that the period simulated within the scope of the ring test exercise did not cover the period in which measurements of pesticide concentrations in the field were made.

Modelling for the Martigny datasets involved i) the simulation of the 'large scale' (12 km^2) monitoring dataset to help in the addition of hydrological data to the 'local scale' dataset (1.5-m^2 experimental plots); and ii) the simulation of pesticide leaching through the soil and the upper groundwater in the experimental plots. The former aspect consisted in the calibration of the MARTHE model using detailed information from seasonal piezometric maps, electrical conductivity maps, automatic head records and borehole logs while the latter approach involved the calibration of root zone models against suction cup data. Root zone models significantly under-estimated the amount of atrazine and isoproturon leached and this was attributed to preferential transport of water and pesticide, which could not be simulated by root zone models used.

The large inter-annual variability in pesticide concentrations observed at Les Trois Fontaines could not be adequately simulated with the MARTHE model. In addition, a very significant spatial variability in pesticide concentrations in groundwater was noted on most sites. This highlights the need for the collection of reliable information on the nature of the compound used in a particular area, the precise location and time of use, and the nature of crop covers in the catchment. Although such detailed information is usually recorded within the scope of research projects aimed at characterising

pesticide transport in the environnement, its availability over decades and for sites which are not followed from a research perspective is clearly problematic. In addition, the failure of models to simulate significant inter-annual variations should lead to further research into the identification of variables determining variations in concentrations from one year to the next. Modelling of the Havdrup dataset demonstrated that the vulnerability to pesticide contamination varies greatly across a given catchment. This has clear implications for the design of monitoring campaigns in terms of the spatial density of sampling points.

The importance of preferential flow in the transport of water and pesticides to depth was found to be a recurring theme during field leaching, field monitoring and modelling activities within PEGASE. Inadequate simulation of plot scale data by models was generally attributed to the inability of most models to account for preferential flow processes or the possibility of bias in the dataset collected due to the bypassing of sampling devices by water moving preferentially down the profile. From an experimental point of view, this suggests that care should be exercised in the field when installing sampling equipment and that attention should be paid to a suitable description of the soil structure when characterising the soil. From a modelling point of view, this suggests that subroutines for preferential flow should be added to existing models if these are to be used for the simulation of water transport and pesticide fluxes in soils other than the coarsest soils. The study of the impact of preferential flow occurring in soil on pesticide concentrations in piezometers or at the outlet of a catchment deserves investigation.

Numerical and conceptual difficulties were encountered when trying to couple root zone models with 3D groundwater models such as MODFLOW. The coupling could only involve the feeding of the predictions of the root zone model to the groundwater model, which represents a major limitation when the water table fluctuates across the fixed boundary depth selected for the coupling of the two models. The integrated models (MARTHE, TRACE, POWER) whose capabilities with regard to pesticide fate were significantly enhanced in the project were found to offer a more viable alternative to modelling water flow and pesticide fate in the soil-unsaturated zone-saturated zone continuum. The addition of the new subroutines means that the integrated models now more or less offer the same capabilities as most root zone models, with the exception of preferential flow modelling, for simulating water and pesticide fluxes in soil. This also means that these integrated tools can be used for modelling across the whole spectrum of modelling activities, from relatively standard root zone modelling to the more demanding 3D modelling.

Chapter 4 -

Socio-economic analysis for agriculture and aquifer management [UVSQ-C3ED]

1. INTRODUCTION

1.1. Principles of the socio-economic analysis

The transition towards policies for sustainability — in agricultural production and aquifer management as in other domains — requires processes of arbitrage between different interests, conflict management and, where possible, reconciliation of multiple criteria for land and water use, landscape features, food product quality, ecosystem integrity, financial viability of farming activity, local community interests, regional development and so on. It means attention to tensions between preoccupations of, and for, present and future generations, different economic sectors and interests, human and non-human communities…

Many different principles, justifications and ethics about what is fair and right, can and will be put up for consideration. Where a single method or principle of good resource management does not prevail, a reasoned and robust base for regulation of resource use must have a reflexive deliberative character. In the search for a possible coexistence of the various interests, the challenge then is to work with a permanent "argumentation" between many contradictory principles of conduct and positions.

The game “Greening the Face of the Cube” is based on a multi-stakeholder multi-criteria scenario evaluation procedure. The players together engage in a deliberation process as “stakeholders” whose goal is to find a scenario for future agricultural activity that is, as far as possible, satisfying to all concerned parties. Through the Cube, presented via an ICT interface, the players are presented with the different scenariis, a spectrum of governance issues, and a variety of stakeholder groups whose preoccupations are to be taken into account. The players may negotiate with each other in order to explore perspectives for a “durable” solution. The key ICT “stage prop” is a three-dimension array called the “Deliberation Matrix” (the Cube) that presents, in a synthetic way, the array of judgements offered by stakeholders concerning alternative perspectives on management of the environmental resource. The Deliberation Matrix concept was formalised in the context of The GOUVERNe Project, "Guidelines for the Organisation, Use and Validation of information systems for Evaluating aquifer Resources and Needs", which is funded under Key Action 1 (Sustainable Management and Quality of Water, RTD Priority 1.1.3 — Operational management schemes and decision support systems) of the Energy, Environment And Sustainable Development theme of the European Commission’s Fifth Framework Programme. It has then been adapted for application within the PEGASE project, as a framework for the presentation of scenarios in a multi-criteria, multi-stakeholder perspective for a (typical) situation of acute water quality degradation due to intensive agricultural practices. The Deliberation matrix has three dimensions:

- the challenges of a sustainable agricultural activities are portrayed via a small number of scenariis each of which expresses distinct technological, economic, environmental and governance features relating to a “crisis” agricultural pollution situation;
- the scenarios of distinct possible futures are evaluated from distinct stakeholder perspectives. A small number of major stakeholder categories are specified (these are based on institutional and interview analyses for the situation being portrayed);

- the stakeholders may make their evaluations of each scenario in terms of a variety of different criteria. The criteria are grouped into a small number of "baskets" corresponding to distinct governance issues.

In brief, each stakeholder class offers a synthetic judgement *(satisfactory, poor, intolerable, etc.)* of each scenario in relation to each of the key governance or decision issues. These judgements are portrayed in a synthetic way in the cells of the Deliberation Matrix, for example using codes of colours *(satisfactory = green; poor = orange; intolerable = red, etc.)*. This makes it possible visually to pin-point which governance issues divide stakeholders and which scenarios are marked by high conflict/oppositions of stakeholders' views.

The players in the game each assume the role of one category of stakeholder or another. They will first contribute to the production or validation of an array of judgements. Once the Matrix is completed and the complete pattern of stakeholders' evaluations is perceived, the players are permitted to reassess the choices and assumptions leading up to the judgement put into each cell. They may, after deliberation, change their own evaluations, and also propose arguments to other players for changes in their evaluations. This places the focus not only on the outcomes of the evaluation procedure (that is, the contents of the cells in the Matrix) but also on the reasoning, performance concepts, priorities, interests, value systems, and knowledge claims that underlie the judgements offered by stakeholders.

A possible resource governance goal would be to implement solutions that are "inclusive" — in the sense of offering a viable future to all recognised stakeholder groups. This can be represented by the objective of finding a scenario that has no red cell. The negotiation game of "Greening the Face of the Cube" thus is a simulation of a stakeholder deliberation process seeking a scenario for future agricultural activity (or, more generally, regional development or other territorial activity) that is broadly acceptable to the full spectrum of stakeholders. Of course, this goal may not be accepted by all the players, or it may not be achievable (or only at the price of modifications to indicators and/or to stakeholders' criteria that strain credibility). Playing the game may nonetheless be stimulating, because the process of filling in the cells of the Matrix and of discussing the basis for different judgements and outcomes, may be an effective way for the protagonists to learn about the key governance issues and of the preoccupations of the various parties.

In order to collect and to organize information related to agriculture and water management to develop the Deliberation Support Tool, we used the Methodology "The Deliberation Cycle in the Theatre of Sustainability" (Fig. 188) for the three case studied: Montreuil-sur-Epte or Brévilles (France), Zwischenscholle (Germany) and Martigny (Switzerland). The seven steps have been achieved only for the Brévilles case study. The first four steps have been reached for the other two sites. A presentation of the work done by the socio-economic team, teams of the consortium or other is presented relating each step to reports, products realised during the PEGASE Project are given in Table 51.

Table 51 - Notes and reports produced within the scope of the socio-economic analysis (see annex 1 for references)

STEPS	BREVILLES (FRANCE)	ZWISCHENSCHOLLE (GERMANY)	MARTIGNY (SWITZERLAND)
STEP 1			
Collecting information	Participation to meetings in Montreuil-sur-Epte, Bibliography, Georges (2000), Baran *et al.* (2002)	Haake (2000), Bibliography	Bibliography, Inteviews of Farmers by K. Meiwirth
Farmers interviews	Paranthoën (1999)	Rainer Harms (2002)	Meiwirth (2002)
STEP 2			
Data	See Work Package 2 for Hydro-Geological Analysis		
Modelling	See Work Package 3 for Hydro-Geological Analysis		
STEP 3			
Environmental Functions	Georges (2000)	Haake (2000)	Bizot & Pistone (2001)
STEP 4			
Governance issues	Georges (2002), Douguet *et al.* (2002), D'Angela & Moers (2001)	Haake (2000)	
STEP 5			
Socio-economic Modelling	Schembri & Douguet (2001)		
Scenarios building	Douguet *et al.* (2001), Leviaud (2002)	Guyonnaud (2002)	
STEP 6			
Building multimedia interfaces	Douguet *et al.* (2003a), Abdellaoui *et al.* (2001a, b), Software PEG@SE		
KQA	GRIC (2002)		
STEP 7			
Methologies: Socio-Economic Analysis	Douguet *et al.* (2003b)		
Dissemination	Development of the PEG@SE CD-ROM; Development of the KERPEGASE On-Line Teaching; Presentation of the socio-Economic Analysis at Schools, Universities, High Schools (see the list below), during exhibition for Sciences		
PEGASE Meetings	See the list in the Description of Work.		
Meetings in Montreuil-sur-Epte	Every 6 months (June 2000 to November 2003)		

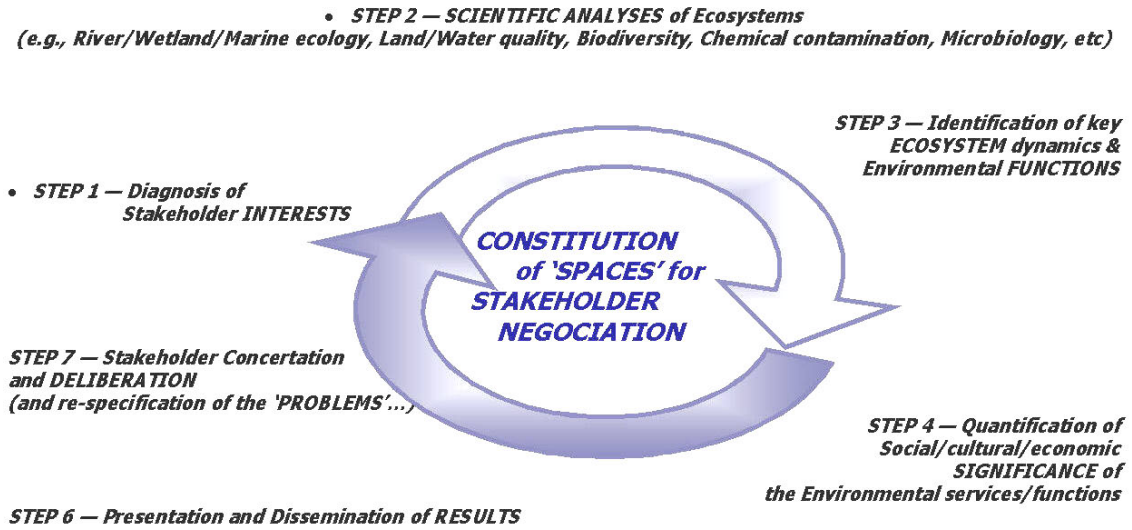


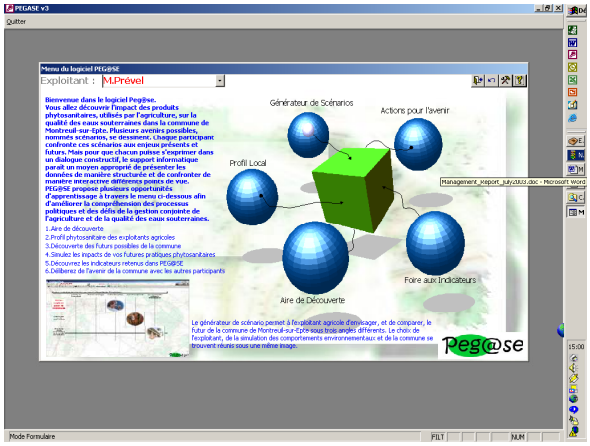
Fig. 188 - The seven steps constituting the Deliberation Cycle in the Theatre of Sustainability.

1.2. The PEG@se software

The PEG@SE software is a deliberation support tool on the Agriculture/Water issues. Information collected for the Montreuil-sur-Epte case study are organized in a multimedia presentation in order to build a bridge between the Scientific Knowledge (measurement made by BRGM, hydro-geological modeling…) and the Society (farmers' behavior, definition of possible scenario, deliberation on governance issues and vision of the future). Generic Concepts used in the software are: the Personal Barometer (to make a farmer profile), the Scenario Generator (to imagine possible futures), the Indicator Dialogue Box (to organize indicators) and the Deliberation Matrix (as a Multiplayer Game). To make the information accessible to a large public, different pedagogic pathways in the PEG@SE software are developed. Six different zones have been defined in the software and are briefly described below. Screen shots of the different zones are provided in Figure 189.

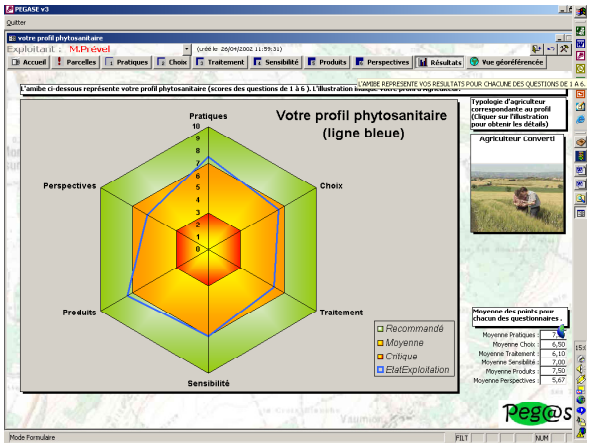
Zone #1: Welcome area
The Welcome area presents the different functionalities of the software. Choose you pedagogical pathway in order to access to information.

Zone #2: the Discovery Zone
The Montreuil-sur-Epte commune and Aquifer are presented in this zone. The idea is to give detailed information concerning the history of the area, technical detailed on the functioning of the aquifer (results of BRGM and INRA research, DDASS data…) to people who do not have any knowledge on this case study.

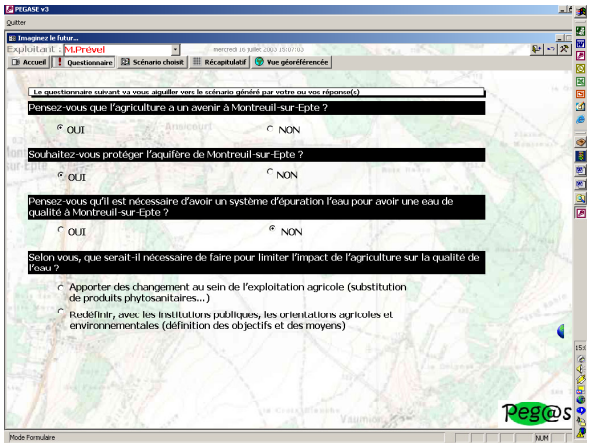


Zone #1: Welcome area

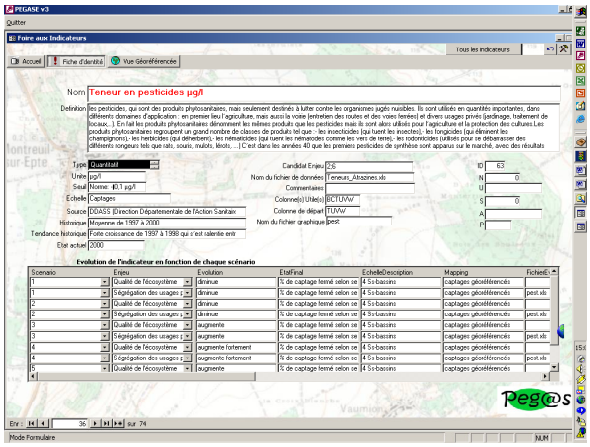
Zone #2: the Discovery Zone



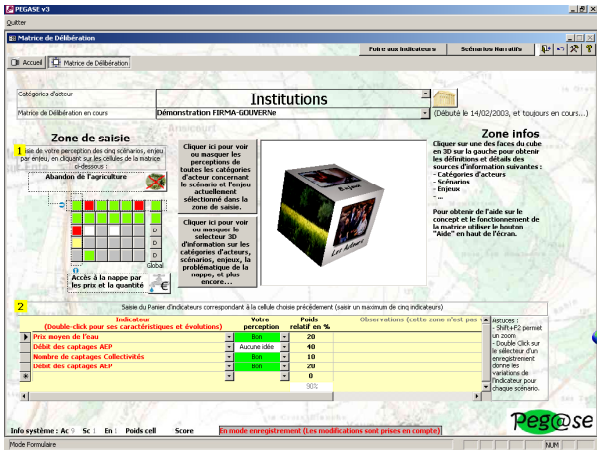
Zone #3: the Personal Barometer



Zone #4: the Scenario Generator



Zone #5: the Indicator Dialogue Box



Zone #6: the Deliberation matrix

Fig. 189 - Screen shots of the different zones of the PEG@ase software.

Zone #3: the Personal Barometer
The aim is to collect information on farmer behavior, and to present a multi-criteria profile of the farmer.

Zone #4: the Scenario Generator
The aim is, at an aggregated level, to access and to present narrative scenarios via a questionnaire and to simulate possible future, using information coming from the economic-environmental and the hydro-geological modeling.

Zone #5: the Indicator Dialogue Box
The IDB is a data base of indicators used in the PEG@SE software. These indicators can be related to the economic, social and ecological (hydro-geological) domains. Each indicator is described in detail and linked, if possible to scenarios. A Knowledge Quality Assessment is also developed for each Indicator (using the NUSAP Methodology, see section 4.2. in the present chapter).

Zone #6: the Deliberation matrix
The deliberation Matrix is a multiplayer game developed to deliberate on agriculture and water issues. It crosses Stakeholders, Governance Issues and Scenarios. Stakeholders have to give their judgment using indicators to characterize the role played by the scenario to respond to governance issues.

This software aims to develop social learning in the case study of Montreuil-sur-Epte. It can also be used in a pedagogic context, in schools (in the Collège Pierre de Coubertin, Chevreuse, France) or at universities and High Schools (University of Versailles, Saint-Quentin-en-Yvelines, Ecole des Mines…, France) or during exhibition for Sciences.

2. THE DELIBERATION MATRIX

2.1. Overview of the structure of the matrix

The PEGASE Project's Deliberation Matrix is a composite indicator that presents, in a synthetic way, the array of judgements offered by stakeholders concerning alternative perspectives on management of the environmental resource. It is constructed on the basis of three powerful methodological choices:

- the management perspectives are portrayed in terms of *a small number of 'decision/policy scenarios'* each of which expresses distinct technological, economic, environmental and governance features;
- the scenarios of distinct possible futures are evaluated from distinct stakeholder perspectives. A *small number of major stakeholder categories* are specified, based on institutional and interview analyses. The procedure of evaluation allows for the existence of diversity within each major stakeholder category (see below);
- the stakeholders' may make their evaluations of each scenario in terms of a variety of different criteria. The criteria are grouped into a small number of 'baskets' corresponding to *distinct governance issues*. Depending on the situation being considered, these may be quite general themes (such as environmental quality or regional development dynamism, etc.), or they may be quite specific features (such as the source of a town water supply).

Therefore, in a matrix representation, the three principal axes of the Deliberation Matrix are :

- the Possible Futures: a small number of Decision/Policy Options and/or Scenarios— the depth Z-axis, moving into the page;
- the Governance Issues: a small number of distinct axes of evaluation — the horizontal X-axis, moving from left to right;
- the Major Types of Stakeholders (or Social Groups, etc.) — the vertical Y-axis, moving from top to bottom.

Thus, any single cell *(x, y, z)* in the matrix represents one dimension of the evaluation *x* by a specified category of stakeholders *y*, of a possible future scenario *z* (Fig. 190).

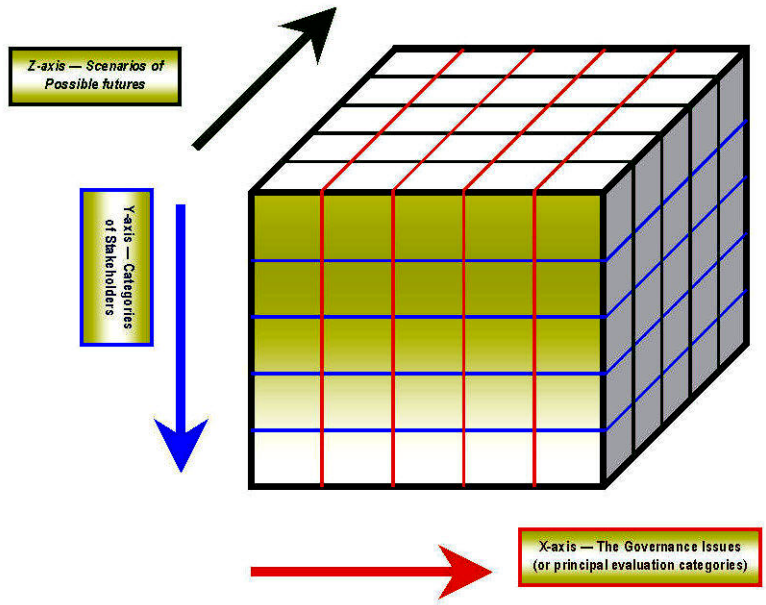


Fig. 190 - The three axes of the Deliberation Matrix.

2.2. Multi-criteria multi-stakeholder evaluation of a scenario

The future is portrayed as a 'fuzzy object' through a set of scenarios. We suppose that, in the overall context of the scenario set, each scenario may be the focus of evaluation, and that each stakeholder group will furnish a distinctive evaluation profile. Take a single scenario. For a given value of *z* (designating the scenario), we have a "slice" of the Cube, a rectangular array of cells *(x, y)* in which each horizontal row represents the evaluations (the categories *x*) by the specified category of stakeholders (the selected *y*) (Fig. 191).

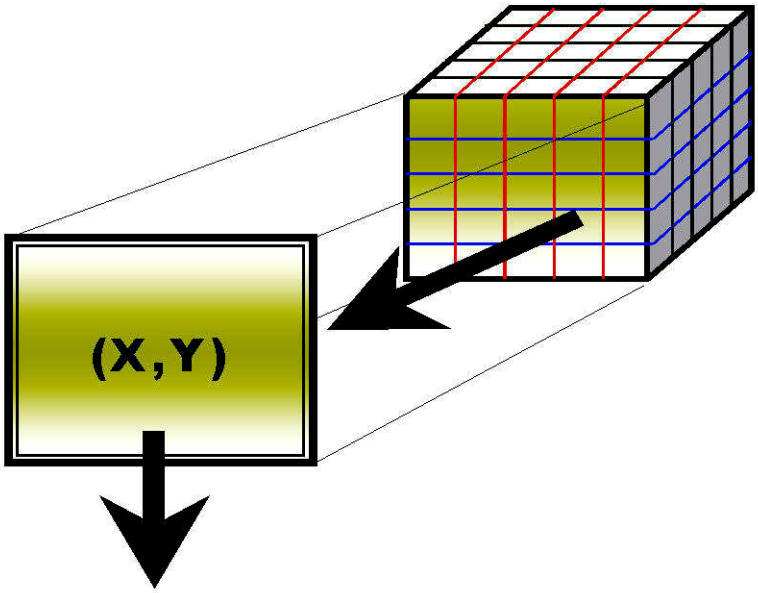


Fig. 191 - Extraction of one scenario (governance-stakeholder, a slice of the cube) from the Deliberation Matrix.

Table 52 - Example of the information held in a slice of the Deliberation Matrix (X = governance issue; Y = categories of stakeholders).

For a given scenario 'Z'

(X,Y)	Governance Issue (I)	Governance Issue (II)	Governance Issue (III)	(…)	Governance Issue (X)	"Overall"
Stakeholder Type A						
Stakeholder Type B	BAD	UNCERTAIN	GOOD	(…)	INDIFFER	DIVIDED
Stakeholder Type C						
(…)						
Stakeholder Type Y						

For discussion purposes, we suppose that the evaluation for each cell is qualitative, *e.g.,* good, indifferent, bad or uncertain; we will also suppose that this can be presented as a symbol of a particular colour (*e.g., green, yellow, red* and *grey*).

2.3. Comparative evaluation of scenarios by a given stakeholder type

The future is portrayed as a 'fuzzy object' through a set of scenarios. We suppose that, in the overall context of the scenario set, each scenario may be the focus of evaluation in relation to the others, and that each stakeholder group will furnish a distinctive view of the relative desirability of the possible futures.

For a given stakeholder category Y, we have a "slice" of the Cube, a rectangular array of cells *(x, z)* in which each horizontal row *(z)* represents a scenario (labelled Alpha, Beta, Gamma, etc.) and each column *(x)* represents the major evaluation categories (the governance issues or axes or evaluation) (Fig. 192; Table 53). The 'colour' of an individual cell shows the rating of a scenario for a single evaluation category, made by the specified category of stakeholders. A row thus portrays the scenario 'scores' for each of the governance issues; and a column portrays the relative performances of each scenario for a single evaluation category.

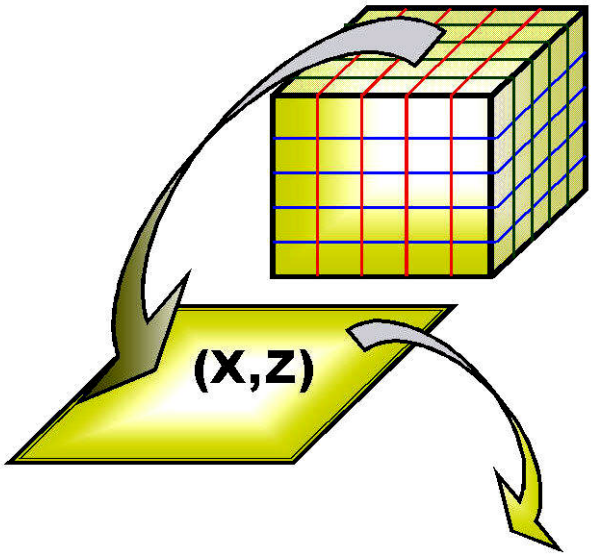


Fig. 192 - Extraction of one slice of the Deliberation Matrix: scenario-evaluation.

Table 53 - Example of the information held in a slice of the Deliberation Matrix (X = governance issue; Z = scenario).

From the point of view of one category of Stakeholder:

(X,Z)	Governance Issue (I)	Governance Issue (II)	Governance Issue (III)	(…)	Governance Issue (X)	"Overall"
Scenario Alpha			BAD			
Scenario Beta	GOOD	INDIFF	GOOD	(…)	BAD	
Scenario Gamma			GOOD			
(…)			(…)			
Scenario Zeta			UNCERTAIN			

2.4. Overview of scenario performance for a given governance/evaluation category

The future is portrayed as a 'fuzzy object' through a set of scenarios.

We suppose that, in the overall context of the scenario set, a focus may be placed on a particular evaluation category (*e.g.,* the question of farmer financial viability; or the question of 'good water quality' under the Water Framework Directive). In this context, each scenario will be assessed in terms of this particular evaluation category, and we may suppose that each stakeholder group will furnish its distinctive assessment of this aspect (*e.g.,* satisfactory, indifferent, bad…).

For a given evaluation category (defined along the X-axis), we will have a "slice of the Cube" (Fig. 193), a rectangular array of cells *(y, z)* in which (as portrayed below) each row corresponds to a scenario (*z*) and each column to the classes of stakeholders (*y*) (Table 54). The use of such a tabular presentation is to enable a rapid appraisal of the

relative performance of each scenario for a chosen criteria or governance issue. (This comparison would appear in the “overall” column on the far right of the table).

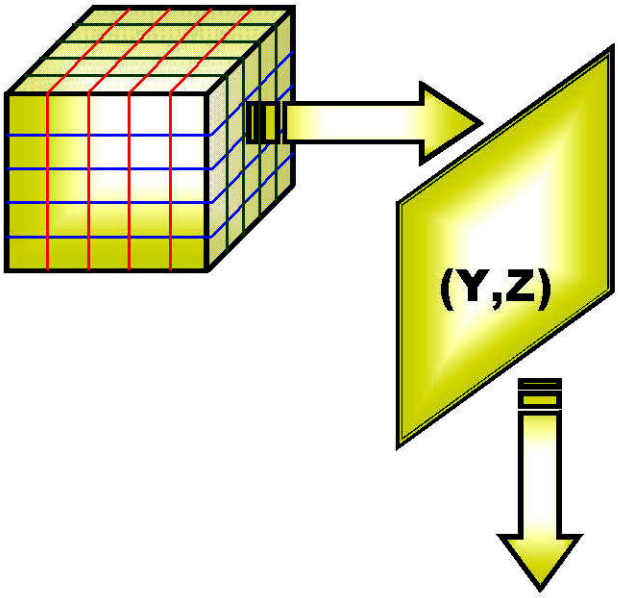


Fig. 193 - Extraction of one slice of the Deliberation Matrix: scenario-stakeholder.

Table 54 - Example of the information held in a slice of the Deliberation Matrix (Y = scenarios; Z = categories of stakeholders).

(Z,Y)	Stakeholder Type A	Stakeholder Type A	Stakeholder Type A	Stakeholder Type A	Stakeholder Type A	“Overall”
Scenario Alpha						
Scenario Beta						
Scenario Gamma	BAD	INDIFF	INDIFF	(…)	BAD	(BAD)
(…)						
Scenario Zeta						

3. ROLES OF THE PLAYERS IN THE GOVERNANCE SCHEME

3.1. A note on the real-life origins of the game

The Deliberation Matrix is, as its name suggests, intended to support a process of discussion, reflection and argument about resource management alternatives. This deliberation can take place, we propose, through a process of appraisal of the different scenarios — their relative merits and demerits, the justifications for and against the choices, interests or value systems that they embody, and so on. The several dimensions of this deliberation process constitute the terrains of choice and negotiation for the players in the Governance Game.

The construction of the Matrix is based on the identification of a small number of key governance or decision issues, and a small number of distinct stakeholder classes.

Each stakeholder class offers a synthetic judgement *(satisfactory, poor, intolerable, etc.)* of each scenario in relation to each of the key governance or decision issues.

For the real-world situation that serves as the reference point for the Gouvernance Game, a diagnostic classification of environmental functions, a qualitative institutional analysis and stakeholder mapping have all been carried out. Six major stakeholders have been identified. These are:

- local farmers and, at a higher scale, the Agricultural sector;
- the Municipality, representing 'traditional' and 'new urban' populations;
- domestic water consumers;
- territorial administrations (at département, region, national and EU scales);
- water distribution companies;
- citizens' associations who represent diverse environmental quality concerns.

Similarly, six major types of governance issues/axes have been identified (Table 55).

Table 55 - The six generic governance issues.

A	Competition for privilege in conditions of access to water defined in terms of PRICE & QUANTITY (economic distribution), *e.g.,* the price consequences of urban water supply piped from an adjacent district
B	Quality degradation (pesticides, nitrates, industrial pollutants…), leading to SEGREGATION of user categories and water users, in terms of QUALITY requirements, *e.g*. farming and industry are not necessarily as exigent as potable water supply to local collectivities
C	Differentiation of SOCIAL STATUS within rural districts between communes/cantons that have their own high quality water and those districts that have polluted water and cannot supply their own, as in the case of Montreuil sur Epte. This is not just a quantity segregation, it also plays at the level of IDENTITY, perhaps of PRESTIGE, linked to collective identity and to notions of patrimony, local economic security and autonomy.
D	LANDSCAPE/ECOSYSTEM QUALITY as a component of SUSTAINABLE DEVELOPMENT. Apart from the degradation of water quality for municipal supply purposes, concerns may be expressed that the intensive agriculture plus contamination of the aquifer may lead to water table, water quality and hence ecological changes that are adverse from the points of view of various recreational uses/users and residents of the region.
E	POLITICAL PROCESS. Rapport de force et mode de decision: will resource governance take place via stakeholder concertation vs. enlightened bureaucrat vs. capture by dominant interests? Which interests will dominate agricultural production, land use, water quality and distribution issues (agricultural sector, local municipalities, EC norms, water companies…)?
F	DEGREE OF ARTIFICIALISATION. *e.g*. the extent to which agricultural production depends on imports of chemicals and energy rather than the natural soil and climate; the extent to which piped, recycled and technically purified water replaces local source supply for communes and industry. This defines the status of water as a natural/cultivated/produced capital and has a bearing on notions of patrimony and ecosystem integrity.

It is important to specify the role of the different scenarios in their game. Their purpose is not to offer predictions about the future, but rather to facilitate learning about the different economic interests, technological choices, societal value judgements and

political coordination challenges (etc.) that surround the questions of “sustainable agriculture”.

In this context, it should be reiterated that the components of the Deliberation Matrix (closely linked to the *IMAGINE* Scenario Generator from the project PEGASE, also to be incorporated in this PEGASE domain implementation) are very directly based on empirical knowledge of the *Montreuil-sur-Epte* case study as well as comparative analysis of a variety of other real world situations.

The governance issues and stakeholder categories are authentic; the contrasting scenarios constituting the ‘fuzzy future’ have been constructed on the basis of a direct consultation over a period of several months with a variety of stakeholders, over and above the standard institutional and documentary analysis (Table 56). The notion of a set of dialectically contrasting scenarios as constituting a “fuzzy future” has been developed in the C3ED’s work on the GOUVERNe and PEGASE projects, which constitute the main precursor studies for the IMAGINE Scenario Generator that is also a key part of the agricultural pollution domain. A comment can be made on the tension between “authenticity” and “idiosyncrasy” in the development of a virtual world as a learning opportunity. We have adopted the choice of a prototype that is recognisably of a specific place, hence “idiosyncratic” to some degrees. However, we already know, for example, that the six categories of governance issues for agriculture/water resource situations are fairly generic. This typology has been established in the context of the GOUVERNe Project, based on observations and analyses of several research teams across several different groundwater management situations in European countries. The C3ED team’s experience in the PEGASE project, although based on a less systematic diagnosis of governance issues, confirms the usefulness of the typology. We do not yet propose it as entirely generic for all and sundry European agriculture/water quality situations; however it is a useful departure point.

Table 56 - The five scenarios of the Governance game.

1. Abandonment of agriculture	This drastic solution reflects the crisis of intensive agriculture in Europe, also the trend of urbanisation / gentrification in favoured districts around major cities. The water quality is progressively improved if non-agricultural pollution sources are controlled.
2. Abandonment of the aquifer	The groundwater is definitely abandoned as a source of drinking qality water. There is investment in a new supply, through a pipe network from another district.
3. Decontamination	Technological means of aquifer water purification are engaged, at substantial cost, to obtain water of drinkable quality. This relaxes the environmental pressure and permits a continuation of agricultural production and also further urbanisation.
4. A 'reasoned' agriculture	Measures are adopted, at the farm level and coordinated through agricultural and territorial administration institutions, for the progressive introduction of production techniques that entail reduced chemical environmental pressures.
5. Towards a new institutional coherence	Agricultural practives evolve radically in the context of a new societal vision seeking to reconcile the multiple values of the landscape, productive agriculture and water quality as cultural and natural patrimony.

Our the intention is, once the Governance Game prototype is functional, to make a careful appraisal of the advantages and limitations of the “authenticity” of this true-to-

life example. On the basis of the C3ED team's work in several multi-partner projects involving case studies in different parts of Europe (notably, the VALSE, CRITINC, GOUVERNe and PEGASE projects), we believe that the prototype experience based on a real case study will directly lead us to be able to specify 'generic' concepts and categories that can be applied for the quick composition of a "Deliberation Matrix" for a wide range of agriculture/pollution/sustainability contexts in different parts of Europe.

The problem situation is based on the real-life case study of the commune of Montreuil-sur-Epte in north-western France. A crisis has emerged due to the cumulative contamination of local groundwater by chemicals deriving (mostly) from agricultural fertiliser and pesticide applications, meaning that this water source can no longer be used for municipal supply. In this context, and reflecting the reality of the debates, changes of practice and investment decisions having to be taken, the five scenario themes described in the table have been defined.

3.2. How to fill the cells of the Matrix?

We turn now to the roles envisaged for the players of the game. For each scenario, we obtain a rectangular array of cells *(x, y)* in which each row represents the evaluations (the categories *x*) furnished by a given class of stakeholders (the selected *y*). However, where do these synthetic judgements come from? How are they arrived at? In the "Greening the Face of the Cube" game context, two types of procedure are pertinent.

The first, which has the role of "initialising" the Matrix, is for the system designer, on the basis of prior experience and analyses, to attribute a judgement by each stakeholder category for a scenario's performance for each governance issue or criterion.

The second procedure envisages more particularly the opportunities for a structured and visible deliberation and "concertation" by the players. It involves a sequence of steps that permits the passage from the identification of candidate indicators and performance concepts to the specification of a synthetic "judgement" such as *"good"* or *"bad"* which is attributed (with a colour, etc.) to a cell of the Matrix.

- For each decision criterion or governance issue, a range of potential indicators are identified as 'candidates' suitable to be used as an element for evaluation judgements. (Some indicators will potentially have relevance for more than one decision or governance issue).
- From the set of potentially useful indicators that has been identified for each governance issue, a subset of a small number (we suggest no more than about 5) of indicators is selected, forming an "indicator basket". In some situations a single indicator may be enough, where a performance or decision criterion is discrete (*e.g.,* the surface cultivated with a particular type of agriculture, or the volume of water of drinking quality allocated to a town supply).
- The observation and the normative interpretation for each indicator in a "basket" must be designated.
- The importance of each indicator for arriving at an overall judgement that is entered into a cell of the Matrix, must be specified.

For the PEGASE prototype, the game developer (that is, the C3ED and associates) assumes the responsibility for the first step, that of identifying and presenting to the players, a range of potentially relevant indicators and performance concepts and the

units/categories of their measurement. It is, however, then envisaged that the players will exercise their own judgement — individually and/or collectively — for the steps numbered (2), (3), (4). This deliberation for the content of each cell of the Matrix can have a dynamic and iterative nature — successive rounds of negotiation, as it were — as each player returns to revise their judgements either individually or on the basis of discussion or observation of the choices exercised by others.

3.3. Combining 'bottom-up' and 'top-down' perspectives in the preliminary selection of candidate indicators

For each decision criterion or governance issue, a range of potential indicators must be identified as suitable to be used as an element for evaluation judgements. As outlined elsewhere in the PEGASE Project methodology, it is important that indicators be able to act as 'bridges' between different scales of representation and as 'common points' permitting exchanges of views between stakeholders having different preoccupations and points of view concerning the resource. Underlying the "game" is a real process of research. That is, the stakeholder categories, the scenarios and the governance issues correspond to a real-world situation with real stakes and people. However, PEGASE seeks to identify 'generic' concepts, not just for the ICT architecture but also for the portrayal of environmental issues to citizens. This is essential if progress is to be made in the exploitation of interactive ICT as supports for environmental learning relevant to large populations in their ordinary walks of life (citizens, school and university students, farmers, office and factory workers, tourists, etc.) and not just for specialised applications having high unit costs and long time frames for realisation. In this context, we re-emphasise that the general research procedure (Fig. 194) has been based on an interfacing of *'bottom up' analyses* based on preoccupations expressed by stakeholders, with a *'top down' perspective* using relatively standardised concepts for the classifications of indicators along economic, environmental and institutional dimensions.

TOP DOWN	*Scientific literature reviews across relevant disciplines (publications, research reports, websites...)*		*Interviews, meetings, discussions with stakeholders and complementary documentary analyses*	BOTTOM UP
Indicator systems based on scientific and political perspectives on sustainability				Indicator proposals based on local perceptions of issues and significance
Think globally act locally				*Think locally, act globally*

Fig. 194 - Overall procedures for selection of candidate indicators combining bottom-up analyses and top-down perspectives.

- The interactions with a cross-section of stakeholders facilitate the identification of a spectrum of relevant indicator categories and operational indicators at the 'local' scale, that is, having meaning to stakeholders in the contexts of their everyday activities and operations.

- The search for 'generic concepts', motivated by considerations of parsimony, clarity and eventual transferability of the methodology to other case studies, is pursued through the attempt at reconciliation of indicator proposals obtained through the 'bottom-up' participatory processes with frameworks based on typologies and analysis categories from state-of-the-art hydrosystem, economic and institutional analyses.

For real-world indicator and evaluation systems, this linking of bottom-up to top-down perspectives is a necessary feature for ensuring the effectiveness in use. It allows stakeholders with local and often site specific preoccupations, to see how their particular concerns are examples of categories of social responsibility and issues addressed by the wider scientific and governance community. The local significance of proposed indicators is transparent and, at the same time, stakeholders can be led to appreciate the role of the indicator systems as a representation of wider societal issues and objectives of economic, environmental and social sustainability.

3.4. Deliberation about indicator selection to fill the cells of the Matrix

Once candidate indicators are organised in their groups, a sequence of steps is required that leads to the specification of a synthetic "judgement" such as "good" or "bad" attributed to each cell of the Matrix. For the "Greening of the Face of the Cube" game, we have proposed that deliberation, on an individual or collective basis, can enter at each step along the way, that is, for the steps numbered:

- the selection of a sub-set of indicators for each basket;
- the normative interpretation (significance) to be attributed to each indicator in a basket;
- the relative or absolute importance of each indicator in relation to the others in the basket, for arriving at a synthetic judgement.

Here we give a simplistic account of the sorts of procedures that might be applied (a full specification will be forthcoming as part of the documentation of the prototype under development). We designate the steps sequentially, but it is clear that anticipation about the end result in the Matrix will, for the developers as subsequently for the players in the game, influence choices along the way.

In the step (2), a user acting 'in the name of' a particular stakeholder category, must select a small number of indicators from the set of 'candidates' that has been identified as potentially relevant for each governance issue. As a rule of thumb, no more than about 5 indicators should go into an "indicator basket".

In the step (3), the normative interpretation for each indicator in a "basket" must be designated. For example, threshold levels of pesticide concentrations in water can be designated (with reference to, *e.g.,* European norms for drinking water quality) in order to specify *"good" (+1), "poor" (0)* and *"unacceptable" (–1)* drinking water quality. If the water quality issue is to be portrayed on a well by well or commune by commune basis, the disaggregated information can be portrayed visually with coloured spots on a map of the relevant territory, such as *green for "good" (+1), yellow for "poor" (0)* and *red for "unacceptable" (–1)* drinking water quality. Then an overall index of water quality performance for a given scenario can be designated with reference to any or all of historical benchmarks, policy goals or trends of change for the scenario time horizon.

In the step (4), the importance of each indicator for arriving at an overall judgement is specified. For example, a simple weighting system may be used. If there are five indicators in a basket and each one is attributed possible values of +1, 0, -1 as in the above example, then a “weighted average” (with weights summing to 100 %) would yield a value somewhere between +1 and -1 for the “judgement” of the performance of the scenario for the decision/governance issue. However this is only an illustration. Other procedures can be used that do not engage linear weights, such as “veto” scores or minimum critical thresholds that, if not achieved, imply that the evaluation judgement for the scenario will be “bad” irrespective of the other indicators in the basket for this decision/governance criterion.

3.5. "Greening the face of the Cube": a simple Governance Simulation game

One of the strong points of multi-criteria analysis is that, appropriately presented, it allows a qualitative appreciation of the principal conflicts of values and of interests characterising the problem. One of the strong points of deliberative processes is that, on the basis of exchanges of views and new understanding, stakeholders can come to revise their opinions and judge differently the options in front of them. The Deliberation Matrix portrays for *each* scenario, a rectangular array of cells *(x, y)* in which *each* row represents the evaluations (*x*) furnished by *each* class of stakeholders (*y*). When comparing scenarios, it is necessary to consider how they rate along each of the different evaluation criteria and according to the different stakeholder perspectives.

In a ‘static’ perspective, mathematical multi-criteria methods of ‘outranking’ (such as *NAIADE*) can be used to identify if any one scenario is ‘inferior’ to all others from all stakeholders’ points of view (for each evaluation category considered separately, or for an “overall” score if this is permitted by the evaluation system). They can also be used to pin-point which governance issues most strongly divide stakeholders and which scenarios are marked by high conflict/oppositions of stakeholders’ views. The tabular formats presented above can be used to display such features, *e.g.,* the patterns of *“green”* versus *“red”* cells for each scenario.

Such results will be presented to the game players, as “data”, enabling them to appreciate the trade-offs between different interests and values that may be associated with different scenario alternatives.

In the ‘dynamic’ game perspective, users of the Deliberation Matrix are able to reassess the choices and assumptions leading up to the judgement put into each cell and, after deliberation, propose new/modified entries into the cells. In effect, a process of stakeholder deliberation is permitted on each of the steps already mentioned: on the selection of which indicators will go into each basket, on the normative interpretation (significance) to be attributed to each indicator in a basket, and on the relative or absolute importance of each indicator in relation to the others in the basket. In this way, for each scenario a new/modified (Stakeholder Type x Governance Issue) evaluation table can be generated, and thus, for the set of scenarios, a new/modified Matrix is obtained.

Suppose, for illustrative purposes, that high importance is attached to avoiding social fracture and implementing, where possible, solutions that are ‘inclusive’ in the sense of offering a viable future to all recognised *(sic)* stakeholder groups. (This may be taken

as close to the European ideal of achieving 'social partnership' and is characteristic of many French territorial governance procedures). In a stylised way this political goal is represented by the task, or objective, of *finding a scenario that has no red cells*.

Once the Deliberation Matrix has been constructed, a simple inspection will reveal whether or not there exists one or more scenario(s) judged "acceptable" on all counts in the sense that there are no red cells (Table 57). The situation portrayed in this game is, characterised by strong tensions where there is not an initial consensus about a good way forward. In this context, strongly contrasting scenarios have been formulated (see earlier Box presentation). As the cells of the Matrix are presented, or are filled in progressively, it will become clear to players that no scenario is judged acceptable from all the stakeholders' points of view. A schematic illustration is given in the table above.

Table 57 - Illustration of stakeholders' opinions on governance issues of a given scenario.

(X,Y)	Governance Issue (I)	Governance Issue (II)	Governance Issue (III)	Governance Issue (X)	"Overall"
Stakeholder Type A	BAD	GOOD	INDIFFER	GOOD	DIVIDED
Stakeholder Type B	GOOD	UNCERTAIN	GOOD	BAD	DIVIDED
Stakeholder Type C	GOOD	INDIFFER	GOOD	BAD	DIVIDED
Stakeholder Type Y	GOOD	UNCERTAIN	GOOD	INDIFFER	(GOOD)
	(opinions divided)	*(uncertain)*	*(good)*	*(opinions divided)*	

These are the sorts of circumstances where a "stakeholder concertation" can usefully be simulated. The game develops as a negotiation process in which the players take roles as stakeholders of different types and engage in reflection and deliberation with the (official) game goal of finding a scenario that has no *"red"* cells. If such a scenario/evaluation outcome can be obtained, this corresponds to achieving the (official) objective of the game, namely, "Greening the Face of the Cube".

In real governance situations, there are two levels at which deliberation might permit the identification of a scenario that is "acceptable to everyone". These are (1) modification of judgements concerning an existing scenario (see Box) and (2) identification of a new favourable scenario.

For each scenario in the set, there can be deliberation on an individual and collective basis concerning: i) the preliminary step of identification of potentially useful indicators and performance concepts; ii) the selection by, or on behalf of each stakeholder category, of a sub-set of indicators for each "governance issue" basket; iii) the nominative interpretation (significance) to be attributed by each stakeholder category to each indicator in their "baskets"; and iv) the relative or absolute importance of each indicator in relation to the others in the basket, for arriving at the synthetic judgement entered in a cell of the Matrix. Exchanges of views between protagonists in the negotiation game may lead to modifications at any or all of these steps, and thus to revisions of the judgements entering the cells of the Matrix table. Stakeholders of one type may try to persuade stakeholders of another type to modify their criteria or relative weighting, etc.

There exists numerous real-world examples where deliberative processes have led to the identification of new policy options that are judged by the protagonists to be superior to the options put in front of them. However, we estimate that obstacles can

rapidly emerge on the conceptual, computational and data places, for any attempted elaboration of a full integrated scenario simulation specification allowing the new scenario to be put on a par with those in a pre-existing set. When a real-world multi-stakeholder deliberative policy process is envisaged, this feature can be accommodated in an iterative procedure, in which a 'technical support' team develops scenario specifications to express the emerging ideas and judgements offered by the deliberating parties. But we do not intend to incorporate such an evolutionary emergent feature within the formal structure of this Governance Game.

For the implementation of the Cube as an ICT stage prop for the Game, a number of technical issues remain to be resolved, which can have an important bearing on the way in which the players may interact. Notably, a decision must be made whether the players should negotiate in a 'real' or in a 'virtual' environment. Both options have some attractive features; however the programming, synchronisation and visualisation requirements are rather distinct in each case.

There are two complementary features of the Governance Game. On the one hand, as the name suggests, there is an interest in the outcomes of the evaluation procedure (that is, the contents of the cells in the Matrix) at successive stages of the negotiation, relating to the societal aspiration of a sustainable agriculture. On the other hand, there is the more subtle, less quantified significance of the inter-subjective experience of the reasons, performance concepts, priorities, interests, value systems, knowledge and lines of reasoning that may underlie the judgements offered by the different players (in their roles of stakeholders).

This latter aspect reflects, indeed mimics, the ideal of deliberative democracy, where it is proposed that opportunities for dialogue and debate be constructed in which the various protagonists communicate their interests and value judgements to others, and also come to appreciate better the positions of the others, in the process of weighing up the alternatives and formulating the crucial decisions. Resource governance is understood as a collective social process in which arguments are put forward by the different protagonists for and against different actions and possible outcomes. Awareness and active participation of citizens, are necessary dimensions of the democratic process. The game "Greening the Face of the Cube" is thus intended to offer learning opportunities that increase understanding, simultaneously, of political processes (the procedural dimension) and of agricultural sector performance challenges (the substantive dimension).

4. KNOWLEDGE QUALITY ASSESSMENT FOR THE GOVERNANCE SCHEME

4.1. Knowledge Quality Assessment work in the PEGASE project

The PEGASE work programme, notably WP4, provides for systematic reviewing of the ICT and modelling products, to ensure their quality as tools to be used by individuals and groups in decision situations and policy formulation. In this context, knowledge quality evaluation entails three complementary dimensions:

- the technical quality of the software products: do the programs work (debugging; system crashes, etc.); do they generate results that seem to be in line with their design specifications; are the visual interfaces stable and do they work; it the

software robust for different operating platform variants and machine specifications, etc.;

- scientific validity and robustness: the classical scientific considerations of rigour, coherence, measurement validation and sensitivity testing for the sequences of data transformation, aggregation and modelling;
- user-oriented considerations of pertinence for framing a decision problem and for supporting a multi-user learning activity.

The first of these concerns, technical quality is firstly the responsibility of the ICT development teams for each environmental domain. However, as a complement to the normal checks on software functioning, programming (etc.) carried out by the ICT development teams, the task of making a technical 'audit' of key features of each of the ICT prototypes (*e.g.,* in order to test for bugs, provide feedback to the developers about technical design and documentation of linkages between datasets, model components, etc) was assigned to them. This technological audit has been conducted in parallel with the final tuning work on the prototypes.

The second of these concerns, scientific validation, is relatively well understood by the scientific community; however it takes on special significance when the envisaged users are not expected to have the same disciplinary or technical expertise as the producers of the knowledge.

The third quality concern, effectiveness and user-friendliness, is related to the need to 'bridge between' different fields of experience: it implies the need for what Funtowicz & Ravetz (1990) have called an "extended peer review" of products by potential users who, most often, are motivated by practical needs and interests with knowledge and judgement requirements that are not fully (or, indeed, not at all) accommodated in a purely scientific review.

The knowledge quality assurance (KQA) tasks envisaged within the PEGASE project are therefore multiple. A formal *Protocol for Quality Assessment* for ICT-based learning tools representing environmental systems and sustainable resource management problems, to serve as a guideline for the KQA procedures, has been produced in the VIRTUALIS project. It should be noted that since the time that the VIRTUALIS project proposal was first drafted, the JRC team (Angela Pereira, Silvio Funtowicz and Serafin Corral) and their collaborators in Europe have addressed these quality assurance questions and produced state-of-the-art implementations of quality assessment procedures appropriate to ICT-based learning/decision support tools representing environmental systems and sustainable resource management problems, notably ULYSSES (see http://www.alba.jrc.it/ulysses) and VISIONS (see http://www.alba.jrc.it/visions/pages/visions.htm), and more recently the NUSAP site (see http://www.nusap.net).

4.2. Applying NUSAP for Scientific Quality Assessment

As envisaged in the PEGASE Project, the scientific knowledge assessment guidelines will be organised in terms of the NUSAP (Numeral Unit Spread Assessment Pedigree) framework which addresses issues of measurement, quantification and spread (error bars, confidence intervals, fundamental uncertainty, etc.) and also the status of underlying theoretical frameworks and quantification conventions for the robustness,

pertinence and acceptance of results by the scientific and stakeholder communities (Fig. 195).

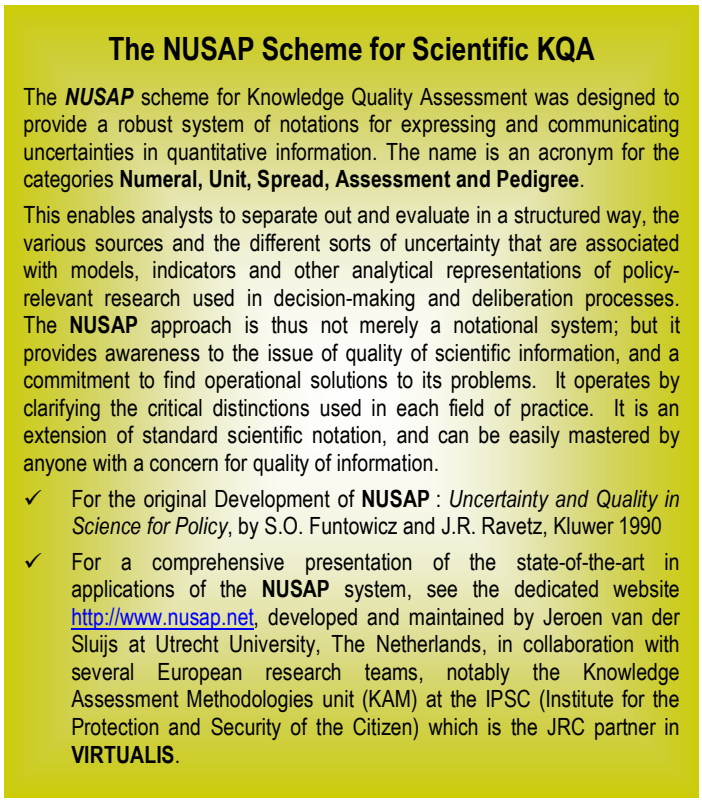


Fig. 195 - Presentation of the NUSAP scheme for Knowledge Quality Assessment.

The complexity of natural systems, the time gaps between exploitation pressure or contamination and cumulative environmental response, and the consequent uncertainties concerning management risks and requirements for long-term stability, pose special problems for scientific quality assurance of any information system. The variety of problems of error and uncertainty (in measurement, classification, aggregation (etc.) associated with measurement and ecosystem description are well known. For the Deliberation Matrix, two main categories of information may be distinguished whose scientific quality is to be assessed. First of all, there are the various measures that are used for the portrayal of scenarios — that is, representations utilising a variety of quantitative indicators (*e.g.,* numerical and visual information specifying agricultural production, pollution emissions, water quality, costs, etc.) that simulate a territorial evolution through time and on a geographically distributed basis, via analytical models, maps and so on. Second, there are the various concepts and measures employed in the 'indicator baskets' used for filling the cells of the Deliberation Matrix. These two categories will overlap, as many of the performance concept used in Matrix indicator baskets will be drawn directly from the scenario descriptions.

NUSAP is quite a flexible tool, and lends itself to applications at the level of individual indicators as well as at the level of complete integrated models. For application to the representations underpinning the "Greening the Face of the Cube" game, we propose

two complementary lines of approach which address, on the one hand the underlying 'integrative' modelling and representation tools and, on the other hand, the indicator systems that are the focus of players' attention.

The integrated modelling tools that underlie the agricultural, hydrological, economic and land-use components of the scenarios, can be subjected to the diagnostic appraisal specified by Risbey, van der Sluijs, Ravetz & Janssen (2001), *A Checklist for Quality Assistance in Environmental Modelling* (see http://chem.uu.nl/www/general/personal/sluijs_a.htm). Based on the results of this appraisal, key features of the modelling and its outputs will be the object of a full NUSAP uncertainty assessment.

The measures and variables that are 'candidate indicators' for the composition of the "indicator baskets" used to generate cells in the Deliberation Matrix, can be characterised by a "NUSAP Profile". This would include a range of indicators that are directly drawn from the scenario simulation modelling and GIS representations, but may also include performance concepts created autonomously.

This two-pronged scientific KQA procedure responds to a variety of communication needs. The software product is intended as a learning opportunity and its quality must be assessed in terms of this function. What is important is that the legitimacy of the learning opportunity should not be undermined by doubts about the realism (in its stylised sense) of the situations and results portrayed. This means firstly to present, or provide access to the documentation about the relevant systems and technologies, etc. It means also to document the main uncertainties and (perhaps) controversies that surround propositions about agricultural production, water pollution and eventual land use futures (etc.). Finally it means to ensure that players of the game can develop awareness of questions that can legitimately be posed about the quality and status of different evaluation claims that appear in the Matrix. A NUSAP Profile attached to each indicator, available as an interactive option to the players, can potentially serve this role of alerting the latter to questions of quantitative (in)exactness and (perhaps controversial) status (or pedigree) of the performance concepts.

4.3. Procedures for 'Extended Peer Review' of the Game

The PEGASE project is conceived as a process that goes from identification of environmental risks and governance issues, to the design and implementation of ICT tools that may help social learning processes about those governance issues. It is obviously very important to make a verification that the these tools are indeed helpful and adequate in the envisaged learning processes and situations, identifying the conditions in which they might work or not and whether they correspond to the users needs – functionality, intuitiveness, black-box free (transparency), perceived as addressing relevant governance issues, and so on.

Thus, complementary to technology quality assessment and the NUSAP-based scientific evaluation, there needs to be a user/stakeholder-based assessment of the ICT. For this, participatory contexts have to be designed and set for bringing together potential users' perspectives into a review process in order to a quality assured technology (Fig. 196).

Tuning Contexts

'Tuning contexts' are the forums where appropriate debate over the design of Information & Communication Technology can be developed and documented. In practice, during group sessions (e.g., *focus groups* or workshop sessions) or through Internet linkages, participants will be invited to evaluate the ICT tools they are interacting with, based on a set of criteria given by the moderators that are related to user and societal needs, system functionality and operability, quality and reliability of the provided information, user interface, etc. The users will also be asked to make recommendations for modifications. These recommendations will be complemented by the moderators based on their own observation of the user's interaction with the applications. Designing the testing procedure, including setting up the participatory framework, involves the following main steps:

- the logistics and resources (e.g. room to carry out sessions, computers and projection equipment, compensation to participants for their time)
- the meeting agenda (exact number of sessions for the two rounds of testing);
- recruitment of the participants to the groups according to some criteria (e.g. age, gender, education, etc.) and definition of the terms of contract with them. Participants should be chosen from 4 different pools: (1) randomly, from the population; (2) Non-Governmental Organisations; (3) schools; (4) stakeholders.

Moderation of Groups' sessions refers to the actual running of the testing phase and includes the following main activities:

- framing the modelling tool into participatory process, i.e. creating a context to use and allow participants to use the software for discussing environmental issues – creating in any case a 'plot' in which the software is tested;
- conduction of groups, monitoring of the social process;
- video-recording of sessions.

Fig. 196 - Presentation of tuning contexts.

For the PEGASE prototype, the testing of the interactive ICT' consist of running a number of sessions with groups, but in a variety of different ways (see GRIC, 2003). In general, the testing phase with potential users takes place in two rounds. After the experimentation in a first round of the first version of software, a second round is used to test a re-engineered version of the software that has incorporated revisions on the basis of experience during the first round. This is what we envisage for the "Greening the Face of the Cube" product.

Software design for learning opportunities necessarily makes presumptions, explicit or implicit, about the character of the learning processes intended to take place. These presumptions and their justifications can be subjected to scrutiny.

An 'extended peer evaluation' of the software engages the participants, interacting in small group settings organised according to an appropriate 'focus group' or 'action-research' social science methodology. For a full peer community evaluation, a typical number of sessions for both runs should be 10 or more, and the number of participants in the groups should be at least 75–100 in total. However, in the process of prototype development it is sometimes also useful to make experiments on a more ad hoc or informal basis.

For the "Greening the Face of the Cube" game, three main types of interactive settings have been distinguished.

- First, where the linkages of project partners to university teaching programmes permit, groups of university students are engaged to experiment with the DST in their early prototype forms. This provides a very effective informal process of 'debugging' and of feedback about the pedagogic effectiveness of the design and interaction capacities of the ICT.
- Second, wide-spectrum groups representing a cross-section of socio-economic classes, will be recruited to make an appraisal of the ICT prototypes in structured 'focus group' settings, following the protocol outlined above. The software users in these experimental settings will offer a range of comments and suggestions on the modelling and visualisation rationales used to represent the physical processes, the socio-economic trends and the 'governance issues'. This feedback, which is fully documented as part of the research/quality assessment process, becomes the basis for "tuning" the Matrix and game procedures for improved effectiveness.
- Third, in formal workshop contexts, panels of people with varied expertise will be invited to experiment with the prototypes. The comments and feedback received at this stage can be the base of a further round of "tuning" before the ICT products are 'released' in the final project dissemination phase.

Setting in motion the process of extended peer evaluation requires, once the small groups are constituted, a succinct introduction to the problem in hand. The procedure to be followed is similar to what is envisaged for an ordinary player of the game once it is brought 'out of the laboratory'. The Deliberation Matrix is intended, precisely, to support and focus process of learning, discussion, reflection and argument about resource management alternatives. So, it can readily be explained, in non-technical terms, how the "Greening the Face of the Cube" game is based on three components: (1) the identification of a small number of key governance or decision issues for the agricultural activity and associated communities, (2) the identification of a small number of distinct stakeholder classes, and (3) the identification (or, more exactly, the construction) of a small number of different scenarios portraying conceivable futures for the agricultural sector and the society concerned by it. This would constitute an effective introduction. For the purposes of software testing, the following procedure could then be applied:

- the participants, after the short general explanation of the overall objectives, are presented with the opportunity to make an appraisal of the different scenarios as presented on the computer. For this to proceed, the range of governance issues and the range of stakeholder categories must be outlined. It must be explained that *each* stakeholder class offers a judgement *(satisfactory, poor, intolerable, etc.)* of *each* scenario in relation to *each* of the key governance or decision issues, leading to a layer of the Matrix, within which each row represents the evaluations (category by category furnished by a given class of stakeholders;
- once these basic notions have been assimilated, the software evaluation proceeds through the step-by-step phase, which can be undertaken on an individual or a collective basis within the group, of the filling in cells of the Deliberation Matrix. This involves decisions based on offered menu selections, about (1) the selection of a sub-set of indicators for each basket; (2) the interpretation (significance) to be attributed to each indicator in a basket; and (3) the relative or absolute importance of each indicator in relation to the others in the basket, for arriving at a synthetic judgement;

- then, the group participants are invited to play the “Greening the Face of the Cube” Governance Simulation Game with the aim of searching out the scenario that achieves a specified game goal.

When harnessed as a software testing process, this group activity permits a rigorous assessment of many different aspects of performance and efficacy of the software interface features (ease of use, clarity, reliability, etc.). The collection and careful review of the experiences of the group (including the facilitators) and their reactions and suggestions, is then the basis for subsequent re-engineering, design modification and ‘tuning’.

Beyond these operational aspects, it also becomes possible to see whether, and to what extent, the game makes a successful bridge between the cognitive frameworks of the analysts whose expert knowledge and methods have contributed to its creation, and the users whose knowledge base, learning interests and life preoccupations are often quite far removed from scientific expertise. The game is based on the hypothesis that individual learning, reflection and exchanges of views between protagonists in a negotiation process may lead to modifications at any or all steps of the judgements leading up to an entry in a cell of the Matrix, and *vice versa*.

To the extent that the game succeeds in its building scenarios in a participatory process, accessing to scientific and vernacular knowledge; the discussion and evaluation of the ICT in testing settings becomes, in itself, an authentic contribution to social learning.

5. SUMMARY

The management of GW resources with reference to quality is often the subject of disagreements among various stakeholders, especially when organic chemicals such as pesticides are involved. A socio-economic analysis of the various alternative management strategies within a sustainable development framework was undertaken within the project. Alternative management scenarios were developed on the basis of the driving forces and solutions envisaged for pesticide management strategies in relation to GW quality for the Brévilles catchments. These scenarios were implemented within a software tool referred to as 'PEG@SE'. The approach and its associated tool are disseminated through a CD-ROM and a dedicated web site (http://st12.c3ed.uvsq.fr /kerpegase/).

Conclusions, perspectives and relevance to policy

1. SUMMARY OF THE PROJECT FINDINGS

The three-year European project PEGASE aimed at i) monitoring the presence of pesticides in a number of representative aquifers; ii) elucidating processes involved in the transport of pesticides from the soil surface to and in groundwater; and iii) developing advanced tools (mathetical modelling tools, but also socio-economic instruments) supporting the management of pesticide usage with regard to the sustainable management of groundwater quality.

Six contrasted aquifers representative of European GW resources (from a sandy aquifer with a GW table <2 m below ground level to a 50 km^2 karst aquifer with GW at >10 m depth) were extensively monitored for water and pesticide fluxes for up to three years. The six study areas were Brévilles (Normandy region, France), Les Trois Fontaines (Centre region, France), Zwischenscholle (North Rhine - Westfalia, Germany), Roswinkel (Drente region, The Netherlands), Martigny (Valay, Switzerland) and Havdrup (Sealand, Denmark). Data collected included information on soils, land use, climate, pesticide usage, hydrogeology and geology. Knowledge about the transport of water and pesticides in soil and in the unsaturated and saturated zones was obtained through field leaching experiments in soil, soil and subsoil coring and sampling of groundwater at various locations and depths.

The **monitoring activities** demonstrated that characterising flow in the subsoil on the basis of experimental observations only remain a challenge despite the large amounts of information which were collected on the soil and the subsoil at the various sites. A potential for a fast transport of pesticides from the soil surface to the groundwater was noted at most study sites, especially when significant rainfall events occured within a few weeks after application. Pesticide concentrations in groundwater exceeding legal thresholds for drinking water were found either for a limited period (*e.g.* isoproturon) or for most of the time (*e.g*. atrazine). Large concentrations (>1 μg/l) were occasionally detected, but these were considered to originate from point source inputs. Very significant spatial and temporal variabilities in pesticide concentrations in the various piezometers were noted at all study sites. This suggests that: i) a network of piezometers should be installed on study areas to grasp the variability in concentrations and to allow an understanding of the transport processes involved; and ii) detailed information on the application of pesticides at the soil surface should be collected as part of the monitoring work. In addition, monitoring activities should be designed so that the duration of monitoring is compatible with the alleged response time of the aquifers.

Sorption **studies in the laboratory** confirmed that the potential for sorption of pesticides in the subsoil is limited. However, sorption in sediments from anaerobic aquifers was found to be significantly larger than that in sediments originating from aerobic aquifers. In contrast to literature results, a significant degradation of MCPP, isoproturon and acetochlor in sediments from the unsaturated zone was found at the Brévilles study area down to a depth of 16 m, except for a particular geological formation. In contrast, atrazine and deethylatrazine were only degraded in the soil. These results may have important implications for pesticide fate modelling activities as modellers traditionally assume that no degradation occurs in the subsoil. In the saturated zone, no degradation of atrazine, deethylatrazine and acetochlor was observed over a two-year period. In contrast, MCPP and isoproturon were degraded, but only in the two aerobic aquifers.

A significant amount of work within PEGASE was dedicated to the refinement and improvement of modelling tools in an effort to further the capabilities of models in the simulation of pesticides to and in the groundwater. This involved i) the refinement of root zone models; ii) the coupling of models, *e.g.* models simulating water and pesticide fluxes in the root zone and groundwater models; and iii) the addition of new subroutines to integrated models thereby allowing the simulation of water transport and pesticide fluxes from the soil surface to and in the groundwater. A revised version of the preferential flow model MACRO was developed. Pesticide fate routines from the GLEAMS model were integrated into the ANSWERS model. MACRO and ANSWERS were combined to two groundwater flow models (MODFLOWT and FRAC3DVS), but difficulties in the coupling of the models were experienced in some instances. The couplings between the various models were restriced to movement of water and pesticide from the root zone model to the groundwater model only. Three 3D integrated groundwater models were adapted to simulate the water transport and pesticide fate from the soil surface to and in the groundwater (MARTHE, TRACE and POWER). This involved the addition of new subroutines to account for pesticide degradation, crop and root development and water and solute uptake by plants. Finally, a simple screening tool with low input requirements, PESTGW, was adapted. Numerics of the various models were improved as part of the refinement work and running times were greatly reduced in numerous instances.

The majority of the new modelling tools developed within the project were applied to reference case studies, numerical solutions or to the datasets collected as part of the project. In a first step, new subroutines implemented in a number of modelling tools considered within PEGASE were subjected to a verification exercise. This involved simulating reference datasets from the literature or comparing model results to analytical solutions. These investigations demonstrated that new subroutines have been correctly implemented in the models and that the new functionalities can be used with confidence. In a second step, the models which were developed or refined within the scope of the project were used to simulate water transport and pesticide fate either at the scale of the soil profile or the groundwater basin based on the data collected during monitoring activities. The large inter-annual and spatial variability in pesticide concentrations was found to be difficult to reproduce in some instances. The importance of preferential flow in the transport of water and pesticides to depth was found to be a recurring theme during field leaching, field monitoring and modelling activities within PEGASE. Inadequate simulation of field data by models was generally attributed to the inability of most models to account for preferential flow processes. Numerical and conceptual difficulties were encountered when trying to couple root zone models with 3D groundwater models such as MODFLOW. In addition, the coupling could only involve the feeding of the predictions of the root zone model to the groundwater model (and not *vice versa*). The integrated models (MARTHE, TRACE, POWER) whose capabilities with regard to pesticide fate were significantly enhanced in the project were found to offer a more viable alternative to modelling water flow and pesticide fate in the soil-unsaturated zone-saturated zone continuum. The addition of the new subroutines means that the integrated models now more or less offer the same capabilities as most root zone models for simulating water and pesticide fluxes in soil while keeping their modelling capabilities of water and pesticide fluxes in the unsaturated and saturated zones in 1-, 2- or 3D. Still, the modelling work undertaken within the project confirmed the challenging nature of simulating water and pesticide fluxes in the combined root, unsaturated and saturated zones.

The management of groundwater resources with reference to quality is often the subject of disagreements among various stakeholders, especially when organic chemicals such as pesticides are involved. A socio-economic analysis of the various alternative management strategies within a sustainable development framework was therefore undertaken within the project. Alternative management scenarios were developed on the basis of the driving forces and solutions envisaged for pesticide management strategies in relation to groundwater quality for the Brévilles catchment. These scenarios were implemented within a deliberation support tool referred to as 'PEG@SE'. The system is designed to create a bridge between scientific and non-scientific knowledge, integrating technical, scientific and social information in a single tool and to help users in formulating their expectations with regard to water quality. The system has been evaluated through interactive demonstrations in schools, universities and local authorities. The approach and its associated tool are being disseminated through a CD-ROM and a dedicated web site.

2. RESEARCH NEEDS

A total of four priority research needs have been identified. First, there is a need for additional information on the distribution of pesticides in the unsaturated and saturated zones. A number of recommendations have been made to support the design of future groundwater monitoring activities. These include i) the adoption of sampling schemes designed to capture the very significant spatial and temporal variability in pesticide concentrations in groundwater which was observed in PEGASE; ii) the collection of detailed data on past pesticide applications (nature of the compounds applied, doses used, but also detailed location of the fields sprayed); and iii) the selection of a monitoring duration which is compatible with the expected response of the aquifer with regard to pesticide contamination. Secondly, laboratory experiments undertaken within the project have revealed that there is a significant potential for pesticide degradation in the unsaturated and saturated zones depending on redox conditions of the aquifer and the nature of the pesticide. These innovative results deserve further investigation as they could lead to a better understanding of the functioning of the aquifer with regard to pesticide contamination and the development of remediation strategies. Thirdly, there is a need to undertake further research into the application of integrated models which can simulate water transport and pesticide fluxes from the soil surface to and in the groundwater. The development of modelling tools with such capabilities is a significant output of the project and these new codes should be thoroughly evaluated to help determining their potential contribution to management strategies for sustaining groundwater quality. Finally, an aspect which should be researched is the connection between preferential flow phenomena in soil and flow processes in the unsaturated and saturated zones. The significant contribution of preferential flow to the presence of pesticides at the bottom of soil profiles has been established, but little is known about the fate of these ‘hot spots’ in the deeper environment and hence the overall contribution of preferential flow phenomena to the contamination of European aquifers by pesticides.

3. RELEVANCE TO POLICY

Some of the findings of the PEGASE project have a direct relevance to current policy initiatives, notably the Water Framework Directive and the Daughter Groundwater Directive. The strong variability in pesticide concentrations in groundwater which translates into significant differences between neighbouring piezometers and between samples taken a few days/weeks apart in a same location should be accounted for in the design of monitoring activities aimed at assessing the status of water resources in the EU. Besides, a common assumption is that the potential for natural attenuation of pesticide concentrations is extremely limited in aquifers. The experiments undertaken to evaluate the potential for pesticide degradation in the unsaturated and saturated zones suggest that significant degradation does occur for some pesticides under specific redox conditions. Full mineralisation of the urea isoproturon leading to the production of carbon dioxyde was even observed in a chalk aquifer. Finally, a range of advanced modelling tools enabling the simulation of the fate of pesticides from the surface of the soil to and in the groundwater through unsaturated and saturated transport have been developed. Although further evaluation of the models is required, it is clear that they offer a significant potential for use as useful tools in the long-term management of groundwater resources in the EU and the achievement or maintaining of good status.

List of references

Abbaspour K.C., Van Genuchten M.T., Schulin R., Schläppi E. (1997) - A sequential uncertainty domain inverse procedure for estimating subsurface flow and transport parameters. *Water Resources Research*, **33**:1879-1892.

Agertved J., Rugge K., Barker J.F. (1992) - Transformation of the herbicides MCPP and atrazine under natural aquifer conditions. *Ground Water*, **30**:500-506.

AGRITOX (2001) - Base de données sur les substances actives phyto-pharmaceutiques, INRA, www.inra.fr/agritox/.

Allen R.A., Walker A. (1987) - The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. *Pesticide Science*, **18**:95-111.

Allen R.G., Pereira L.S., Raes D., Smith M. (1998) - Crop Evapotranspiration: Guidelines for computing crop water requirements. Irrigation and Drainage Paper 56, Food and Agriculture Organization of the United Nations, Rome, 300 p.

Bailey G.W., White J.L. (1970) - Factors influencing the adsorption, desorption and movement of pesticides in soil. *Residue Reviews*, **32**:29-92.

Baker M., Puustinen M., Lund K. (2003) - An evaluation of PEGASE: A personal barometer and a scenario generator. Contribution to D3A3, Document of Work for the European Commission DG Information Society, Contract n° IST-2000-28121, GRIC, France.

Balinova A.M. (1997) - Acetochlor: a comparative study on parameters governing the potential for water pollution. *Journal of Environmental Science and Health*, **32**:645-658.

Banton O., Larocque M., Lafrance P., Montminy M., Gosselin M.A. (1997) - Développement d'un outil d'évaluation des pertes environnementales de pesticides : intégration d'un module PestiFlux au logiciel AgriFlux. Scientific report INRS-Eau. Ste-Foy, Québec, Canada. 144 p.

Baran N. (1999) - Transit de l'isoproturon et de l'atrazine dans un système hydrologique karstique de la craie (Gâtinais-France) : de la station pédologique expérimentale à l'échelle du système. Documents BRGM 284, Editions BRGM, 329 p.

Barbash J.E., Thelin G.P., Kolpin D.W., Gilliom R.J. (2001) - Major herbicides in ground water: results from the national water-quality assessment. *Journal of Environmental Quality*, **30**:831-845.

Bauer P., Attinger S., Kinzelbach W. (2001) - Transport of a decay chain in homogenous porous media: analytical solutions. *Journal of Contaminant Hydrology*, **49**:217-239.

Bebgley D.B., Huggins L.F., Monke E.J. (1980) - ANSWERS: a model for watershed planning. *Transactions of the ASAE*, **23**:938-944.

Birkinshaw S.J., Ewen J. (2000) - Nitrogen transformation component for SHETRAN catchment nitrate transport modelling. *Hydrological Science*, **230**:1-17.

Boesten J.J.T.I., Van Der Pas (2000) - Movement of water, bromide ion and the pesticides ethoprophos and bentazone in a sandy soil : description of the Vredepeel dataset. *Agricultural water management*, **44**:21-42.

Bouraoui F. (1994) - Development of a continuous, physically-based, distibuted parameter, non-point source model. Doctoral thesis (PhD), Faculty of Agricultural Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia, USA, 110 p.

Bouraoui F., Vachaud G., Haverkamp R., Chen T., Dillaha T.A. (1997b) - A GIS-integrated distributed approach for non point source pollution modelling. *IAHS*, **240**:377-384. Proceedings of the Rabat Symposium, April 1997.

Bouraoui F., Vachaud G., Haverkamp R., Normand B. (1997a) - A physical approach for surface-subsurface water transport modeling in agricultural watersheds. *Journal of Hydrology*, **203**:75-88.

Brakensiek D.L., Rawls W. (1994) - Soil containing rock fragments: effects on infiltration. *Catena*, **23**:99-110.

Bröholm M.M., Rügge K., Tuxen N., Højbjerg A.L., Mosbæk H., Bjerg P.L. (2001a) - Fate of herbicides in a shallow aerobic aquifer: A continuous field injection experiment (Vejen,Denmark). *Water Resources Research*, **37**:3163-3176.

Bröholm M.M., Tuxen N., Rügge K., Bjerg P.L. (2001b) - Sorption and degradation of the herbicide 2-methyl-4,6-dinitrophenol (DNOC) under aerobic conditions in a sandy aquifer in Vejen, Denmark. *Environmental Science and Technology*, **35**:4789-4797.

Brooks R.H., Corey C.T. (1964) - Hydraulic properties of porous media. Hydrology Paper 3. Colorado State University, Fort Collins, CO, 27 p.

Carsel R.F., Mulkey L.A., Lorber M.N., Baskin L.B. (1985) - The Pesticide Root Zone Model (PRZM): a procedure for evaluating pesticide leaching threats to groundwater. *Ecological Modelling*, **30**:49-69.

Carter A., Brown C., Glover H., Beard G., Siddons P., Gunther P., Trevisan M., Capri E., Padovani L., Van der Linden T., Cornelese A., Gomez de Barreda D., Kreuger J., Jarvis N., Delmas A., Remy B., Van Zanen N. (1997) - Further analysis on the presence of residues and impact of plant protection products in the EU. Report for the Commission of European Communities & The Dutch Ministry for the Environment, Possibilities for future EC environmental policy on plant protection products. PES-A/Phase 2.

Celia M.A, Bouloutas E.T., Zarba R.L. (1990) - A general mass conservative numerical solution for the unsaturated flow equation. *Water Resources Research*, **26**:1483-1496.

Cerejeira M.J., Viana P., Batista S., Pereira T., Silva E., Valério M.J., Silva A., Ferreira M., Silva-Fernandes A.M. (2003) - Pesticides in Portuguese surface and ground waters. *Water Research*, **37**:1055-1063.

Chilton P.J., Stuart M.E., Goody D.C., Williams R.J., Williamson A.R. (1995) - The occurrence of herbicides in and the modelling of their transport to the chalk aquifer beneath arable land in southern England. *In*: Pesticide movement to water (eds. A. Walker, R. Allen, S.W. Bailey, A.M. Blair, C.D. Brown, P. Günther, C.R. Leake & P.H. Nicholls), BCPC Monograph no. 62, p. 111-116.

Cho C.M. (1971) - Convective transport of ammonium with nitrification in soils. *Canadian Journal of Soil Science*, **51**:339-350.

Ciocanaru M., Harms R., Nitzsche O., Englert A., Vereecken H. (2002) - Site characterization of the Julicher Zwinschescholle area for the PEGASE Project. Forschungszentrum Julich, Germany, Internal Communication, 12 p.

Clark L., Turrell J., Fielding M., Oakes D.B., Wilson I., Taylor L. (1996) - Pesticides in Major Aquifers, Report for the National Rivers Authority. WRc plc, R&D Report 17.

Clay S.A., Moorman T.B., Clay D.E., Scholes K.A. (1997) - Sorption and degradation of alachlor in soil and aquifer material. *Journal of Environmental Quality*, **26**:1348-1353.

Darling W.G., Bath A.G. (1988) - A stable isotope study of recharge processes in the English chalk. *Journal of Hydrology*, **101**:31-46.

Dillaha T.A, Bebgley D.B. (1983) - Distributed parameters modelling of sediment movement and particle size distributions. *Transactions of the ASAE*, **26**:1772-1777.

Doorenbos J, Pruitt. W.O. (1977) - Crop Water Requirements. FAO. Irrigation and Drainage Paper 24, Rome, Italy.

Döring U. (1997) - Transport der reaktiven Stoffe Eosin, Uranin und Lithium in einem heterogenen Grundwasserleiter, ph.D. thesis, Christian Albrechts Universität Kiel, 118 p.

Duffield G.M., Benegar J.J., Ward D.S. (2001) - MODFLOWT A modular three-dimensional groundwater flow and transport model: User's manual Version 1.23. GeoTRANS, Inc. Sterling, Virginia.

Duwig C., Normand B., Vauclin M., Vachaud G., Green S., Becquer T. (2003) - Evaluation of the WAVE-model on two contrasted soil and climate conditions. Submitted to Vadose Zone Journal.

EEC (1991) - European Communities Council Directive 91/414/EEC concerning the placing of plant protection products on the market. Official Journal of the European Communities L230:1-32.

Elrick D.E., Mermoud A., Monnier T. (1994) - An analysis of solute accumulation during steady-state evaporation in an initially contaminated soil. *Journal of Hydrology*, **155**:27-38.

Englert A. (2003) - Mesurement, estimation and modelling of groundwater flow velocity at Krauthausen test site, Ph.D. thesis, RWTH Aachen, 89 p.

Feddes R.A., Bresler E., Neuman S.P. (1974) - Field test of a numerical model for water uptake by root systems. *Water Resources Research*, **10**:1199-1206.

Feddes R.A., Kowalik P.J., Zaradny H. (1978) - Simulation of field water use and crop yield, Simulation Monographs, Wageningen, 188 p.

Feng P.C.C. (1991) - Soil transformation of acetochlor via glutathione conjugation. *Pesticide Biochemistry and Physics*, **40**:136-142.

FOCUS (1995) - Leaching models and EU registration. EC document reference 4952/VI/95, 123 p.

FOCUS (2000) - FOCUS groundwater scenarios in the EU plant protection product review process. Report of the FOCUS Groundwater Scenarios Workgroup, EC document Sanco/321/2000 rev. 2, 202 p.

Funtowicz S.O., Ravetz J.R. (1990) - Uncertainty and quality in science for policy. Dordrecht: Kluwer Academic Publishers.

Gardner W.R. (1958) - Some steady state solutions of the unsaturated moisture flow equation with application to evaporation from a water table. *Soil Science*, **85**:228-232.

Geake A.K., Foster S.S.D. (1989) - Sequential isotope and solute profiling in the unsaturated zone of British chalk. *Hydrological Sciences Journal*, **34**:79-95.

Germann P. (1985) - Kinematic wave approach to infiltration and drainage into and from soil macropores. *Transactions of the ASAE*, **28**:745-749.

Golaz C. (2001a) - Comparison of two simulations made with LEACHP and MARTHE models on the Vredepeel dataset, internal unpublished report.

Golaz C. (2001b) - Données nécessaire pour une modélisation distribuée avec MARTHE, document BRGM, 2 p.

Golaz C. (2001c) - Exercice : nappe-rivière en transitoire, document BRGM, 1 p.

Golaz C. (2001d) - Principaux fichiers de MARTHE, document BRGM, 1 p.

Goode D.J., Konikow L.F. (1989) - Modification of a method-of-characteristics solute transport model to incoporate decay and equilibrium-controlled sorption or ion exchange. U.S. Geological Survey Water-Resources Investigations Report 89-4030, 65 p., Reston, Virginia.

Green W.H., Ampt G. (1911) - Studies of soil physics. Part 1: the flow of air and water through soils. *Journal of Agricultural Science*, **4**:1-24.

Grochulska J., Kladivko E.J. (1994) - A two-region model of preferential flow of chemicals using a transfer function approach. *Journal of Environmental Quality*, **23**:498-507.

Grove D.B., Stollenwerk K.G. (1984) - Computer model of one-dimensional equilibrium-controlled sorption processes. U.S. Geological Survey Water-Resources Investigations Report 89-4059, 58 p.

Güntner A., Olsson J., Calver A., Gannon B. (2001) - Cascade-based disaggregation of continuous rainfall time series: the influence of climate*. Hydrology and Earth System Sciences*, **5**:145-164.

Haria A.H., Hodnett M.G., Johnson A.C. (2003) - Mechanisms of groundwater recharge and pesticide penetration to a chalk aquifer in southern England. *Journal of Hydrology*, **275**:122-137.

Haverkamp R., Parlange J.Y., Cuenca R., Ross P.J., Steenhuis T.S. (1998) - Scaling of the Richards' equation and its application to watershed modeling. In Scale Invariance and Scale Dependence in Hydrology, Ed. G. Sposito, Cambridge University Press, New York, USA., ISBN 0-521-57125-1, chapter 7, p. 190-223.

Haverkamp R., Zammit C., Bouraoui F., Rajkai K., Arrúe J.L., Heckmann N. (1998) - GRIZZLY, Grenoble Catalogue of Soils: Survey of soil field data and description of particle-size, soil water retention and hydraulic conductivity functions. Laboratoire d'Etude des Transferts en Hydrologie et Environnement (LTHE), Grenoble Cedex 9, France.

Haverkamp R., Braud I., de Condappa D., Debionne S., Gandola F., Ross P.J., Vachaud G., Varado N., Zin I. (2003a) - POWER, Planner Oriented Watershed modeling system for Environmental Responses, Introductory Report. Laboratoire d'Etude des Transferts en Hydrologie et Environnement (LTHE), Grenoble Cedex 9, France, p. 1-69.

Haverkamp R., Leij F.J., Fuentes C., Zin I., Ross P.J. (2003b) - Soil water retention, I: Development of a shape index. *Soil Science Society of America Journal*, submitted.

Herbst M., Ciocanaru M., Hardelauf H., Harms R., Vereecken H. (2003) - Modelling the regional scale transport of pesticides, Tagungsbeiträge zum 6. Workshop zur hydrologischen Modellierung, Kassel University Press, Magdeburg, 167-176.

Heron G., Christensen T.H. (1992) - Degradation of the herbicides mecoprop in an aerobic aquifer determined by laboratory batch studies. *Chemosphere*, **24**:547-557.

Hill B.D., Miller J.J., Chang C., Rodvang S.J. (1996) - Seasonal variation in herbicide levels detected in shallow Alberta groundwater. *Journal of Environmental Science and Health*, **B31**:883-900.

Hoffmann-Riem H., Van Genuchten M.T., Flühler H. (1999) - General model for the hydraulic conductivity of unsaturated soils. *In*: Characterization and measurement of the hydraulic properties of unsaturated porous media, (eds. M.T. van Genuchten; F.J. Leij; L. Wu), p. 31-42, Univ. California, Riverside, CA, USA.

Holman I., Hollis J. (2001) - CAMSCALE: upscaling, predictive models and catchment water quality. Final Report ENV4-CT97-0439. SSLRC, Cranfield University, UK.

Hoyningen-Huene J.V.F (1983) - Die Interzeption des Niederschlages in landwirtschaftlichen Pflanzenbeständen. Schriftenreihe des Deutschen Verbandes für Wasserwirtschaft und Kulturbau e.V. 57, 65 p.

Huang K., Mohanty B., Leij F., Van Genuchten M.Th. (1998) - Solution of the nonlinear transport equation using modified Picard iteration. *Advances in Water Resources*, **21**:237-249.

Huang K., Mohanty B.P, Van Genuchten M.Th. (1996) - A new convergence criterion for the modified Picard iteration method to solve the variably saturated flow equation. *Journal of Hydrology*, **178**:69-91.

Huggins L.F., Monke E.J. (1966) - The mathematical simulation of the hydrology of small watersheds, Techn. Rep. N°1, Water Resources Res. Center, Purdue Univ., 130 p.

Hutson J. (2000) - LEACHM – Model description and user's guide, available upon request: (john.hutson@flinders.edu.au), 143 p.

Hutson J.L., Wagenet R.J. (1992) - LEACHM: Leaching Estimation And Chemistry Model. A process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Version 3, Department of Soil, Crop and Atmospheric Sciences. Research series no. 92-3, Cornell University, NY, USA.

I.U.P.A.C. (1987) - IUPAC report on pesticides no. 23. Potential contamination of ground water by pesticides. *Pure & Applied Chemistry*, **10**:1419-1446.

IFEN (2002) - Les pesticides dans les eaux. Bilan annuel 2002. Etudes & Travaux 36. IFEN, Orléans, France. 23 p.

Issa S., Wood M. (1999) - Degradation of atrazine and isoproturon in the unsaturated zone: a study from southern England. *Pesticide Science*, **55**:539-545.

Jahn R. (2002) - Erstellung eines hydrogeologischen modells for die Jülicher Zwischenscholle. Master Thesis University Aachen. 79 p.

Janssen P.H.M., Heuberger P.S.C., Sanders R. (1992) - UNCSAM 1.1: a software package for sensitivity and uncertainty analysis. Report nr. 959101004, National Institute of Public Health and Environmental Protection (RIVM), Bilthoven, Netherlands.

Jarvis N. (2001) - The MACRO Model (Version 4.3). Technical Description.SLU, Department of Soil Sciences, Box 7014, 750 07 Uppsala.

Jarvis N.J. (1994) - The MACRO model (Version 3.1). Technical description and sample simulations. Reports and Dissertations, 19, Dept. Soil Sci., Swedish Univ. Agric. Sci., Uppsala, Sweden, 51 p.

Jarvis N.J. (2002) - Macropore and preferential flow. *In*: The Encyclopedia of Agrochemicals, (ed. J. Plimmer), vol. 3, 1005-1013, J. Wiley & Sons, Inc.

Jarvis N.J., Jansson P.E., Dik P.E., Messing I. (1991) - Modelling water and solute transport in macroporous soil. I. Model description and sensitivity analysis. *Journal of Soil Science*, **42**:59-70.

Jayachandran K., Steinheimer T.R., Somasundaram L., Moorman T.B., Kanwar R.S., Coats J.R. (1994) - Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *Journal of Environmental Quality*, **23**:311-319.

Johnson A.C., Besien T.J., Lal Bhardwaj C., Dixon A., Gooddy D.C., Haria A.H., White C. (2001) - Penetration of herbicides to groundwater in a unconfined chalk aquifer following normal soil applications. *Journal of Contaminant Hydrology*, **53**:101-117.

Johnson A.C., White C., Bhardwaj C.L. (2000) - Potential for isoproturon, atrazine and mecoprop to be degraded within a chalk aquifer system. *Journal of Contaminant Hydrology*, **44**:1-18.

Jørgensen P., McKay L.D., Spliid N.H. (1998) - Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed columns and numerical modeling. *Water Resources Research*, **34**:539-553.

Jørgensen *et al.* (2002) - Monitoring and modeling of flow and transport of bromide and pesticides (MCPP, metsulfuron, and prochloraz) in till and local aquifer from field injection of pesticides. *Water Resources Research*.

Jørgensen *et al.* (2003) - Evaluation and implication of conventional pesticide monitoring techniques in clayey till.

Jørgensen P., McKay L.D., Kistrup J.P. (2003) - Aquifer vulnerability to pesticide migration through till aquitards. *Groundwater*, in press.

Jørgensen *et al.* (2004a) - Evaluation and comparison of suitability of equivalent porous (EPM), dual porosity (DP (CXTFIT, MODFLOW/MT3D)) and discrete fracture matrix diffusion (DFMD (FRAC3Dvs)) modeling approaches to predict solute transport during variable flow rate and time. *Journal of Contaminant hydrology*.

Jørgensen *et al.* (2004b) - Evaluation of key-parameters (geological, hydrological, pesticide properties) evaluation of aquifer vulnerability under clay-rich till aquitards, accepted for publication in *Ground Water*.

Jury W.A., Sposito G., White R.E. (1986) - A transfer function model of solute transport through soil. 1. Fundamental concepts. *Water Resources Research*, **22**:243-247.

Kalkhoff S.J., Kolpin D.W., Thurman E.M., Ferrer I., Barcelo D. (1998) - Degradation of chloroacetanilide herbicides: The prevalence of sulfonic and oxanilic acid metabolites in Iowa groundwaters and surface waters. *Environmental Science & Technology*, vol. 32.

Kimmeier F. (2001) - 3-D Groundwater Flow Modeling in Heterogeneous Geologic Media: Integrated Approach Using Spatial and Temporal Database, Geostatistics and GIS, Thèse, Centre d'hydrogéologie, Université de Neuchâtel.

Kimmeier F., Bouzelboudjen M., Ababou R., Ribeiro L. (2001) - Travel path uncertainty: a case study combining stochastic and deterministic hydraulic models in the Rhône valley, Switzerland. 3rd International Conference on Future Groundwater Resources At Risk, Lisbon, Portugal, 15 p., 9 fig., 1 ann.

Kimmeier F., Bouzelboudjen M., Ornstein P., Weber I., Rouiller J.D. (2001) - Geohydrological parameter identification and groundwater vulnerability to pollution: A Swiss case study. 3rd International Conference on Future Groundwater Resources At Risk, Lisbon, Portugal, 16 p.,12 fig., 1 tab., 1 ann.

Klosterman J. (1992) - Das Quartär der Niederrheinischen Bucht. Geologische Landesamt Nordrhein-Westfalen, Krefeld.

Knisel W.G. (1980) - CREAMS, A field scale model for chemical, runoff, and erosion from agricultural management systems. Conservation Res. Report, USDA-SEA.

Knisel W.G. (1993) - GLEAMS, Groundwater Loading Effects of Agricultural Management Systems. Version 2.10, Model documentation. Univ. of Virginia, USDA, ARS, Tifton, Georgia, USA..

Knisel W.G., Davis F.M., Leonard R.A. (1992) - GLEAMS Version 2.0, User Manual. USDA-ARS, Southeast Watershed Research Laboratories, Tifton, GA, USA.

Kolpin D.W., Nations B.K., Goolsby D.A., Thurman E.M. (1996) - Acetochlor in the hydrologic system in the midwestern United States, 1994. *Environmental Science and Technology*, **30**:1459-1464.

Kolpin D.W., Thurman E.M., Linhart S.M (1998) - The environmental occurrence of herbicides; the importance of degradates in ground water. *Archives of Environmental Contamination and Toxicology*, vol. 35, no. 3, p. 385-390.

Konda L.N., Pásztor Z. (2001) - Environmental distribution of acetochlor, atrazine, chlorpyrifos, and propisochlor under field conditions. *Journal of Agricultural Food and Chemistry*, **49**:3859-3863.

Kristensen G.B., Sørensen S.R., Aamand J. (2001) - Mineralization of 2,4-D, mecoprop, isoproturon and terbuthylazine in a chalk aquifer. *Pest Mangement Science*, **57**: 531-536.

Larsbo M., Jarvis N.J. (2003) - MACRO5.0. A model of water flow and solute transport in macroporous soils. Technical description. Emergo 2003:5. Studies in the Biogeophysical Environment. Department of Soil Sciences, SLU, Uppala, Sweden, 48 p.

Larsen L., Sørensen S.R., Aamand J. (2000) - Mecoprop, Isoproturon, and Atrazine in and above a Sandy Aquifer: Vertical Distribution of Mineralization Potential. *Environmental Science, Technology*, **34**:2426-2430.

Lasne E. (1992) - Etude du système hydrologique karstique des sources des Trois Fontaines (Saint-Loup-de-Gonois, Loiret). Contribution à la connaissance de la structure, du fonctionnement et de l'évolution de l'aquifère crayeux du Gâtinais (Sud est du Bassin de Paris). Thèse de l'Université d'Orléans, 453 p.

Leij F.J., Alves W.J., Van Genuchten M.Th., Williams R.J. (1996) - The UNSODA - Unsaturated Soil Hydraulic Database. User's Manual Version 1.0. Report EPA/600/R-96/095. National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268: 1-103.

Leistra M., Boesten J.J.T.I. (1989) - Pesticide contamination of groundwater in Western Europe. *Agricultural Ecosystems and Environment*, **26**:369-389.

Levy J., Chester G. (1992) - Simulation of atrazine and metabolite transport and fate in a sandy till aquifer. *Journal of Contaminant Hydrology*, **20**:67-88.

Li K.Y., de Jong R., Boisvert J.B. (2001) - An exponential root-water-uptake model with water stress compensation. *Journal of Hydrology*, **252**: 189-204.

Libra R.D., Hallberg G.R., Hoyer B. (1987) - Impacts of Agricultural Chemicals on Ground Water Quanlity in Iowa. In Ground Water Quality and Agricultural Practises; Lewis Publisher Chelsea, Michigan: 1987; Chapter 14.

Loague K.M., Green R.E. (1991) - Statistical and graphical methods for evaluating solute transport models: overview and application. *Journal of Contaminant Hydrology*, **7**:51-73.

Madsen L., Lindhardt B., Rosenberg P., Clausen L., Fabricius I. (2000) - Pesticide sorption by low organic carbon sediments: A screening for seven herbicides. *Journal of Environmental Quality*, **29**:1488-1500.

Manning R. (1891) - On the flow of water in open channels and pipes. *Transactions, Institution of Civil Engineers of Ireland, Dublin*, **20**:161-207.

McDonald M.G., Harbaugh A.W. (1988) - A modular three-dimensional finite-difference groundwater flow model. US Geological Survey Techniques of Water-Resources Investigations, book 6, Chap. A1, 586 p. (3): 489-494.

McMahon P.B., Chapelle F.H., Jagucki M.L. (1992) - Atrazine mineralization potential of alluvial-aquifer sediments under aerobic conditions. *Environmental Science & Technology,* **26**:1556-1559.

Meiwirth K. (2003) - Regional and local scale pesticide transport in the alluvial plain of the swiss Rhône river valley, EPFL, Thesis No 2869, 110 p.

Miller E.E., Miller R.D. (1955) - Physical theory for capillary flow phenomena. *Journal of Applied Physics*, **27**:324-332.

Mills W.C., Leonard R.A. (1984) - Pesticide pollution probabilities. *Transactions of the ASAE*, **27**:1704-1710.

Monteith J.L. (1975) - Vegetation and the atmosphere. Academic Press. 439 p.

Moreau C., Mouvet C. (1997) - Sorption and desorption of atrazine, deethylatrazine and hydroxyatrazine by soil and aquifer solids. *Journal of Environmental Quality*, **26**:416-424.

Morel-Seytoux H.J., Meyer P.D., Nachabe M., Touma J., van Genuchten M.T., Lenhard R.J. (1996) - Parameter equivalence for the Brooks-Corey and van Genuchten soil characteristics.

Nash J.E, Sutcliffe J.V. (1970) - River flow forecasting through conceptual models: Part I – A discussion of principles. *Journal of Hydrology*, **10**:282-290.

Neuendorf O. (1996) - Numerische 3-D Simulation des Stofftransports in einem heterogenen Aquifer. Ph.D. thesis, RWTH Aachen, 305 p.

Nicholls P.H. (1994) - PETE – Physico-chemical Evaluation: The Environment – expert system for pesticide preregistration assessment. Proceedings BCPC, Pest and Diseases, Brighton, UK, 1337-1342.

Nofziger D.L., Hornsby A.G. (1986) - A micro-computer base management tool for chemical movement in soil. *Applied Agricultural Research*, **1**:50-56.

Nordmeyer H., Pestemer W., Rahman A. (1992) - Sorption and transport behaviour of some pesticides in groundwater sediments. *Stygologia*, **7**:3-11.

Normand B. (1996) - Etude expérimentale et modélisation du devenir de l'azote dans le système sol-plante-atmosphère. 190 p. Ph.D. diss. Joseph Fourier Univ., Grenoble, France.

Normand B., Recous S., Vachaud G., Kengni L., Garino B. (1997) - Nitrogen-15 tracers combined with tensio-neutronic method to estimate the nitrogen balance of irrigated maize. *Soil Science Society of America Journal*, **61**:1508-1518.

Olsson J. (1998) - Evaluation of a scaling cascade model for temporal rainfall disaggregation. *Hydrology and Earth System Sciences*, **2**:19-30.

Organisation for Economic Co-operation and Development. (1993) - OECD guidelines for testing of chemicals. 106 Adsorption/desorption. OECD, Paris, France.

Pasquarell G.C., Boyer D.G. (1996) - Herbicides in karst groundwater in southeast West Virginia. *Journal of Environmental Quality*, **25**:755-765.

Pedersen P.G., Arildskov N.P., Albrechtsen H.J. (2002) - Atrazine removal in Danish anaerobic aquifers. Ground water Quality 2001. Conference held at Sheffield. UK. IAHS Publ. No. 275.

Pothuluri J.V., Moorman T.B., Obenhuber D.C., Wauchope R.D. (1990) - Aerobic and anaerobic degradation of alachlor in samples from a surface-to-groundwater profile. *Journal of Environmental Quality*, **19**:525-530.

Pütz T (1993) - Lysimeterversuche zum Verlagerungsverhalten von Methabenzthiazuron und gelöstem organischen Kohlenstoff in einer Parabraunerde, Aufbau von zwei Klimameßstationen und Untersuchungen zur Validierung des Lysimetersystems. Thesis. University Bonn. 223 p.

Rao P.S.C., Hornsby A.G., Jessup R.E. (1985) - Indexes for ranking the potential for pesticide contamination of groundwater. *Soil and Crop Science Society of Florida Proceedings*, **44**:1-8.

Rawls W., Brakensiek D.L. (1985) - Prediction of soil water properties for hydrologic modelling. *American Society of Civil Engineers*, 293-299.

Rawls W.J., Brakensiek D.L. (1989) - Estimation of soil water retention and hydraulic properties. *In*: Morel-Seytoux H.J., (Ed.), Unsaturated Flow in Hydraulic Modelling: Theory and Practice, NATO ASI Series C, vol. 275. Kluwer, Dordrecht.

Rawls W.J., Brakensiek D.L., Saxton K.E. (1982) - Estimation of soil water properties. *Transactions of the ASAE*, **25**:1316-1330.

Reggiani P., Sivapalan M., Hassanizadeh M. (1998) - A unifying framework of watershed thermodynamics: balance equations for mass, momentum, energy and entropy and the second law of thermodynamics. *Advances in Water Resources*, **22**:367-398.

Reggiani P., Sivapalan M., Hassanizadeh S.M. (2000) - Conservation equations governing hill-slope responses: exploring the physical basis of water balance. *Water Resources Research*, **36**:1845-1864.

Richards L.A. (1931) - Capillary conduction of liquids through porous media. *Physics*, **1**: 318-333.

Risbey J., van der Sluijs J., Ravetz J., Janssen P. (2001) - A Checklist for Quality Assistance in Environmental Modelling, Dept. of Science, Technology and Society, Utrecht University. 22 p. NWS-E-2001-11.

Ritchie J.T. (1972) - A model for predicting evapotranspiration from a row crop with incomplete cover. *Water Resources Research*, **8**:1204-1215.

Ross P.J. (2002) - Modeling soil water and solute transport - Fast, simplified numerical solutions. ASA Special Symposium "The soil-plant-atmosphere continuum: gaps and unresolved issues", Charlotte, N. Carolina, USA, October 21-25.

Ross P.J. (2003) - Modeling soil water and solute transport - Fast, simplified numerical solutions. *Agronomy Journal*, in press.

Rügge K., Juhler R.K., Broholm M.M., Bjerg P.L. (2002) - Degradation of the R- and S-enantiomers of the herbicides MCPP and dichlorprop in a continuous field injection experiment. *Water Research*, **36**:4160-4164.

Rutter A.J., Kershaw K.A., Robins P.C., Morton A.J. (1971) - A predictive model of rainfall interception in forests 1. Derivation of the model from observations in a plantation of corcican pine. *Agricultural Meteorology*, **9**:367-384.

Ryan M., Meiman J. (1996) - An examination of short-term variations in water quality at a karst spring in Kentucky. *Ground water*, **34**:23-30.

RZWQM Team (1992) - Root Zone Water Quality Model, Version 1.0. Technical documentation. GPSR Technical Report no. 2., USDA-ARS-GSPR, Fort Collins, USA.

Salvucci G.D., Entekhabi D. (1994) - Equivalent steady soil moisture profile and the time compression approximation in water balance modelling. *Water Resources Research*, **30**:2737-2749.

Schwarze H, Jaeckel U., Vereecken H. (2001) - Estimation of macrodispersion by different approximation methods for flow and transport in randomly generated heterogenous media. *Transport in Porous Media*, **43**, 265-287.

Smith M., Allen R., Pereira L. (1996) - Revised FAO Methodology for crop water requirements. FAO-Report. 10 p.

Soutter M. (1996) - Prédiction stochastique à l'échelle régionale des risques de contamination des eaux souterraines par des pesticides. Ph.D. thesis n° 1487, DGR-EPFL, Lausanne.

Spitters C.J.T., van Keulen H., van Kraalingen H. (1988) - A simple but universal crop growth simulation model, SUCROS87. In R. Rabbinge, H. Van Laar & Ward (ed), Simulation and system management in crop protection. Simulation Monographs. PUDOC, Wageningen.

Springer A.E., Bair E.S. (1998) - Natural-gradient transport of bromide, atrazine and alachlor in an organic-rich aquifer. *Journal of Environmental Quality*, **27**:1200-1208.

Stralher A.N. (1957) - Quantitative analysis of watershed geomorphology. *Transactions of the American Geophysical Union*, **38**:913-920.

Stralher A.N. (1964) - Quantitative geomorphology of drainage basins and channel networks. In Handbook of Hydrology, Ed. V. T. Chow, McGraw-Hill, New York, chap. 4-11.

Tappe W., Groeneweg J., Jantsch B. (2002) - Diffuse atrazine pollution in German aquifers. *Biodegradation*, **13**:3-10.

Tarboton D.G. (1997) - A new method for the determination of flow directions and contributing areas in grid digital elevation models. *Water Resources Research*, **33**:309-319.

Thiéry D. (1990) - Logiciel MARTHE – Modélisation d'Aquifère avec maillage Rectangulaire, Transport et HydrodynamiquE, version 4.3 Rapport BRGM R 38210, 330 p.

Thiéry D. (1993a) - Hydrological modelling of the Saone Basin. Sensitivity to the soil model. Physics and Chemistry of the Earth.

Thiéry D. (1993b) - Modélisation des aquifères complexes. Prise en compte de la zone non saturée et de la salinité. Calcul des intervalles de confiance. *Hydrogéologie*, **4**:325-336.

Thiéry D. (1994a) - Logiciel MARTHE – Nouvelles fonctionnalités de la version 5.4, Rapport BRGM R 38085 HYT/DR/94, 330 p.

Thiéry D. (1994b) - Modélisation 3D des écoulements en zone non saturée avec le logiciel MARTHE Version 5.4, BRGM report, R38108 HYT/DR 94, 114 pp, in French.

Thiéry D. (1995) - Modélisation 3D du transport de masse avec le logiciel MARTHE Version 5.4, BRGM report, R38149 HYT/DR 95, 171 pp, in french.

Thiéry D. (2001) - Couplage Nappe-Rivière dans le modèle MARTHE et Couplage Nappe-Drains, unpublished, 12 p.

Thiéry D. (2002a) - Couplage Nappe-Rivière dans le modèle MARTHE et Couplage Nappe-Drains, unpublished, 16 p.

Thiéry D. (2002b) - Didacticiel du pré-processseur WinMarthe v1.1, unpublished, 43 p.

Thiéry D., Golaz C. (2002) - Consideration of vegetation effects in version 6.2 of the MARTHE model, BRGM/RP-51988-FR, 48 p.

Thiéry D., Schwartz J., Berge J., Totoohi F., Konstantopedos K., Lambe M. (1995) - Un système d'aide à la gestion des ressources en eaux souterraines. Application au site de Bordeaux. *Hydrogéologie*, **1**:129-139.

Tiktak A., van der Linden A.M.A., Merkelbach R.C.M. (1996) - Modeling pesticide leaching at a regional scale in the Netherlands. RIVM report No. 715801008, Bilthoven, the Netherlands, 1996.

Tiktak A., van den Berg F., Boesten J.J.T.I., van Kraalingen D., Leistra M., van der Linden A.M.A. (2000) - Manual of FOCUS PEARL version 1.1.1. RIVM report 711401 008, Alterra report 28, Bilthoven, Wageningen, The Netherlands.

Tiktak A., De Nie D., Van der Linden T., Kruijne R. (2002) - Modelling the Leaching and Drainage of Pesticides in the Netherlands: The GeoPEARL model. *Agronomie*, **22**:373-387.

Toräng L., Nyholm N., Albrechtsen H.J. (2003) - Shifts in biodegradation kinetics of the herbicides MCPP and 2,4-D at low concentrations in aerobic aquifer materials. *Environmental Science and Technology*, **37**:3095-3103.

Tuxen N., de Lipthay J.R., Albrechtsen H.J., Aamand J., Bjerg P.L. (2002) - Effect of exposure history on microbial herbicide degradation in an aerobic aquifer (Vejen, Denmark). *Environmental Science and Technology*, **36**:2205-2212.

Vachaud G., Chen T. (2002) - Sensitivity of computed values of water balance and nitrate leaching to within soil class variability of transport parameters. *Journal of Hydrology*, **264**:87-100.

Van Dam J.C., Huygen J., Wesseling J.G., Feddes R.A., Kabat P., Van Walsum P.E.V., Groenendijk P., Diepen C.A. (1997) - Theory of SWAP version 2.0 Department of water Resources, Report 71, Wageningen Agriculture University, Wageningen, The Netherlands.

Van Genuchten M.T. (1980) - A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*, **44**:892-898.

Van Heemst H.D.J. (1988) - Plant data values required for simple crop growth simulation models: review and bibliography. Simulation Report CABO-TT nr. 17, Wageningen. 107 p.

Vanclooster M., Boesten J.J.T.I., Trevisan M., Brown C.D., Capri E., Eklo O.M., Gottesbüren B., Gouy V., van der Linden A.M.A. (2000) - A European test of pesticide leaching models: methodology and major recommendations. *Agricultural Water Management*, **44**:1-19.

Vanclooster M., Armstrong A., Baouroui F., Bidoglio G., Boesten J.J.T.I., Buraeul P., Capri E., De Nie D., Fernandez E., Jarvis N., Jones A., Klein M., Leistra M., Linnemann V., Pineros Garcet J.D., Smelt J.H., Tiktak A., Trevisan M., Van den Berg F., Van der Linden A.M.A., Vereecken H., Wolters A. (2003) - Effective approaches for predicting environmental concentrations of pesticides: The APECOP project. Proceedings of the XII International Symposium Pesticide Chemistry, 4-6 June 2003, Piacenza, Italy, 923-931.

Vanclooster M., Pineros-Garcet J.D., Boesten J.J.T.I., van den Berg F., Leistra M., Smelt J., Jarvis N., Roulier S., Burauel P., Vereecken H., Wolters A., Linnemann V., Fernandez E., Trevisan M., Capri E., Padovani L., Klein M., Tiktak A., van der Linden A., De Nie D., Bidoglio G., Bouraoui F., Jones A., Armstrong A. (2003) - Effect approaches for predicting environmental concentration of pesticides. EU-FP5, Quality of Life, Final report. Université Catholique de Louvain.

Vaughan P.C., Verity A.A., Mills M.S., Hill I.R., Newcombe A.C., Simmons N.D. (1999) - Degradation of the herbicide, acetochlor in surface and sub-surface soils under field and laboratory conditions p.481-490. Proceedings of the XI symposium Pesticide Chemistry, September 11-15, Cremona, Italy. La Goliardica Pavese.

Vereecken H., Maes J., Feyen J., Darius P. (1989) - Estimating the soil moisture retention characteristic from texture, bulk density and carbon content. *Soil Science*, **148**: 389-403.

Vereecken H., Maes J., Feyen J. (1990) - Estimating unsaturated hydraulic conductivity from easily measured soil properties. *Soil Science*, **149**:1-12.

Vereecken H., Lindenmayr G., Neuendorf O., Döring U., Seidemann R. (1994) - TRACE A mathematical model for reactive transport in 3D variably saturated porous media, Internal Report KFA-ICG-4-501494, Jülich, 67 p.

Vereecken H., Kaiser R. (1999) - Analysis of multi-step outflow data and pedotransfer functions to characterise soil water and solute transport at different scales. In: M. Th. van Genuchten, F.J. Leij and L. Wu (ed.) Characterization and measurement of the

hydraulic properties of unsaturated porous media, part 2. Riverside, California, 1089-1102.

Vereecken H., Döring U., Hardelauf H., Jaeckel U., Hashagen U., Neuendorf O., Schwarze H., Seidemann R. (2000) - Analysis of solute transport in a heterogeneous aquifer: the Krauthausen field experiment. *Journal of Contaminant Hydrology*, **45**:329-358.

Vogel T., van Genuchten M.T., Cislerova M. (2001) - Effect of the shape of the soil hydraulic functions near saturation on variably-saturated flow predictions. *Advances in Water Resources*, **24**:133-144.

Voss C.I. (1984) - SUTRA - A Finite-Element simulation model for saturated-Unsaturated, Fluid-Density-Dependent Groundwater Flow with Energy Transport or Chemically Reactive Single species solute transport. U.S. Geological Survey National Center. Reston, Virginia.

Wagner J.J. (1970) - Elaboration d'une carte d'anomalie du Bouger. Etude de la vallée du Rhône de St-Maurice à Saxon (Suisse). Thèse n° 1483, Université de Genève.

Walker A. (1987a) - Evaluation of a simulation model for prediction of herbicide movement and persistance in soil. *Weed Research*, **27**:143-152.

Walker A. (1987b) - Herbicide persistence in soil. *Reviews in Weed Science*, **3**:1-17.

Wauchope R.D., Yeh S., Linders J.B.H.J., Klowskowski R., Tanaka K., Rubin B., Katayama A., Kordel W., Gerstl Z., Lane M., Unsworth J.B. (2002) - Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Management Science*, **58**:419-445.

Wellings S.R., Cooper J.D. (1983) - The variability of recharge of the English chalk aquifer. *Agricultural Water Management*, **6**:243-253.

Widmer S.K., Spalding R.F. (1995) - A natural gradient transport study of selected herbicides. *Journal of Environmental Quality*, **24**:445-453.

Williams G.M., Harrison I., Noy D.J., Crowley O., Kalin R.M. (2001) - Use of Enantiomeric Ratios to Identify Natural Attenuation of Chiral Mecoprop in the Lincolnshire Limestone. Report no P2-151/TR, Environment Agency, Rio House, Bristol.

Williams J.B., Nicks A.D., Arnold J.G. (1985) - Simulator for water resources in rural basins. *Journal of Hydraulics Engineering*, *Transactions of the ASCE*, **111**:970-986.

Willmott C.J. (1981) - On the validation of models, Physical Geography, 2.

Wilson J.T., McNabb J.F., Balkwill D.L., Ghiorse W.C. (1983) - Enumeration and characterization of bacteria indigenous to a shallow water-table aquifer. *Ground Water*, **21**:134-142.

Yeh G. (1987) - 3DFEMWATER, a three dimensional finite element model of water flow through saturated-unsaturated media. report ORNL-6386. Oak Ridge.

Yeh G.T., Sharp-Hansen P., Lester B., Strobl R., Scarbrough J. (1992) - 3DFEMWATER/ 3DLEWASTE: Numerical codes for delineating wellhead protection areas in agricultural regions based on the assimilative capacity criterion, U.S. Environmental Protection Agency, GA 30613, Athens.

Zheng C., Wang C. (1998) - MT3DMS A modular three-dimensional multispecies transport model for simulation of advection, dispersion and chemical reactions of contaminant in groundwater systems. Documentation and User's Guide. Waterways Experiment Station. US Army Corps of Engineers Vicksburg, Mississippi 39187.

Zheng H., Ye C. (2002) - Adsorption and mobility of acetochlor and butachlor on soil. *Bulletin of Environmental Contaminants and Technology*, **68**:509-516.

APPENDIX 1

Bibliography related to the 7 steps of the method "The Deliberation Cycle of the Theatre of Sustainability" (see chapter 4) and dissemination activities

STEP 1 :

For Montreuil-sur-Epte (France):

Georges E. (2000) - Quelles informations pour la gestion d'un problème de pollution des eaux souterraines par les produits phytosanitaires ? Le cas de Montreuil-sur-Epte. Rapport de stage, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 110 p.

Paranthoen S. (1999) - Pollution des eaux par les produits phytosanitaires en Ile de France – Etude de quelques sites spécifiques. Mémoire INA-PG – Agronomie-Environnement – Stage à la Direction Régionale et Interdépartementale de l'Agriculture et de la Forêt d'Ile-de-France.

Baran N., Mouvet C. (2002) - Sources des Brévilles — Montreuil-sur-Epte (95). Bilan des activités jusqu'à décembre 2001 et suivi parcellaires pour l'année culturale 2000. Rapport BRGM RP?, p. 58.

For Juelich (Germany):

Haake J. (2000) - Case study of the Jülich aquifer 'Zwischenscholle' - socio-economic part. Unpublished report, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 35 p.

Harms R. (2002) - Interviewers of farmers in Schwischenscolle (Germany). Unpublished report, UFZ.

For Martigny (Switzerland):

Meiwirth K. (2002) - Interviewers of farmers in Martigny (Switzerland). Unpublished report, EPFL.

STEP 2:

See Work Packages 2 & 3.

STEP 3:

For Montreuil-sur-Epte (France):

Georges E. (2000) - Quelles informations pour la gestion d'un problème de pollution des eaux souterraines par les produits phytosanitaires ? Le cas de Montreuil-sur-Epte. Rapport de stage, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 110 p.

For Juelich (Germany):

Haake J. (2000) - Case study of the Jülich aquifer 'Zwischenscholle' - socio-economic part. Unpublished report, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 35 p.

For Martigny (Switzerland):

Bizot X., Pistone I. (2001) - Etude de cas sur la nappe aquifère de Martigny (Suisse). Unpublished report, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France 15 p.

STEP 4:

For Montreuil-sur-Epte (France):

Georges E. (2000) - Quelles informations pour la gestion d'un problème de pollution des eaux souterraines par les produits phytosanitaires ? Le cas de Montreuil-sur-Epte. Rapport de stage, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 110 p.

D'Angela L., Moers D. (2001) - Etude de cas sur la nappe de Montreuil-sur-Epte (France). Unpublished report, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 15 p.

Douguet J.M., O'Connor M., Schembri P., Lanceleur P., Abdellaoui A., Chakiri M. (2003) - Scénarios concernant un usage alternatif des pesticides pour les études de cas retenus. Livrable n° 19 pour le Work Package 4, réalisé dans le cadre du projet européen PEGASE (2000-2003), n° EESD-ENV-99-1, coordonné par C. Mouvet (BRGM, France), pour la DG de l'Environnement, Commission Européenne dans le cadre du 5ème Programme Cadre de Recherche et de Développement, 36 p.

For Juelich (Germany):

Haake J. (2000) - Case study of the Jülich aquifer 'Zwischenscholle' - socio-economic part. Unpublished report, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 35 p.

STEP 5:

FOR THE MODELLING:

Schembri P., Douguet J.M. (2001) - Le PEGASE-Exploitation, une modélisation structurelle dynamique au niveau de l'exploitation agricole. Application au cas de Montreuil-sur-Epte. Unpublished report, C3ED, University of Versailles - Saint-Quentin-en-Yvelines, France, June 2001, 30 p.

FOR SCENARIOS BUILDING:

For Montreuil-sur-Epte (France):

Douguet J.M., O'Connor M., Schembri P., Lanceleur P., Abdellaoui A., Chakiri M. (2003) - Scénarios concernant un usage alternatif des pesticides pour les études de cas retenues. Livrable n° 19 pour le Work Package 4, réalisé dans le cadre du projet européen PEGASE (2000-2003), n° EESD-ENV-99-1, coordonné par C. Mouvet (BRGM, France), pour la DG de l'Environnement, Commission Européenne dans le cadre du 5ème Programme Cadre de Recherche et de Développement, 36 p.

Levieaud A. (2002) - Evolution de la politique de gestion de l'eau et de la politique agricole en Europe: application aux scénarios développés pour Montreuil-sur-Epte

dans le cadre du projet européen PEGASE. Report, University of Versailles — Saint-Quentin-en-Yvelines, France.

For Juelich (Germany):

Guyonnaud M. (2002) - Scenarios for the case of the German aquifer "ZWISCHENSCHOLLE". Unpublished draft report, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 5 p.

STEP 6:

THE MULTI-MEDIA INTERFACE:

PEG@SE software. (2003) - Version 3.2, Realised by the C3ED for the PEGASE Consortium, C3ED-UVSQ, Guyancourt, France.

Abdellaoui A., Douguet J.M., Schembri P. (2001a) - Phytosis: Présentation. Published brochure, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 1 p. It is a short presentation of Phytosis. The aim is to give them to stakeholders or during meetings.

Abdellaoui A., Douguet J.M., Schembri P. (2001b) - Imagine: Présentation. Published brochure, C3ED, University of Versailles — Saint-Quentin-en-Yvelines, France, 1 p. It is a short presentation of Imagine. The aim is to give them to stakeholders or during meetings.

Douguet J.M., O'Connor M., Schembri P., Lanceleur P. (2003a) - Evolution possible des concentrations de pesticides dans les aquifères retenus. Livrable n° 20 pour le Work Package 4, réalisé dans le cadre du projet européen PEGASE (2000-2003), n° EESD-ENV-99-1, coordonné par C. Mouvet (BRGM, France), pour la DG de l'Environnement, Commission Européenne dans le cadre du 5ème Programme Cadre de Recherche et de Développement, 66 p.

KNOWLEDGE QUALITY ASSESSMENT:

Pustinnen M., Baker M., Lund K. (2002) - An Evaluation of PEGASE: A Personal barometer and a scenario generator. Unpublished report, GRIC ULL2-CNRS, University of Lyon 2, France.

During C3ED Seminar (3 times per year, 2000-2003), University of Versailles - Saint-Quentin-en-Yvelines, France.

Communication of preliminary results to other PEGASE partners, to local stakeholders and to policy stakeholders in order to establish a basis for scenario re-specification and full evaluation analysis: Meeting at Montreuil-sur-Epte (November 22th 2001); Presentation of the interactive interface in Montreuil-sur-Epte (January 11th 2002); April 2002.

Presentation of the interactive interface in Saint-Quentin-en-Yvelines during a seminar with INRA, French institute on Agronomy (January 17th 2002); Evaluation by students of the University of Versailles - Saint-Quentin-en-Yvelines (January and February 2002).

STEP 7:

METHODOLOGY:

Douguet J.M., O'Connor M. (2003b) - Evaluation socio-économique des implications des scénarios alternatifs développés pour les aquifères retenus. Livrable n° 21 pour le Work Package 4, réalisé dans le cadre du projet européen PEGASE (2000-2003), n° EESD-ENV-99-1, coordonné par C. Mouvet (BRGM, France), pour la DG de l'Environnement, Commission Européenne dans le cadre du 5ème Programme Cadre de Recherche et de Développement, 50 p.

DISSEMINATION OF THE SOCIO-ECONOMIC ANALYSIS:

Products: CD-RoM PEGASE: (which is composed by PEG@SE software + pedagogic supports + information concerning the PEGASE European project), produced by the C3ED for the PEGASE Consortium, University of Versailles - Saint-Quentin-en-Yvelines, France (2003).

Teaching on line: http://st12.c3ed.uvsq.fr/kerpegase/, produced by the C3ED, University of Versailles - Saint-Quentin-en-Yvelines (2003).

TEACHINGS:

ICT in School:

Presentation of the GAS and PEGASE Software at the Collège Pierre de Coubertin (Chevreuse, France).

ICT in University (2001, 2002, 2003, 2004):

Presentation of ICT in the University of Versailles - Saint-Quentin-en-Yvelines (France), during teaching on Integrated Analysis Economy-Environment and information System, Master on Integrated Sustainable Development.

Presentation in the C3ED seminars (3 times per year), October-February 2002, 2003, 2004.

ICT in High School: The use of ICT in the socio-economic evaluation process.

Ecole des Mines de Douai (High school of ingeneur): 29 janvier 2003; In 2004 (date not defined).

Supélec (High school in electronics): le 11 février 2003; 2004 (date not defined).

INTERNATIONAL WORKSHOP AND SYMPOSIUM:

Douguet J.M., Schembri P. (2001) - Analyse prospective des systèmes de production agricole et des politiques environnementales. 2nd international symposium of the A.P.R.E.M.A, *Sustainable Development and Valuation-decision process*. Université de Corse, Corte, 22-23 mai 2001.

Douguet J.M., Schembri P. (2000) - Systèmes agraires et soutenabilité : l'utilisation des nouvelles technologies d'information et de communication dans le processus d'évaluation, paper presented to the Colloque de la Société Française de l'Evaluation, Groupe de Travail "Environnement, Infrastructures et Evaluation", Rennes, 15-16 juin 2000.

Poster in order to present the PEGASE Project for the conference of Lille 3 "Europe of water, Water of the Europeans", group La mise en place du volet économique de la DCE - Expériences dans les bassins pilotes, 9-10 October 2003.

Fête de la science at Antibes (October 12-14, 2003):
Presentation of the PEGASE software.

Fête de la science at Saint Quentin-en-Yvelines (October 15-18, 2003):
Presentation of the PEGASE software.

Presentation of the PEG@SE prototype during a workshop on Sustainable development and aquaculture, CEMAGREF, Paris, France (January 29th, 2003).

International Society of Ecological Economics biennal Symposium, Tunisia 2002: Presentation of the PEG@SE software (developed in PEGASE and Virtualis projects).

Interfaces between Science & Society Milano (Organized by the European Commission, JRC ISPRA, on November 27-28, 2003).