REGIONAL AND LOCAL PESTICIDE TRANSPORT IN THE ALLUVIAL PLAIN OF THE SWISS RHÔNE RIVER VALLEY

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ABSTRACT

The herbicide transport and the groundwater vulnerability to pesticide contamination were studied in the alluvial aquifer of the Rhône River Valley near Martigny (Southwest Switzerland). The low clay and organic matter content of the soil, the intensive agricultural use, and the low depth of the groundwater table, lead to an alleged high vulnerability of the groundwater to contamination. Groundwater is used for irrigation, drinking water supply, and industrial purposes; it is of great economic and ecological importance which makes it particularly interesting to study.

The work consists of local scale transport experiments and a regional monitoring of the groundwater over a two year period.

At the local scale, two herbicides (atrazine and isoproturon) and a tracer were applied to instrumented field plots (4 m^2) in two consecutive years and the transport through the vadose zone was studied in detail. Water flow and solute transport are closely linked to climatic factors. After the application, the pesticides remain at the soil surface as long as no precipitation occurs. Following to the first heavy rainfall, the chemicals are quickly transported through the vadose zone and part of them reaches the groundwater in a short time. During dry periods, the concentrations decrease steadily in the soil profile and the groundwater. After further rainfall, additional concentration peaks are observed in the groundwater, while only small peaks appear near the soil surface. Approximately 2.5 months after the application, the chemical concentration in the soil and in the groundwater has decreased considerably. The experimental results have been used to evaluate a mechanistic deterministic root zone model (HYDRUS-1D). The aim of the simulations was to define the processes involved in pesticide transport and, if possible, to predict the fate of chemicals applied at the soil surface. The MIM (mobile-immobile water) concept was used in order to account for the rapidity of the observed transport. In the study area, the shallow groundwater influences considerably the water conditions in the unsaturated zone; apparently, in such cases the use of a one-dimensional model to simulate the water flow and the chemical transport in the vadose zone is hindered due to difficulties in defining the lower boundary condition. Groundwater flow is typically three-dimensional and therefore, a global (saturated - unsaturated) 3-D model or the coupling of an unsaturated 1-D model to a 3-D saturated model would be more appropriate. Nevertheless, HYDRUS-1D allowed to describe qualitatively the observed results and to confirm the assumption that accelerated flow occurs on the experimental plots.

At the regional scale, 13 piezometers were installed in an observation area (400 ha), and the groundwater was regularly analysed for the concentration of 6 herbicides (atrazine, terbutylazine, simazine, deethylatrazine, isoproturon, and diuron). Herbicides were detected in 12 piezometers, sometimes at high 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 for the observation of herbicides. Near the Rhône river, high hydraulic gradients quickly dilute chemicals leaching from the fields above and herbicides coming from more distant fields may also be observed. Near the slope, an inflow of contaminated water from the hill side (vineyards) contributes to the groundwater contamination. Within the plain, high concentrations of herbicides applied to an

above located field can temporarily be observed. Contaminations are confined in time and space and different substances are detected from one piezometer to another. This lack of continuity in pesticide concentrations will complicate the prediction of the solutes' fate in the groundwater, and a very precise knowledge of the pesticides use, both in space and time, is required.

RÉSUMÉ

Les processus de transport d'herbicides et la vulnérabilité de la nappe à des contaminations chimiques ont été étudiés dans une zone de la plaine du Rhône alluviale valaisanne située près de Martigny, au Sud-Ouest de la Suisse. Les faibles teneurs en argile et en matières organiques du sol, l'utilisation agricole intensive et la faible profondeur de la nappe souterraine laissent à penser que la nappe, d'une grande importance économique et écologique, est exposée à des risques de contamination par des substances appliquées à la surface du sol.

L'étude repose sur l'association d'essais à l'échelle locale et d'observations à l'échelle régionale effectués pendant une période de deux ans.

A l'échelle locale, deux herbicides (atrazine et isoproturon) et un traceur ont été appliqués sur des sites expérimentaux (4 m^2) largement instrumentés pendant deux années de suite et le transport à travers la zone non saturée a été suivi de façon systématique. Il apparaît que les mouvements d'eau et le transport de solutés sont étroitement liés aux facteurs climatiques. Après l'application, et en l'absence de précipitations, les herbicides demeurent à la surface du sol. Lors de la première pluie importante, les herbicides sont transportés rapidement à travers la zone non saturée et une fraction atteint la nappe très rapidement. Durant les périodes sèches qui suivent, les concentrations diminuent régulièrement dans tout le profil de sol. A la suite d'autres événements pluvieux, de nouveaux pics de concentration sont observés dans la nappe, alors que seuls de très faibles pics sont détectés dans la zone non saturée près de la surface du sol. Environ 2.5 mois après l'application, les concentrations en herbicides dans le sol et dans la nappe ont diminué considérablement. Les résultats des expériences à l'échelle locale ont été utilisés pour évaluer un modèle de type mécaniste déterministe (HYDRUS-1D) en vue de mieux comprendre les processus impliqués dans le transport de pesticides et de prédire le devenir des substances chimiques appliquées à la surface du sol. Vu la rapidité des processus de transport observés, il a été fait appel au concept MIM qui suppose qu'une partie de l'eau du sol est immobile, alors que l'autre fraction est mobile. Dans la zone d'étude, la nappe peu profonde influence considérablement le comportement de l'eau dans la zone non saturée. Il ressort des simulations que dans telles situations, le recours à un modèle uni-dimensionnel pour simuler les transferts d'eau et le transport de solutés dans la zone non saturée se heurte à la difficulté de définir correctement la condition à la limite inférieure. L'écoulement dans la nappe étant tri-dimensionnel, un modèle global (saturé - non saturé) à trois dimensions ou, éventuellement, un modèle uni-dimensionnel pour la zone non saturée couplé à un modèle tri-dimensionnel pour la zone saturée, seraient sans doute plus appropriés. Cela étant, le modèle HYDRUS-1D a permis de décrire, au moins qualitativement, les résultas observés et de confirmer la plausibilité de l'hypothèse que de l'écoulement accéléré se produit aux sites expérimentaux.

A l'échelle régionale, 13 piézomètres ont été installés dans une zone d'observation de 400 ha et des échantillons d'eau ont été prélevés régulièrement en vue de la détermination de leur concentration en 6 herbicides (atrazine, terbutylazine, simazine, deethylatrazine, isoproturon et diuron). La présence d'herbicides a été détectée dans 12 piézomètres, parfois à forte concentration, mais durant une brève période (entre mi mai et mi juin); le reste du temps, les concentrations étaient très faibles. Les principaux résultats des essais sur sites expérimentaux (rapidité du transport, importance des conditions climatiques, diminution rapide des pics de concentration) se confirment à l'échelle régionale. Par ailleurs, les caractéristiques de la nappe influencent notablement le devenir des herbicides. A proximité du Rhône, les gradients de charge hydraulique

élevés diluent et entraînent rapidement les herbicides issus des parcelles sus-jacentes; par ailleurs, des substances provenant de sources plus éloignées peuvent également être observées. Près du versant, l'apport d'eau contaminée en provenance du coteau (vignobles) peut contribuer significativement aux pics de concentration. Au centre de la plaine, de fortes teneurs en herbicides appliqués sur les parcelles sus-jacentes peuvent être détectées temporairement. Les contaminations sont limitées dans le temps et dans l'espace et des substances différentes sont observées d'un piézomètre à l'autre. Cette absence de continuité des concentrations laisse entrevoir des difficultés pour prédire le devenir des substances dissoutes dans la nappe et la nécessité de connaître précisément le régime d'application des pesticides.

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INTRODUCTION

In the early 1980s, isolated traces of pesticides detected in the groundwater attracted public attention. Since then, the pesticide contamination of soils, sediments, and water resources has become an increasing problem as a consequence of the growing agricultural production and man's growing awareness for environmental and health concerns (ISENBECK-SCHROETER et al., 1997). In the first decades of pesticide use, scientists assumed that the soil prevented the passage of pesticides into the groundwater by adsorption and degradation. Users' primary concern was that pesticides should not harm crops. Since the discovery of pesticides in the groundwater, however, the perspectives have changed considerably. The EU established the drinking water limit of 0.1 µg l^{-1} for individual substances and several pesticides have been banned in a number of countries. Moreover the occurrence of the fairly immobile chemicals in the groundwater has led to enhanced research on the transport and fate of pesticides in soils (e.g., KLADIVKO et al., 1991; FLURY et al., 1995).

The behaviour of a chemical in the environment depends on its structure and its physico-chemical characteristics (e.g., water solubility and distribution coefficient; MC BRIDE, 1994). The form, intensity, and frequency of the application are other important aspects. Relations between specific application strategies and water pollution have to be investigated. Regional characteristics such as climate, geology, morphology, and hydrology also play an important role for the fate of chemicals. Heavy rainfall for example may transport the chemicals deep into the vadose zone, especially in highly porous or fractured soils. The soil's organic matter and clay content are important parameters for the sorption of pesticides while the temperature influences the chemical's degradation. Chemicals that are ineffectively retained or rapidly transported through the vadose zone may reach the groundwater. Shallow groundwater tables are especially vulnerable for pesticide contamination (FLURY, 1996).

Pesticides are usually thoroughly tested in the laboratory prior to their registration. Experiments are driven at several scales, e.g. batch experiments and soil column experiments (e.g., ZHANG, 2003). Results obtained in the laboratory, however, may not always be applied to the field situation due to spatial variability and heterogeneity phenomena (JURY & FLÜHLER, 1992). In many field studies, pesticides moved deeper into the soil than expected from laboratory measurements (FLURY, 1996). Results from different field studies can hardly be compared because experimental conditions such as soil type and amount and timing of rainfall vary between the sites. Thus, experimental conditions have to be thoroughly taken into account when evaluating the results (ISENBECK-SCHROETER et al., 1997).

In order to analyse laboratory or field experiments, numerical models are used. The movement of chemicals in the vadose zone is simulated with Root Zone Models, while their transport in the saturated zone is simulated using Groundwater Models. Parameters may be directly entered into the model or deduced by fitting calculations to measured data points (inverse modeling). A model has to be validated by comparing the calculated values to the experimental data before reliable predictions can be made (LOAGUE & GREEN, 1991). A quantification of the pesticide transport on a regional scale is generally difficult, because the parameters vary in time and space.

The present study was realised in the Rhone River Valley between Martigny and Charrat, in the Valais Canton. The agricultural zone is intensively cultivated with vegetables, fruit, and corn; vineyards are located on the slope of the valley. The groundwater is used for irrigation (frost

protection and summer irrigation), drinking water, and industrial supply. Consequently, the aquifer is of great economic interest. The intensive agricultural use, the low clay and organic matter contents of the soil, and the shallow groundwater table, lead to an alleged high vulnerability of the groundwater (GW) to contamination (SOUTTER, 1996) and make the area particularly interesting to study.

Nevertheless, only two isolated measurement campaigns of pesticide concentration in the GW have previously been performed, one during summer when the GW level is high and another one during winter when the water table position is lower. Out of 27 analysed pesticides, traces of atrazine, isoproturon, and terbutylazine have been detected in some of the piezometers during the summer campaign. In the winter, the concentrations were below the detection limit. Such a low level of contamination is surprising considering the presumed high vulnerability of the GW to contamination.

The purposes of this study are:
- to evaluate the contamination risks of the alluvial aquifer
- to study in detail the fate of some selected herbicides in the unsaturated zone and to depict important processes governing their transport from the soil surface to the groundwater table

Consequently, the investigations are carried out at two scales:
- a systematic monitoring of the groundwater contamination at a regional scale (~ 400 ha)
- a detailed study of the pesticide transport in the vadose zone at local field sites (4 m^2)

The results of the local experiments were used to evaluate a root zone model (HYDRUS-1D). Simulations were meant to clarify the dominant processes involved in pesticide transport from the soil surface to the GW table. The local scale results and the model help to interpret the regional scale observations and allow to evaluate the risk of groundwater contamination in the aquifer.

The study is part of a European project (PEGASE: Pesticides in European Groundwaters, detailed study of representative Aquifers and Simulation of possible Evolution scenarios). The general objective of PEGASE is to make advances in the understanding of pesticide contaminations in representative European GW systems. The main contribution of the HYDRAM laboratory was to study the contamination processes and pollution risks of an alluvial aquifer with a shallow groundwater table (tasks 1, 2 and 3 of the PEGASE project[1]).

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1. Principal objectives and tasks of the PEGASE projects are:
    1. Selection of experimental sites representative of most European aquifers for detailed study of pesticide uses and fate from the soil to the GW
    2. Intensive and extensive monitoring of those systems according to consensual protocols
    3. Detailed high quality data sets, including soil, vadose zone, and aquifer characterisation to identify critical parameters and enable later modeling
    4. Development of tools enabling the modeling of pesticide contamination of GWs at various spatial (from 1 ha to several km^2) and conceptual (mechanistic or semi-empirical) scales
    5. Assessment of the performance of those tools applied to systems ranging from small and simple aquifers to large complex systems
    6. Application of these tools to predict possible evolution of GW contamination at the experimental sites with or without changes in agricultural practices
    7. Assessment of socio-economic implications of alternative scenarios aiming at GW quality restoration or protection.

The document is organized in three parts: a theoretical part, the local study, and the regional survey. The local scale experiments are presented before the regional scale study, because the interpretation of the regional observations relies to a great extent on the results of the local experiments. The content is further subdivided into 6 chapters:

Major interaction and transport mechanisms of chemicals in soils as well as the outcome of some recent studies are presented in Chapter 1.

Chapter 2 introduces the fundamental mathematical equations describing water flow and solute transport in porous media that are used in this study.

The local transport experiments are described in Chapter 3. The soil properties, the field instruments and their functioning, and some properties of the applied herbicides are illustrated.

Chapter 4 presents the results of the local transport experiments: the soil hydraulic properties and variables as well as the concentrations in the vadose zone and in the GW are described, further investigations that help explaining the observations are illustrated, and the results are finally summarized and discussed.

The numerical modeling of the transport experiments is presented in Chapter 5. The calibration of the hydraulic model is first illustrated and the water fluxes are examined. The results of the transport simulations are described and analysed thereafter.

Chapter 6 is devoted to the regional monitoring study. Some information about geographical, hydrogeological, climatic, and agricultural aspects of the Rhône River Valley and the observation area is given, before the methods of the groundwater monitoring are briefly described. Then, the results are presented and discussed in detail.

In a final conclusion, the results from the experimental study and the numerical modeling are compared to the regional observations, and the vulnerability of the groundwater in the observation area is assessed.

SOLUTE TRANSPORT IN SOILS

Chapter 1

Transport of Pesticides and Groundwater Contamination

When applied to a soil surface, three major processes govern the fate of chemicals in the environment: transport, transformation, and retention (MC BRIDE, 1994). Since the discovery of pesticides in the groundwater, several experimental studies were conducted to elucidate the transport and transformation mechanisms of pesticides in soils. Moreover, public concern has risen dramatically and the number of groundwater monitoring studies increased (ISENBECK-SCHROETER et al., 1997). In this chapter, we will briefly describe the important transport mechanisms of pesticides in the vadose zone before giving an overview of some recent experimental studies. Finally, some groundwater monitoring studies will be summarized.

1.   Principal Processes in the Vadose Zone

When a pesticide is applied to the soil surface, it may follow different transport or loss pathways (Fig. 1). Part of the chemical is possibly washed to surface waters by runoff, another part infiltrates into the vadose zone where it partitions into the three phases: gaseous, solid, and liquid (MARINO et al., 2002).
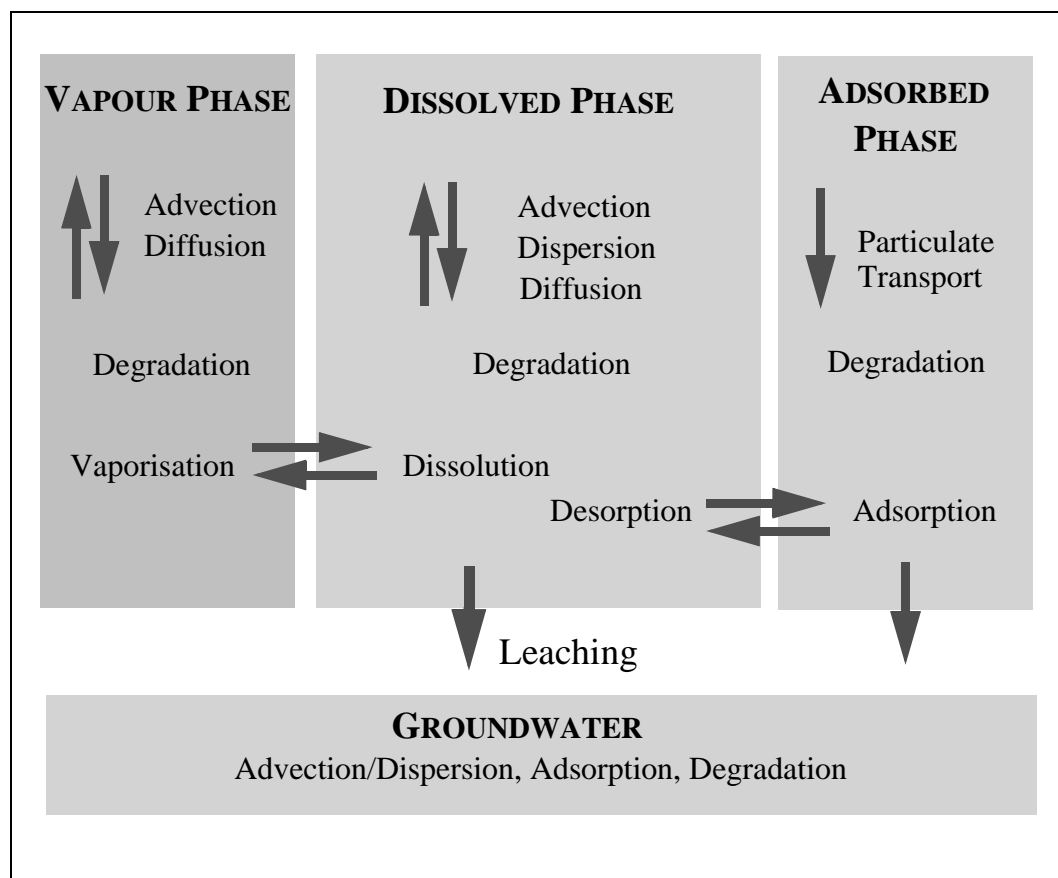
Figure 1: Simplified scheme of pesticide transport and loss pathways in a soil profile

In the vapour phase pesticides are transported by advection and gaseous diffusion within the air-filled portion of the soil voids. At the soil surface volatilization leads to the migration of pesticides into the atmosphere. When sunlight is available, the molecules may be photochemically degraded. There is a constant exchange between the vapour phase and the dissolved phase by vaporization and dissolution of the chemicals (MC BRIDE, 1994).

Another fraction of the applied pesticides may adsorb onto soil particles. At the soil surface, these particles can be transported to surface waters by erosion, while within the soil they may be carried into deeper layers with the advective water flow. Pesticides adsorbed to solids may be decomposed to metabolites by chemical and microbial transformation processes (GROVER, 1988).

Finally, a big fraction of the applied pesticides will remain in the dissolved phase and be transported deeper into the soil profile by gravity driven advection and by dispersion. During dry periods, however, the water flow and transport may be directed upwards to sustain evaporation. Dissolved pesticides may also be chemically and biochemically degraded (MC BRIDE, 1994).

The fraction of the pesticides that is not irreversibly retained or degraded in the vadose zone will leach into the groundwater. While highly volatile chemicals may leach into the groundwater as vapour phase compounds (PASTERIS et al., 2002), this process plays only a minor role for chemicals with low vapour pressures like most pesticides (GROVER, 1988). A more important process is the leaching of pesticides adsorbed to colloids and soil particles that are advectively transported to the groundwater (SETA & KARATHANASIS, 1997). Nevertheless, the principal fraction of pollutants generally leaches into the groundwater in the dissolved phase.

The importance of each of these processes varies according to the physicochemical properties of the pesticide, the climatic conditions, the soil characteristics, e.g., its texture, its chemical composition, its hydraulic properties, and others (MARINO et al., 2002).

2.   Pesticides and their Interaction with Soil

Pesticides are a heterogeneous set of organic substances. They can be classified according to their use as fungicides, fumigants, insecticides, rodenticides, growth regulators, and herbicides or according to their chemical structure (triazines, ureas, carbamates, etc., ISENBECK-SCHROETER et al., 1997). In this study, we will often use the term pesticides, even if we are referring to the subgroup of herbicides. Some important properties of the herbicides considered in this study are listed in Tab. 1.

The migration of herbicides into the atmosphere depends on the vapour pressure that varies over a wide range for the different substances (e.g., 2800 mPa for EPTC; GROVER, 1988, and 0.003 mPa for simazine, Tab. 1). Nevertheless, even maximal vapour pressures of herbicides are low in comparison to familiar organic compounds like alcohols or ethers (vapour pressures ~10^5 Pa; GROVER, 1988). Therefore, volatilization generally plays a minor role for the environmental fate of pesticides.

Table 1: Properties of the herbicides considered in this study. n.a.: no information available

Herbicide	Molecular Formula	Vapour Pressure [mPa]	Water Solubility [mg l^{-1}]	pK$_b$ values [-]	Half Life, T$_{1/2}$ [d]	Soil Organic Carbon Sorption Coefficient, K$_{oc}$ [ml g^{-1}]
Atrazine	C$_8$H$_{14}$Cl N$_5$	0.0385[h]; 0.04[a]	33[b], 30-70[h]	12.32[b,h]	60[c]; 64[k]; 82[e]; 18-120[h]; 13-402[b]	100[b,c]; 160[k], 172[j]; 38-174[h]
Simazine	C$_7$H$_{12}$Cl N$_5$	0.00295[h]; 0.003[b]	3.5[b,h]; 5[k]; 6.2[c,h]	12.38[b] 12.35[h]	60[c]; 75[k]; 28-149[h]; 126-186[b]	138[b,j]; 140[k]; 4-2200[h]
Terbutylazine	C$_8$H$_{16}$Cl N$_5$	0.15[f]	8.5[f]	12.0[l]	n.a.	323[g], 360[k]
Diuron	C$_9$H$_{10}$Cl$_2$N$_2$O	0.0092[b,h]	37[a]; 42[b,h]	n.a.	90[b,c] 30-328[h], 328[k]	351, 380[k]; 383[j]; 477[b]; 29-902[h]
Isoproturon	C$_{12}$H$_{18}$N$_2$O	0.0033[f]	55[f], 65[d]	protonation not relevant[d]	15[e], 6.5-30[i]	48[i]; 130[k]

a.) GROVER, 1988
b.) USDA-ARS
c.) LEONARD et al., 1987
d.) TUXEN et al., 2000
e.) JOHNSON et al., 2000
f.) DR. EHRENSTORFER, 1997
g.) KAUNE et al., 1998
h.) HORNSBY et al., 1996
i.) WALKER et al., 2001
j.) WAUCHOPE et al., 2002
k.) RAO & DAVIDSON, 1980
l.) FLURY et al., 1995

Adsorption and desorption of organic molecules in soils is controlled by the chemical properties of the molecules and the surface properties of the soil material. The most important soil components for adsorption of herbicides are clay minerals and organic matter (MC BRIDE, 1994). Clay minerals have large negatively charged surfaces with a high density of hydroxyl groups and exchange ions. Internal surfaces of the phyllosilicates can become accessible for molecules of suitable size (GROVER, 1988). Even more important for the adsorption of pesticides is the organic material in the soil. It consists of aromatic polymers with carboxyl or hydroxyl functional groups and has a more hydrophobic character than clay minerals. As clay minerals, organic matter may have considerable surfaces (MC BRIDE, 1994).

Both, clay minerals and organic matter, have the potential to adsorb organic molecules by various mechanisms, e.g, ion exchange, hydrogen bondings, or hydrophobic interaction (GROVER, 1988). Ion exchange can be significant for triazines that are weak bases and may bind a hydrogen atom to form cations in acidic water. Maximum adsorption occurs if the pH of the soil solution is close to the conjugate pK$_a$ of the cationic form (14-pK$_b$, Tab. 1, HORNSBY et al., 1996).

The conjugate pK_a of triazines varies from 1.62 for simazine to more than 4 (Terbutryn). Although these values are low compared to the pH of most soil solutions, clay minerals can be strong proton donators so that ion exchange may locally become an important process (GROVER, 1988). Hydrogen bonds appear when a hydrogen covalently bound to an electronegative atom (like N) is electrostatically attracted by another electronegative atom to form a bridge. Triazines and Ureas contain groups that have the potential to form the low energy hydrogen bonds. In many soils, though, hydrophobic interaction is by far the most important mechanism governing the adsorption not only of molecular but also of ionized pesticides (MARTINS, 1988). Site specific parameters that may influence the adsorption of herbicides are mainly the soil structure and texture, the aeration, the water content, and the temperature (MARTINS, 1988).

Because of their relatively low solubility in water, pesticides are predominantly adsorbed at low concentrations. The different adsorption mechanisms cannot be determined separately; sorption is therefore illustrated by isotherms that describe the relation between the concentration in solution and the corresponding adsorbed concentration without differentiating the mechanisms.

Pesticides may be chemically or microbially degraded, either in the liquid or in the solid phase. An important process for triazine and urea degradation is dealkylation, where methyl or other alkyl groups are biologically removed from a nitrogen atom (GROVER, 1988). Hydrolysis is the cleavage of molecules by water and may be considered as a chemical or biological degradation process. The persistence of pesticides in a soil is usually expressed in terms of half-life, $T_{1/2}$, the length of time required for one half of the original quantity to break down. As microbial degradation depends on many soil specific and biological parameters (e.g., oxygen content, density of microorganisms), the half-life values found in the literature vary significantly (Tab. 1) and degradation rates should be determined experimentally for each soil.

3.   Experimental Transport Studies

Experiments to elucidate the fate of pesticides in soils are conducted at different scales. Physical and chemical properties of the agrochemicals are usually tested in the laboratory, i.e., the distribution coefficient and the degradation constant are determined in batch experiments. Laboratory transport studies use soil columns of different sizes. An ever increasing number of field experiments involving pesticide transport have been carried out since the 1970s that use different sampling techniques. In many field studies, pesticides moved deeper into the soil than expected based on laboratory measurements, indicating that results obtained in the laboratory may not always be applied to field situations (FLURY, 1996). Spatial variability and preferential flow phenomena have been hypothesized to be responsible for the inconsistencies between many laboratory and field studies (JURY & FLÜHLER, 1992).

3.1.   Experimental Techniques and Results

The sampling method used in a local transport experiment may influence the interpretation of the results; none of the existing methods is ideal for solute sampling in natural media and the choice of a specific instrument has to be based on the research goal.

Agricultural fields that contain subsurface drains are frequently used for field transport studies (KLADIVKO et al., 1991; TRAUB-EBERHARD et al., 1994; LARSSON et al., 1999; ZEHE, 1999). The collection of water from drains is relatively easy and the sampling is non-destructive.

KLADIVKO et al. (1991) observed leaching of pesticides through a silt loam with low organic matter content under typical agricultural management practices. They found high concentrations in the drains during the spring following the application, while only isolated traces were found in later periods. In a similar field experiment, TRAUB-EBERHARD et al. (1994) observed a breakthrough of herbicides in a loamy silt soil with the first drainflow only two days after the application. In both studies the transport was found to be event driven with high concentrations appearing after heavy precipitations. The concentration of different pesticides in the drainflow followed the rank-order of their distribution coefficients, but all substances were detected at the same time. The authors concluded that only a small fraction of the pore volume was active in the rapid transport and that non-equilibrium adsorption occurred in the flow pathways. Moreover, TRAUB-EBERHARD et al. (1994) compared the leaching after a spring and an autumn application and concluded that considerably higher concentrations reached the drains after autumn application because of the higher drainflow and reduced evaporation during winter. LARSSON et al. (1999) examined the leaching to tile drains of the non-reactive tracer bromide in a water repellent sandy soil. They simulated the observed data and found good agreement when employing a two-region preferential flow model. Also from a tile drain experiment, ZEHE (1999) reported flow velocities that were 10^3 to 10^4 times higher than expected for the loamy soil matrix; here again, the high velocity was attributed to preferential flow phenomena. A disadvantage of tile drains in transport experiments is that the soil has to be disrupted when the drains are installed and that the sampling is sensitive to seasonal variations of the water table (RICHARD & STEENHUIS, 1988). Tile drains contain representative samples of the cumulative loss of a chemical through leaching on a field scale; they can however not reveal local concentration differences or spatial variability of the concentration.

Many studies use soil cores to analyse the concentration distribution of chemicals along a profile (BUTTERS et al., 2000). Soil samples provide well-defined concentrations at a given time, but as sampling is destructive no further measurements can be realised at the same location. Additionally, holes created by the cores have to be refilled to prevent artificially accelerated flow. A further problem is that soil cores are likely to miss the leading edge of chemicals in a transport experiment and thus may not be representative. Consequently, soil sampling often serves as a complementary analysis together with other techniques like tile drains (LARSSON et al., 1999) or dye tracing experiments (GHODRATI & JURY, 1990; FLURY et al., 1995).

Dye tracing techniques allow to visualize the water flow paths and can thereby reveal heterogeneous flow patterns. Preferential flow through blocky soils and earthworm burrows has often been demonstrated using dye tracing (FLURY et al., 1998). Notwithstanding, the technique is destructive because a pit must be dug, and it does not supply any information about solute concentrations or transport velocities. When coupled with soil sampling, on the other hand, dye tracing experiments may give more precise informations. FLURY at al. (1995) applied a dye tracer and herbicides to a structured loamy soil and an unstructured sandy soil; soil samples were taken at the stained flow paths only. They found that different herbicides moved equally deep into the soil profile of the structured loamy soil, while the chemicals hardly penetrated into the unstructured sandy soil. These results are in contradiction to the study of LARSSON et al. (1999), who did a dye tracing experiment and soil sample analyses in a sandy soil. The dye tracer clearly indicated the existence of preferential flow pathways and the soil samples proved that accelerated flow generated a lateral redistribution of bromide near the surface of the sandy soil soon after application. The same was reported by GHODRATI & JURY (1990) who analysed the transport of a dye tracer in a loamy sand. They found irregular flow patterns even if the soil profile was not visibly heterogeneous.

The use of ceramic suction cups to sample the soil solution is a non-destructive method allowing to sample concentration profiles in a soil at nearly any time. Initial soil disruption is less drastic than for tile drains (FLURY et al., 1998). Suction cups integrate the pesticide concentration in their sphere of influence at the depth they are placed. Thus, installing numerous suction cups at different depths allows for a rough estimation of the concentration's spatial distribution. Temporal concentration differences will be easier and better displayed than with soil cores. A disadvantage of suction cups is that a good contact of the ceramic with the soil pores has to be assured and that the sphere of influence is generally unknown. CLOSE et al. (1998) installed several suction cups at different depths in a silt loam and a fine sandy loam. In the silt loam, they observed higher concentrations in suction cups at greater depth than at shallow depth early after application. In the sandy loam a quick pulse of pesticides appeared at 40 cm quickly after the application, while the main chemical peak arrived only later. The depths specific measurement of the chemical concentration allowed for the conclusion that preferential flow occurred at both sites.

3.2.   Factors affecting Pesticide Leaching

From the cited experiments it follows that a comparison of different field studies is difficult because the experimental conditions such as sampling procedures, soil type, and amount and timing of rainfall or irrigation vary. Nevertheless, some general factors affecting pesticide leaching can be pointed out.

The effect of surface preparation on the leaching of chemicals has been investigated by several authors. GHODRATI & JURY (1990) found enhanced leaching in a structureless loamy sand when the surface was disturbed with a trencher prior to the chemical application. PETERSEN et al. (2001), on the other hand, found that ploughing the surface of a structured sandy loam soil decreased leaching of the dye. It is likely that leaching through preferential flow pathways is more pronounced with no-tillage since the soil structure (e.g., root channels or earthworm burrows) is conserved (FLURY et al., 1994). In unstructured or coarse textured soils, however, it can be expected that surface preparation has less influence on pesticide leaching.

The initial water content is another factor affecting pesticide leaching. RAO et al. (1974) suggested that pesticides applied to a dry aggregated soil were transported into the aggregates by the first rainfall event following the application. Adsorption within the aggregates could then limit the leaching. ISENSEE & SADEGHI (1994), however, observed enhanced leaching of pesticides applied to a dry macroporous soil after high intensity rainfall. BROWN et al. (1995) explained limited pesticide leaching through a wet clay by reduced macropore flow in the wet soil. FLURY et al. (1995) observed leaching to greater depth in an initially wet loamy soil, while LARSSON et al. (1999) predicted a high risk for leaching through accelerated flow pathways in an initially dry sandy soil. In conclusion, the effect of the initial water content on pesticide leaching seems to depend on the soil structure.

Irrigation techniques can have an effect on solute transport in soils. In dye tracer experiments FLURY et al. (1994) and GHODRATI & JURY (1990) found much faster water flow under ponded irrigation than under sprinkler irrigation. Similarly, TROIANO et al. (1993) observed increased leaching of atrazine under ponded irrigation compared to sprinkler irrigation in an unstructured sandy soil. They concluded that during sprinkler irrigation more water evaporates compared to ponded irrigation and, consequently, less water is available for deep percolation. Yet, the results

obtained from irrigation studies are not consistent. Nevertheless, it can be expected that the effect of irrigation becomes more pronounced as the soil structure increases (FLURY, 1996).

The time of pesticide application together with the time of subsequent rainfall are important factors for pesticide leaching. EDWARDS et al. (1993) suggested that the mass of pesticides leached is inversely proportional to the time elapsed before the first strong rainfall event. FLURY (1996) supposed that since adsorption of pesticides is a rate limited process, leaching is largest when heavy rainfall occurs shortly after application of the chemicals; longer periods between the application and a rainfall event will result in less leaching.

Obviously, the soil type and structure are very important factors for pesticide leaching. FLURY et al. (1994) studied the flow characteristics of different soils after application of a dye tracer. The soils varied from structureless to strong in grade and from fine granular to very coarse in type. In most soils, water bypassed a portion of the soil matrix, but the extend of the bypassing differed. Generally, the dye penetrated deeper into structured than into non structured soils; two extreme flow patterns emerged: a structured silty loam, with several cracks and earthworm channels where the infiltrating solution bypassed the soil matrix and reached the subsoil, and a structureless sandy soil, where the dye penetration was confined to the top 10-20 cm and the stained pattern was relatively homogeneous. This is not consistent with the findings by GHODRATI & JURY (1990) and LARSSON et al. (1999) described above. Moreover, JARVIS & MESSING (1995) also report evidence for accelerated flow in sandy soils. In conclusion, structured soils are clearly susceptible to pesticide leaching, while information about leaching in unstructured soils is contradictory.

3.3.   Non-Equilibrium Flow and Transport

In the above mentioned studies, chemicals often moved deeper into the soil than expected. Researchers generally explained this by "preferential flow" where the solutes are transported through only a small portion of the soil volume. Though, the term "preferential flow" is not used in a consistent manner, and its meaning can change from one study to another (FLURY, 1996).

For SIMUNEK et al. (2003), preferential flow is opposed to uniform flow and results in irregular wetting of the soil profile as a direct consequence of water moving faster in certain parts of the soil than in others. HENDRICKX & FLURY (2001) described preferential flow as a phenomenon where water and solutes move along certain pathways, while bypassing a fraction of the porous matrix. According to JARVIS (1998), preferential flow implies that for various reasons, infiltrating water does not have the time to equilibrate with the slowly moving resident water of the soil matrix. The author suggests that such physical non-equilibrium can occur in virtually all types of soils and may result in similar consequences for the solute leaching although the underlying mechanisms can be different. Consequently, in the present study we will refer to non-equilibrium flow and transport rather than to preferential flow.

The probably most obvious mechanism for non-equilibrium flow and transport is the migration of water and solutes through large channels (macropores). Macropore flow is the process by which infiltrating water rapidly moves downwards within structural pore spaces such as shrinkage cracks, worm channels, and root holes. Macropores can also form by weathering, e.g., freeze-thaw cycles (WHITE, 1985). Because there is no sharp break in the size distribution of pores in soils, the choice of a lower size limit for macropores is arbitrary. BEVEN & GERMANN (1982) defined macropores as pores ranging from 30 to 3000 mm in diameter. Even if macro-

pores comprise only a small fraction of the total soil volume (0.001-0.05; WHITE, 1985), they can have a profound effect on the rate of infiltration and redistribution of water and solutes. In an attempt to find a functional definition of macroporosity based on transport characteristics or hydraulic conductivity, SKOPP (1981) distinguished macropores and matrix pores: macropores provide flow paths so that mixing with the remaining pores is limited, while matrix pores transmit water and solute at a slow rate so that mixing and transfer of molecules between pores is possible. Other authors demonstrated the existence of macropore systems in soils by fitting bimodal or multi-modal hydraulic functions to measurements of water retention and/or soil hydraulic conductivity (WILSON, 1992; JARVIS & MESSING, 1995). Accelerated flow and transport in structured media can be described using dual-permeability models (SIMUNEK et al., 2003) in which the soil is divided into domains of larger pores and finer matrix pores. Advective flow is assumed to take place in both, the rapidly conducting macropores and the slowly conducting matrix pores (VANDERBORGHT et al., 1997; SIMUNEK et al., 2003).

When pesticides move deeper than expected into unstructured soils (without visible macropores), accelerated flow is attributed to a flow through only a small portion of the soil volume. GHODRATI & JURY (1990) explained non-equilibrium flow in a sandy loam by channeling of water through soil regions with higher than average permeability. According to FLURY et al. (1998), physical non-equilibrium may occur in many field soils and may be caused by water repellency and spatial variability. LARSSON et al. (1999) noted non-equilibrium flow and transport within the matrix of a sandy soil and proposed air pressure built up ahead of a wetting front, water repellency, or spatial variation in the soil texture as possible mechanisms. Accelerated transport in the matrix of coarser-textured field soils and in aggregated media is often simulated using the mobile-immobile water concept (JARVIS, 1998; VANDERBORGHT et al., 1997). In this concept (MIM: Mobile-Immobile Model, see Ch. 2, 2.3) proposed by VAN GENUCHTEN & WIERENGA (1976), soils are described as a formation of slowly and rapidly conducting pore sequences. In the aggregates containing slowly conducting pores (immobile region) solute displacement is dependent upon diffusion, while in pores that contain mobile water advective movement is assumed. The exchange of solutes between the two regions is described as a first order kinetic diffusion process. Thus, an early breakthrough of chemicals is explained by the fast transport in the pores between the aggregates, and tailing is a result of the chemical's diffusion into and out of the aggregates (VANDERBORGHT et al., 1997). BUTTERS et al. (2000) fitted the MIM successfully to observed field data. VANCLOOSTER et al. (1993) found that in undisturbed sandy soil columns the two-region model fitted well the observed breakthrough curves, while the conventional convection-dispersion equation failed to describe the solute transport. Further models and statistical techniques to describe the fate of pesticides in a two-region soil have been developed (HANTUSH et al., 2002); they show that lateral diffusive mass tranfer into immobile-water regions and advection relative to dispersion in the mobile-water region can affect significantly the leaching and degradation of organic chemicals.

3.4.   Colloid Associated Transport

The hydrochemical significance of pesticide transport with colloidal-size particles has been realized in field and laboratory studies that showed faster contaminant migration over large distances and at higher concentrations than model predictions suggest (PULS & BARCELONA, 1996). Colloids susceptible to transport pesticides are suspended clay particles, inorganic precipitates (iron or aluminium oxides), and natural organic matter (humic acids and other organic macromolecules). BACKHUS et al. (1993) defined mobile colloids to be in the size range of 0.1-1 μm. In order to remain mobile, colloid particles have to resist coagulation or flocculation. The

surface properties of the colloid particle, its size, the ionic strength of the solution, and the porosity of the matrix material play a major role for the co-transport of pesticides.

BACKHUS et al. (1993) used turbidity measurements to quantify the colloid content of groundwater as a function of the pumping rate. They found that the concentration of organic pollutants increased with increasing turbidity (and thus increasing colloid content) at high pumping rates. SETA & KARATHANASIS (1997) found that the presence of smectite and organic carbon enhanced atrazine transport through soil columns, while kaolinite particles were too large with a relatively small surface to contribute to the atrazine transport. Interestingly, they found that the co-transport with colloids was not the only possible mechanism for enhanced atrazine leaching. The presence of colloids could also accelerate the transport of dissolved atrazine. Colloid particles may block adsorption sites in the soil matrix that would otherwise be available for the adsorption and retention of the pesticides. This blocking mechanism can be either physical, if colloids plug micropore entries, or chemical, if cations associated with the colloids are preferentially adsorbed reducing the available surface charge of the soil matrix. In a tile drain experiment, ZEHE (1999) observed isoproturon concentrations exceeding the solubility product. He concluded that at least part of the isoproturon was transported adsorbed to clay particles and humic substances. Consequently, he suggested that using agrochemicals with high sorption coefficients might not always guarantee their retention in the upper soil layers, but rather contribute to a rapid transport and thus to groundwater contamination.

In conclusion, colloidal particles may act as highly mobile contaminant carriers and contribute significantly to the contamination of groundwater.

4.   Pesticide Monitoring Studies

4.1.   Pesticide Contamination of Groundwaters

In the early 1980s, isolated traces of pesticides detected in the groundwater attracted public attention. As a consequence, the EU established the drinking water limit of 0.1 µg l^{-1} for individual substances as a tolerable concentration and several pesticides have since been banned in a number of countries (ISENBECK-SCHROETER et al., 1997).

Whereas in some cases accidental spills, industrial usage, or inappropriate disposal are responsible for groundwater contamination, most of the pesticides in groundwater result from agricultural use with subsequent leaching through soils. In order to evaluate the pesticide content in groundwater systems, many national and federal agencies have initiated monitoring programs.

A comparison of the studies is difficult because of differences in the monitoring programs. Nevertheless, a summary of pesticide monitoring studies in different european countries shows that atrazine is the most abundant herbicide found in the groundwater (Tab. 2, ISENBECK-SCHROETER et al., 1997). In Great Britain, atrazine was found more often in 1994 than in 1993, when the maize cultivation was increased in southwest England. In Denmark, atrazine was the most commonly found herbicide between 1989 and 1994.

Table 2: Summary of pesticide monitoring studies in different european countries in the 1990s
(according to ISENBECK-SCHROETER et al., 1997)

Country	Aquifer Types	Agricultural Land Use [km^2]	Mean Precipitation [mm y^{-1}]	Herbicide Use [t y^{-1}][a]	% of Samples > 0.1 μg l^{-1} (Total Number of Samples)	
Dk	moraines and glacial outwash	28 442	400-800	3 400	Atrazine Isoproturon Simazine Diuron Terbutylazine	1.19 (586) 0.45 (447) 0.38 (523) 0 (81) 0 (488)
D	diverse	125 002	500-2000	14 800	Atrazine Isoproturon Simazine Diuron Terbutylazine	4.7 (2200) 0.3 (2200) 0.6 (2200) 0.9 (2200) 0.3 (2200)
F	diverse	330 000	600-840[b]	30 000	Atrazine Isoproturon Simazine Diuron Terbutylazine	0.22 (180) 0.02 (180) 0.01 (180) 0 (180) 0 (180)
UK	chalk/karst	72 000[c]	1000	19 500	Atrazine Isoproturon Simazine Diuron	12 (600) 2.8 (170) 1.8 (600) 3.9 (30)

a.Mass of active ingredients in herbicides sold per year. Values from different years in the 1990s.
b.from http://www.eventsworldwide.com/c-france.htm
c.from http://www.icid.org/v_uk.pdf

In Germany, atrazine is prohibited since 1991 (HÄFNER, 1994); nevertheless, it was still present in the groundwater according to a monitoring study performed in 1996 indicating that the groundwater system reacts very slowly to outward circumstances. Atrazine even exceeded 0.1 μg l^{-1} in 2.85 % of the samples taken from drinking water in 1995 (ISENBECK-SCHROETER et al., 1997). According to the same authors, the hydrogeological context is one of the most important regional characteristics for the groundwater contamination by herbicides. Consequently, in Great Britain with its extremely vulnerable chalk aquifers, high herbicide concentrations were measured in many samples. Moreover, a monitoring study in the Netherlands has shown a close relationship between pesticide detection and the distance of the groundwater from the soil surface with higher concentrations occurring in shallow aquifers. In France, the most pronounced pesticide findings were limited to unconfined aquifers with shallow groundwater tables (ISEN-BECK-SCHROETER et al., 1997).

In the USA, herbicides were the largest category of pesticides sold in 1982 with a total mass of 162 000 t of active ingredient (RITTER, 1990); atrazine and alachlor were most commonly used. As a consequence, atrazine was more widely detected in the groundwater than any other herbicide. A maximum atrazine concentration of 88 μg l^{-1} was measured in Nebraska in 1980. Peak concentrations appeared at the end of the irrigation season in shallow wells. In an agricultural watershed in Virginia, atrazine had the highest mean concentration (0.46 μg l^{-1}) of 20 pesticides analysed in 129 samples (RITTER, 1990). In a similar study in Pennsylvania, atrazine was detected in 14 out of 20 wells at concentrations ranging from 0.013 to 1.1 μg l^{-1}, while simazine

was found in 35% of the wells at concentrations between 0.01 and 1.7 µg l^{-1} (RITTER, 1990). In Iowa, pesticides were present as well in karst areas and carbonate aquifers as in alluvial and Pleistocene aquifers. Eight chemicals were detected in the groundwater of 31 counties, although many of the sampled wells served for public water supply. While most of the contaminations appear under normal agricultural use, extremely high concentrations were found in the vicinity of farm chemical suppliers (RITTER, 1990). According to the review of RITTER (1990), field conditions susceptible for groundwater contamination by pesticides are unconfined aquifers below a porous soil and a total groundwater recharge exceeding 250 mm y^{-1}.

DOMGALSKI & DUBROVSKY (1992) found simazine in the eastern part of the San Joaquin Valley (Central California) where it was intensively used, but not in areas with a deep groundwater table. Atrazine was found in some of the same locations as simazine, but its distribution rather corresponded to the use for weed control on roadways. Diuron contaminations were restricted to areas of high agricultural use. The leaching was attributable to a combination of coarse-grained soils with low total organic carbon and shallow groundwater depth (< 30 m). Finally, the authors stated that the most vulnerable areas in the San Joaquin Valley were alluvial fans, deltas, and sand dunes.

In conclusion, herbicides are increasingly present in american and european groundwaters even under normal agricultural use. Atrazine was still the most commonly detected herbicide; its concentrations exceeded by far the drinking water limit. Characteristics that influence the vulnerability of aquifers for pesticide contamination are primarily the soil properties, the depth of the groundwater table, and the climatic conditions.

4.2.   Characteristics and Limits of Monitoring Studies

A comparison of pesticide monitoring studies is difficult, because of different data qualities, monitoring strategies, and interpretation methods. The reliability of a study depends to a great extent on the sampling method and the laboratory analysis. A groundwater sample has to be representative of the aquifer, care has to be taken not to contaminate the groundwater samples by unclean sampling devices, and the water has to be stored correctly until it is analysed. National directions for groundwater sampling procedures exist, e.g., the USEPA's detailed "Ground Water Issue" (PULS & BARCELONA 1996), Germany's "Entnahme und Untersuchungsumfang von Grundwasserproben" (DVWK, 1992), or are in progress, e.g., in Switzerland, where a working group is developing practical guidelines for groundwater sampling and measurement (http://www.ssh.ethz.ch/english/groups/sampling.html). Research about correct sampling of groundwater is going on (BACKHUS et al., 1993; CREASY & FLEGAL, 1999). The analysis of pesticide concentrations also yields a high risk of false positive findings due to analytical interferences with other organic substances. Analyses therefore have to be checked according to plausibility criteria (HÄFNER, 1994). Varying monitoring strategies can effect the results significantly. Sampling sites may be randomly or systematically chosen and the number of sampling locations and the sampling frequency influences the study's outcome. Only a restricted number of different substances can be analysed and their choice may influence whether a groundwater sample is considered contaminated or not. For example, in a groundwater study in South Jutland samples were analysed for 18 different pesticides and one or more substances were found in 75 % of the wells. With the national monitoring program that confines itself to only 8 different substances, positive results would have been found in only 15 % of the wells (ISENBECK-SCHROETER et al., 1997). Finally, the data of monitoring studies are summarized in various ways: statistical overviews, regional descriptions, or development over time. The interpretation may or not correlate

the groundwater contamination to various factors, such as climatic, geological, and morphological features.

5.   Conclusion

The results of experimental transport studies in the unsaturated zone are strongly influenced by the sampling method and sampling intensity. In most experiments spatial variability cannot be detected or quantified. The parameters are site specific and variable in time and space, and consequently, the results of an experiment can hardly be transferred to other sites or circumstances. Nevertheless, some general factors can be defined that influence the transport of pesticides through soils, especially the soil type and structure, the pesticide properties, the climatic conditions, the initial water content of the soil, and the surface preparation.

Pesticide observation studies vary in their monitoring strategies, the data quality, and the interpretation methods and are therefore difficult to compare. Reliable studies should be based on reproducible sampling methods and analytical procedures, they should have a comprehensive monitoring strategy, a precise target, and a transparent interpretation.

Chapter 2

Mathematical Description of Water and Solute Transfer

The movement of water as well as the transport of chemicals in a soil are generally quantified using some fundamental physical and chemical equations. Assuming that the processes are free of random variations, these equations lead to a unique result (mechanistic-deterministic approach, see Ch. 5, 1.1). In this chapter, the flow and transport equations used in the present study are briefly described.

1.   Variably Saturated Water Flow

1.1.   Flow Equation

Water flow in a variably saturated porous medium is described by the Richard's equation, a combination of Darcy's law and the continuity equation. For one-dimensional, vertical flow it is written as:

$$\frac{\partial \theta}{\partial t} - R(z, t) = \frac{\partial}{\partial z}\left(K(h)\frac{\partial H}{\partial z}\right) \tag{2.1}$$

where θ is the volumetric water content $[L^3 \, L^{-3}]$
    t is the time $[T]$
    z is the depth in the soil profile (positive downwards) $[L]$
    $R(z,t)$ represents soil water uptake by plants $[T^{-1}]$
    $K(h)$ is the unsaturated hydraulic conductivity function $[L \, T^{-1}]$
    H is the hydraulic head $[L]$ defined as

$$H = h - z \tag{2.2}$$

    h is the soil water pressure head $[L]$

1.2.   Unsaturated Soil Hydraulic Properties

Equation 2.1 contains two interdependent state variables, the soil water content, θ, and the pressure head, h. Their relation is described by the highly non-linear soil water retention function, $\theta(h)$. The hydraulic conductivity depends on the pressure head as described by the hydraulic conductivity function, $K(h)$. Various parametric forms have been proposed to describe the soil water retention function and the hydraulic conductivity function. The soil water retention function proposed by VAN GENUCHTEN (1980) is one of the most popular (VANCLOOSTER et al., 2000a):

$$S_e = [1 + |\alpha h|^n]^{-m}$$
(2.3)

with
$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

where S_e is the effective water content [-]

θ_r and θ_s are the residual and saturated volumetric water contents, respectively $[L^3 L^{-3}]$

n [-] and α $[L^{-1}]$ are independent empirical parameters

$m = 1 - n^{-1}$ $n > 1$

VAN GENUCHTEN (1980) used the statistical pore size distribution model of MUALEM (1976) to obtain the equation for the unsaturated hydraulic conductivity function:

$$K(h) = K_s S_e^l \left[1 - \left(1 - S_e^{\frac{1}{m}} \right)^m \right]^2$$
(2.4)

where K_s is the saturated hydraulic conductivity and l is a parameter describing the pore connectivity [-], estimated to be 0.5 as an average for many soils (MUALEM, 1976).

2.   Solute Transport

2.1.   Adsorption and Degradation

When chemical equilibrium is assumed between the solid phase and the solution, the Freundlich Isotherm may be used (VAN GENUCHTEN & WIERENGA, 1976):

$$S = KC^N$$
(2.5)

where S is the adsorbed concentration $[M\ M^{-1}]$

C is the solute concentration and $[M\ L^{-3}]$

$K\ [L^3\ M^{-1}]^N$ and N [-] are constants

For pesticides, a reversible linear adsorption is commonly assumed in which case N = 1 and equation 2.5 reduces to:

$$K_d = \frac{S}{C}$$
(2.6)

The distribution coefficient, K_d [L^3 M^{-1}], describes the linear division of a chemical between the liquid and the solid phase. A linear correlation between the organic carbon content of the soil and the K_d value is sometimes observed. In these cases, the K_d of the chemical may be calculated from the soil organic carbon sorption coefficient, K_{oc} [L^3 M^{-1}] (WAUCHOPE et al., 2002):

$$K_d = f_{oc} K_{oc} \tag{2.7}$$

where f_{oc} is the organic carbon fraction of the soil [M M^{-1}]

When the pesticides interact with the solid phase, their transport is retarded. For linear adsorption, the retardation is proportional to the extend of adsorption and is described by the retardation factor, R [-]:

$$R = 1 + \rho \frac{K_d}{\theta} \tag{2.8}$$

where ρ is the bulk density of the soil [M L^{-3}]

Microbial and chemical degradation of an organic substance in a soil are generally grouped and described by a first order degradation law:

$$C = e^{-\lambda t} C_0 \tag{2.9}$$

where C_0 is the initial solute concentration of the chemical [M L^{-3}]
     λ is the first oder degradation constant [T^{-1}]

The half life, $T_{1/2}$ [T], of a chemical is defined as the time needed to degrade half of its initial concentration. It is given by:

$$T_{1/2} = \frac{\ln 2}{\lambda} \tag{2.10}$$

2.2.   Convection-Dispersion Equation

Displacement of solutes is generally described by the convection-dispersion equation (CDE). For one-dimensional vertical transfer in a variably saturated medium where neither adsorption nor degradation occurs it is written as:

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial \nu \theta C}{\partial z} \tag{2.11}$$

where C is the solute concentration [M L^{-3}]

      D is the hydrodynamic dispersion coefficient [L^2 T^{-1}]

      ν is the average pore water velocity [L T^{-1}] with $\nu = q/\theta$, q being the water flux [L T^{-1}]

Hydrodynamic dispersion describes the scattering or spreading of particles which is composed of diffusion and dispersion. In stagnant water, a concentration front tends to diffuse because of the Brownian motion described by the diffusion coefficient. In flowing water, a concentration front also spreads because the water moves around soil particles of different sizes and surface properties. This spreading is described by the dispersivity, a characteristic property of each medium. In most cases, dispersion is far more important than diffusion.

When adsorption and first order degradation in the liquid phase are accounted for, equation 2.11 becomes:

$$\frac{\partial \rho S}{\partial t} + \frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z} - \nu \theta C\right) - \theta \lambda C \tag{2.12}$$

For conditions of uniform water flow in homogeneous soils (ν and θ are constant in time and space), equation 2.12 reduces to:

$$\frac{\rho}{\theta}\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - \nu\frac{\partial C}{\partial z} - \lambda C \tag{2.13}$$

By combining 2.8 and 2.13, the CDE further reduces to:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - \nu\frac{\partial C}{\partial z} - \lambda C \tag{2.14}$$

Equation 2.14 does not take into account the temperature dependence of the dispersion coefficient, D, of the distribution coefficient, K$_d$, and of the degradation constant, λ. It further assumes that the solutes applied to the soil surface mix completely with the soil water, and hence the dispersion of the solutes, induced by heterogeneous pore water velocities can be described by a Fickian diffusion law (APPELO & POSTMA, 1994).

2.3.   Two-Region Transport Model

The dual-porosity model assumes that the liquid phase is partitioned into a mobile (flowing) and an immobile (stagnant) region (physical non-equilibrium). Advection and dispersion take place in the mobile region, while solute transport in the immobile phase is possible by diffusion only

(MIM-Model, VAN GENUCHTEN & WIERENGA, 1976). For a two-region, dual-porosity type solute transport, equation 2.12 becomes:

$$\frac{\partial}{\partial t}(\theta_m C_m) + \frac{\partial}{\partial t}(\theta_{im} C_{im}) + \frac{\partial}{\partial t}(f\rho S_m) + \frac{\partial}{\partial t}(1-f)\rho S_{im}$$

$$= \frac{\partial}{\partial z}\left(\theta_m D \frac{\partial C_m}{\partial z}\right) - \frac{\partial}{\partial z}(v\,\theta_m C_m) - \theta_m \lambda_m C_m - \theta_{im}\lambda_{im} C_{im}$$

(2.15)

where the subscripts m and im refer to mobile and immobile regions, respectively

$f = \theta_m\,\theta^{-1}$ [-] is equivalent to the fraction of adsorption sites in contact with the mobile liquid

v is the average water velocity in the mobile region, $v = q\,\theta_m^{-1}$

Introducing linear adsorption and assuming uniform water flow in a homogeneous soil leads to:

$$(\theta_m + f\rho K_d)\frac{\partial C_m}{\partial t} + (\theta_{im} + (1-f)\rho K_d)\frac{\partial C_{im}}{\partial t}$$

$$= D\theta_m\left(\frac{\partial^2 C_m}{\partial z^2}\right) - v\theta_m\frac{\partial C_m}{\partial z} - \theta_m\lambda_m C_m - \theta_{im}\lambda_{im} C_{im}$$

(2.16)

Diffusional transfer of solutes between the two water regions is modelled as a first order process; first order degradation is assumed to take place in the immobile region:

$$\theta_{im}\frac{\partial C_{im}}{\partial t} + (1-f)\rho K_d\frac{\partial C_{im}}{\partial t} + \theta_{im}\lambda_{im} C_{im} = \alpha(C_m - C_{im})$$

(2.17)

where α is the mass transfer coefficient [T^{-1}]

Introducing 2.17 into 2.16 finally yields:

$$(\theta_m + f\rho K_d)\frac{\partial C_m}{\partial t} = D\theta_m\left(\frac{\partial^2 C_m}{\partial z^2}\right) - v\theta_m\frac{\partial C_m}{\partial z} - \theta_m\lambda_m C_m - \alpha(C_m - C_{im})$$

(2.18)

Equation 2.18 describes solute transport in a two-region flow system considering adsorption and degradation in both, mobile and immobile regions. It has, however, the same restrictions as equation 2.14.

The above equations are used to analyse laboratory and field experiments and to predict water and solute movement in the vadose zone. Processes like volatilization, photolysis and their kinetics as well as chemical non-equilibrium adsorption are not taken into account. In the present

work, water flow and solute transport will be simulated with the mobile-immobile water concept that seems better adapted to the specific conditions in the study area.

LOCAL FIELD EXPERIMENTS

Chapter 3

Materials and Methods

Based on laboratory experiments, soil has long been assumed to retain organic chemicals, thereby preventing groundwater from being polluted. But the occurrence of pesticides in groundwater made clear that under field conditions chemicals may move down to considerable depths. Whether a chemical reaches the groundwater, depends not only on the water flow, but also on various processes affecting the solute in the vadose zone. In this study, the transport processes of pesticides from the soil surface to the groundwater table were investigated. Experimental field plots were equipped with various instruments installed at different depths. Two herbicides and an inert tracer were applied in two consecutive seasons and the solute movement through the unsaturated zone was studied. The experimental plots are situated in the Rhône River Valley near Martigny. A detailed description of the region is given in Chapter 6.

1. Experimental Setup

1.1. Principle

The transport of chemicals through the unsaturated zone is closely linked to the water movement. The water flow through a porous medium as described by Darcy's law depends on the soil hydraulic conductivity and the hydraulic gradient. While the soil hydraulic conductivity is a function of the volumetric water content, θ (equations 2.3 and 2.4) , the hydraulic charge can directly be calculated from the soil pressure head, h (equation 2.2). Therefore, if the hydraulic conductivity function is known, the simultaneous measurement of the state variables θ and h at different times and depths will allow to quantify the water flow in a soil. In this study, tensiometers and TDR probes (Time Domain Reflectometry) were installed at different depths to quantify the water flow.

The movement of solutes is described by the convection-dispersion equation (CDE). The transport of a non-reactive solute depends on the water flux and on the dispersion coefficient, D (equation 2.11). For pesticides, however, the transport also depends on their adsorption to the soil solid phase and on degradation. In the CDE, adsorption is accounted for by the retardation factor, R, and degradation is generally described by a first order degradation law (equation 2.14). Both parameters are soil dependant and can be estimated from laboratory experiments. Therefore, if pesticides are applied together with an inert tracer, the tracer will unveil the dispersion coefficient, while the difference in the pesticide's movement relative to the tracer will reveal the extent of adsorption and degradation processes. In order to observe the transport of the chemicals, the solute concentration has to be measured at different times and depths. The concentration can either be measured on soil solution samples collected in suction cups or on soil samples obtained from soil cores. In contrast to soil samples, the use of soil water samplers is a non destructive and repeatable method (Ch. 1, 3.1). In this study, only few soil samples were taken; most concentrations were measured in soil solution and GW samples.

1.2.   Site Description

The experimental site consisted of four plots (termed plot 1 to 4) 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 fixed at 10, 20, 40, 60 and 85 cm depth (Fig. 2). Additionally, stainless steel piezometers were installed on the plots 3 and 4. A rain gauge was placed between the plots.
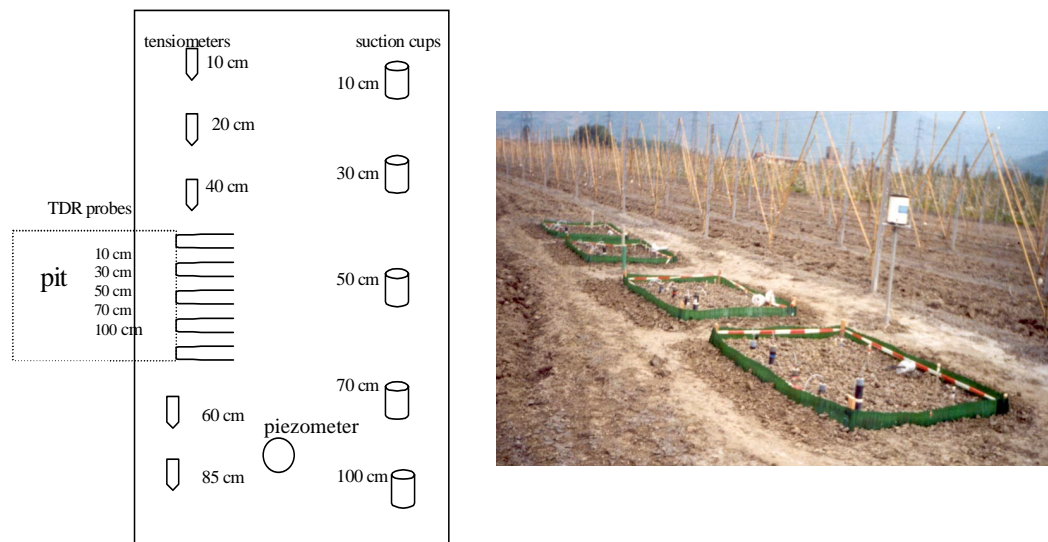

Figure 2: Scheme of one of the plots and view of the experimental site

2.   Soil Properties

The soil of the experimental plots was analysed on disturbed and undisturbed soil samples taken at 10, 30, 50, 70 and 100 cm depth in April 2001 at the occasion of the instrument installation. Basic soil properties such as particle size distribution, organic carbon content, bulk density, and porosity were determined in the laboratory.

2.1.   Soil Profile and Grain Size

The soil profile was determined visually and by tactile evaluation in the field and later by particle size analysis in the laboratory (Appendix 3.1) according to the standard method described e.g. in GEE & BAUDER (1986). The soil was classified according to the USDA system (U.S. DEPARTMENT OF AGRICULTURE) as a silt loam from the surface to a depth of about 0.90 m. Between 0.90 and 1.30 m, the silt and clay contents increase, whereas below 1.30 m a higher percentage of sand is observed (Tab. 3). The limits of these intercalated coarser grained layer are not exactly known, because the samples were taken with a spacing of 20 cm. Below 1.50 m depth, light brown dots indicate the influence of oxidation due to groundwater level changes, and at 2.00 m depth the soil turns into a dark grey coloured silt.

Table 3: Soil profile determined through visual, tactile, and laboratory analysis

Depth	Visible/Tactile	% Clay/Silt/Sand	Classification
0 - 0.90 m	brown silt loam	9/63/27 (mean of 8 samples)	silt loam
0.90 - 1.30 m	brown silt loam	12/76/12 (mean of 4 samples)	silt/silt loam
1.30 - 1.50 m		2/48/50 (mean of 2 samples)	sandy loam
> 1.50 m	light brown dots		
> 2.00 m	dark grey silt (permanently water saturated)		

2.2.   Organic Carbon and Clay Content

The organic carbon content measured on 10 soil samples taken between 0.10 and 1 m depth varied between 5.5 and 12 mg g^{-1}; no tendency with depth could be observed. ZHANG (2003) analysed 55 soil samples taken between 0.15 and 0.85 cm depth at a nearby site and found organic carbon contents between 5.3 and 14.6 mg g^{-1}. Smaller values appeared at lower depths and a slight increase was observed between 0.55 and 0.85 m depth.

Within the upper 0.90 m of the soil profile the clay content varies between 6 and 11 %; between 0.90 and 1.30 m slightly higher values occur varying between 11 and 14 % (Tab. 3). Below 1.30 m the clay content decreases significantly, but a high percentage is observed again from 2.00 m on where the soil becomes finer. Yet, no particle size analysis was carried out at this depth.

2.3.   Density and Porosity

Density and porosity were measured independently on 60 undisturbed soil samples. 3-7 sample replicates were taken at each location (Appendix 3.2). The density was calculated as the mass of dry soil per sample volume, the porosity was measured on the same samples by the pycnometer method (DANIELSON & SUTHERLAND, 1986).

The mean density varies between 1.49 and 1.43 g cm^{-3} and decreases with depth (Tab. 4). Such a trend is unusual in a relatively uniform soil, because the material is supposed to settle at greater depth resulting in a higher density. The mean porosity varies between 0.47 and 0.50 (Tab. 4). The general increase with depth (except for porosity at 1 m) is in agreement with the decreasing density.

Table 4: Density, ρ, and porosity, η, measured on undisturbed soil samples taken at different depths (12-15 samples per depth)

Depth [m]	ρ [g cm^{-3}]	η [cm^{3}cm^{-3}]
0.10	1.49[a] (1.42;1.54)[b]	0.47 (0.45;0.51)
0.30	1.48 (1.40;1.54)	0.48 (0.46;0.53)
0.50	1.47 (1.39;1.50)	0.49 (0.45;0.50)
0.70	1.46 (1.38;1.53)	0.50 (0.47;0.55)
1.00	1.43 (1.33;1.55)	0.49 (0.45;0.54)

a. mean value
b. minimum and maximum values

3.   Field Measurements and Methods

The water movement in the vadose zone was quantified by measuring the soil water content, θ, with TDR probes and the soil water pressure head, h, by means of tensiometers. The chemicals were applied to the soil surface in the spring of two successive years. In order to study the solute transport, groundwater and soil solution samples were repeatedly taken during each summer. The samples were analysed in the EPFL laboratory for their herbicide and tracer contents. In this section, we will describe the methods and discuss their general limits.

3.1.   Water Content Measurement

Time Domain Reflectometry (TDR) is a fast and non-destructive method that allows for repetitive measurement at a specific location. With TDR the water content of a soil is determined through its dielectric number, ε. The dielectric number is related to the volumetric water content, θ, of the soil by an empirical relation (TOPP et al., 1980)

$$\theta = -5.3 \cdot 10^{-2} + 2.92 \cdot 10^{-2} \cdot \varepsilon - 5.5 \cdot 10^{-4} \cdot \varepsilon^2 + 4.3 \cdot 10^{-6} \cdot \varepsilon^3 \qquad (3.1)$$

TDR probes can either be installed vertically in the soil profile or horizontally at a specific depth. When installed vertically, the TDR probe measures the depth integrated water content. Horizontally installed probes, on the other hand, will prospect a region within a small depth interval whose dimensions depend on the rod diameter, spacing, and length. It is commonly accepted that the horizontal orientation should be preferred, when depth specific humidity is to be analysed (NADLER et al., 2002). Yet, the accuracy of the resulting humidity profile will depend on the number of probes one is willing to install.

In this study, two-rod TDR probes were installed horizontally at 10, 30, 50, 70, and 100 cm depth. The length and spacing of the rods was 30 and 4 cm, respectively.

Deviations of the $\theta(\varepsilon)$ relation from the TOPP equation (3.1) are sometimes observed in natural systems and can be attributed to (NADLER et al., 2002)

- the presence of rare clay minerals
- high organic matter contents
- experimental errors stemming from the positioning of the probes (e.g., variations in the spacing of the probes) or formation of a cavity at the rod tips
- variability in texture and non-uniform soil density
- significant temperature fluctuations (WRAITH & OR, 1999)

Time Domain Reflectometry can also be used to determine the relative apparent bulk electrical conductivity of a soil. For low salt concentrations a linear relationship exists between the bulk electrical conductivity and the signal impedance (TOPP et al., 1988). There are conflicting reports about the effect of salinity on the apparent dielectric permittivity and thus on θ. Some studies suggest that a high salinity level of the soil solution results in an overestimation of θ (WYSEURE et al., 1997; DALTON, 1992). Other authors report no significant effect on the accuracy of TDR measured humidity (TOPP et al., 1988; NADLER et al., 1991). Because the soil of the Rhône River Valley is known to be highly saline (Ch. 6, 1.2), the validity of the $\theta(\varepsilon)$ relation was studied by comparing gravimetric water contents to TDR measurements (Fig. 3). Although some deviations are considerable, the slope of the regression line is close to one, indicating that the TOPP relation is valid in principle. The relatively wide spreading (correlation coefficient, $r^2 = 0.7$) is probably due to spatial heterogeneity and measurement inaccuracies.
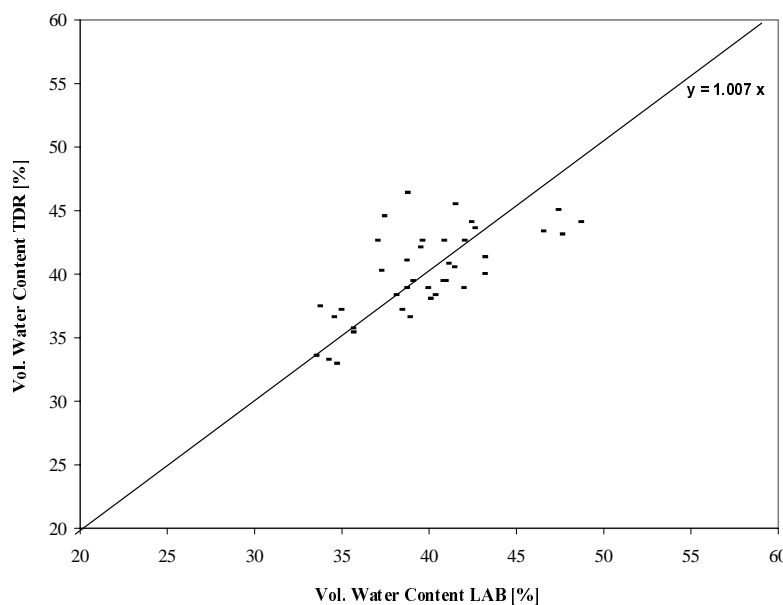
Figure 3: Relationship between volumetric water contents obtained in the laboratory and TDR measurements using the TOPP equation.

3.2.   Soil Water Pressure Head

The pressure head, h, measured with tensiometers reflects the influence of the soil matrix's adsorptive forces and capillary effects on the pore water pressure; it decreases with decreasing water content. The suction, Ψ, is the absolute value of the pressure head.

The tensiometers used in this study had an inner diameter of 18 mm, a ceramic tip length of 54 mm, and a pore diameter of 2.5 μm. The bubbling pressure was 1 bar. The response time of the tensiometers lies in the order of 1 minute (CASSELL & KLUTE, 1986). The instruments were installed at 10, 20, 40, 60, and 85 cm depth. They were inserted into a hole that was refilled with a sludge of soil and water to ensure a good contact between the tip and the soil.

Tensiometers usually allow to measure suctions up to 850 hPa. Problems may occur when the contact between the ceramic tip and the soil is not perfectly established or when air enters the tensiometer making the system unoperational, e.g., if dissolved gases come out of solution as the pressure in the tensiometer is reduced or if the pressure exceeds the bubbling pressure. FAYBISHENKO (2000) found that atmospheric air can even diffuse through the saturated porous tip into the tensiometer tube, if the soil water pressure drops to less than -300 or -400 hPa causing an underestimation of the soil suction. In highly saline soils the ceramic tip may fill with precipitates leading to an increased response time of the system. But according to ALAM & ROGERS (1997) the tip porosity remains satisfactory for several years in most soils. It has to be kept in mind that tensiometers provide punctual measurements of the soil suction. Spatial variability in heterogeneous soils will hardly be detected unless many tensiometers are installed.

3.3.   Soil Solution Sampling

Soil solution samplers (or suction cups) are commonly used for collecting soil solution in transport monitoring studies. A vacuum is applied to the suction cup for a specific period of time before the soil solution is taken out with a syringe. The rate at which the soil solution flows into the sampler depends on the soil properties, the vacuum in the sampler, and the properties of the ceramic tip (its pore size and hydraulic conductivity). In order to collect representative and reproducible soil solution samples, identical initial vacuums and short sampling periods should be used for all instruments at each sampling campaign (HANSEN & HARRIS, 1975). Nevertheless, suction cups are limited to their sphere of influence and spatial variability effects in heterogeneous soils (e.g., non-equilibrium flow) can hardly be detected. Different intake rates and sampling volumes, as well as bypassing processes may influence the composition of soil solution samples (SILKWORTH & GRIGAL, 1981; HANSEN & HARRIS, 1975).

Before installation, the new samplers were cleaned with diluted hydrochloric acid and water to remove chemicals resulting from the manufacture. In order to verify that the organic chemicals do not adsorb to the instrument material, a solution of known concentration was sucked into the sampler and analysed for its herbicide concentration (DVWK, 1990). No adsorption was observed and no chemicals susceptible to interfere with the herbicide analysis were detected.

Once cleaned and tested, the soil water samplers with an inner diameter of 54 mm were installed in tight contact with the soil at depths of 10, 30, 50, 70, and 100 cm: a hole was drilled with a hand auger, a sludge of soil and water was poured into the hole, and the sampler was immediately inserted. The remaining empty volume around the tube was filled with the sludge and the soil was tamped firmly to prevent water from flowing down along the instrument. After the first

year of experiments, the samplers were cleaned again, but none of them was plugged. They were re-installed with a bentonite sealing to avoid flow along the tubing. At each sampling an initial vacuum of 400 hPa was applied and the instruments were allowed to set for 3 to 5 hours, according to the soil water content.

3.4.   Groundwater Sampling

The sampling of the piezometers is described in detail in Chapter 6, 2.2. At the experimental site, the hydraulic conductivity was too low to allow for continuous pumping. Consequently, the water volume in the piezometers was entirely removed twice before the sample was taken. This sampling method is not depth specific and the collected water is an unknown mixture of groundwater between the water table and the lower and of the piezometers (2.5 m). Nevertheless, considering the low depth of the piezometers, the water sample stems from the upper part of the aquifer. The temperature, pH, and electrical conductivity were measured immediately and the sample was stored in a certified clean glass bottle at 4°C (PULS & BARCELONA, 1996) until analysis.

3.5.   Solute Application and Time Schedule

Two herbicides and an inert tracer were applied to the soil surface in the springs 2001 and 2002 at the following formulations and concentrations:

- atrazine as Gesaprim Quick, 0.39 g m^{-2} commercial product (c.p.), 90 % active ingredient (a.i.)
- isoproturon as Graminon IPU, 0.65 ml m^{-2} c.p., 50 % a.i.
- in 2001: Bromide (Merck, pro analysis), 19 g m^{-2}
- in 2002: Iodide (Merck, pro analysis), 15 g m^{-2}

The substances were dissolved in 400 ml of water and applied as an aerosol to the manually tilled soil surface with a hand driven spray bar device (2.5-3 bar pressure). To measure the spatial variability of the application, 5 small plastic trays, each with an area of 0.005 m^2, were placed on the soil surface before spraying. The trays were rinsed with a known volume of distilled water and the samples were analysed for tracer concentration. A uniformity factor was calculated according to

$$CU = 100\left(1 - \frac{\Sigma|c_i - c_m|}{nc_m}\right)$$

(3.2)

where

c_i is the concentration on each of the trays

c_m is the mean concentration on the trays

n is the number of trays, n = 5

In 2001, the application took place on May 11 at 7 a.m. on the four plots; the uniformity factor varied between 80 and 90 %. Plots 3 and 4 were irrigated with 15 mm of water subsequent to the application, while plots 1 and 2 were left under natural climatic conditions. Samples of the

soil solution were taken once a week; at this occasion the soil water content and the pressure head were also measured. The groundwater sampling started 2 weeks after the chemical application and continued once a week.

In 2002, the chemicals were applied on May 24 at 7 a.m., but only on plot 3 and 4; the uniformity factors were 63 % and 74 %, respectively. The reason for the lower uniformity factor compared to 2001 may be a slight wind at the time of the application. In 2002, the plots were not irrigated and the sampling frequency was intensified. The suction cups were sampled approximately twice a week and groundwater samples were collected from the first day on, once or twice a week. The soil water pressure head was measured every day in the late afternoon during May and June.

Before each application, the concentration of atrazine, isoproturon, and the tracer was measured in the soil solution and in soil samples, but only traces of the substances were detected.

3.6.   Chemical Analysis

The water samples from the unsaturated and the saturated zones were analysed in the EPFL laboratory. The herbicide concentration was determined using HPLC with a UV-detector (HEWLETT PACKARD SERIES 1050) and a C18 column of 25 cm length (VYDAC). As suggested by BACKHUS et al. (1993), the samples were not filtered but particles were allowed to sediment. The samples were preconcentrated by Solid Phase Extraction. The solutions were run through a 3 ml C18 cartridge (SUPELCO, USA) at a flow rate of 100 to 200 ml h^{-1} and the organic substances were adsorbed to the solid phase. Subsequently, the herbicides were washed off the dried solid phase using methanol and the resulting sample was further concentrated by evaporating the methanol. The analysis instructions are given in Appendix 3.3. The original volume of the samples was 1 l for groundwater and 10 to 400 ml for soil solution. Consequently, the samples were preconcentrated up to 2500 times according to the original sample volume. The detection limit of the HPLC for the preconcentrated samples was 0.05 mg l^{-1} for atrazine and 0.03 mg l^{-1} for isoproturon; consequently, the final detection limit varied between 2 µg l^{-1} and 20 ng l^{-1}.

Bromide concentrations were determined by ionchromatography in the Pedology laboratory (EPFL). For that purpose, 1-2 ml of water were filtered through a 0.45 µm cellulose filter. Because the salt content was extremely high, most samples were diluted 10 times before injection. Iodide was analysed by HPLC using the chromatographic conditions described by ANDERSSON & FORSMAN (1997).

4.   Characteristics of Atrazine and Isoproturon

Atrazine [$C_8H_{14}Cl\,N_5$] a substance of the triazine group and isoproturon [$C_{12}H_{18}N_2O$], a urea, were applied to the instrumented plots. Basic properties of both herbicides are listed in Tab. 1 (p. 9). Half-life values reported in the literature vary between 13 and 402 days for atrazine and between 6.5 and 30 days for isoproturon. JOHNSON et al. (2000), however, found a degradation potential for isoproturon under aerobic conditions in a Chalk aquifer, but no degradation of atrazine. Furthermore, important spatial variations of degradation rates may appear in a single field (JOHNSON et al., 2000; WALKER et al., 2001). The soil organic carbon sorption coefficient, K_{oc}, of atrazine lies in the range of 38-174 ml g^{-1}, the K_{oc} of isoproturon varies between 48 and

$130 \, ml \, g^{-1}$ (Tab. 1). Some studies, however, suggest that isoproturon may also adsorb to mineral surfaces (TUXEN et al., 2000; JOHNSON et al., 1998) indicating that the K_{oc} could not be used to predict adsorption. Moreover, triazines may adsorb to a greater extend as cations at low pH-values (WAUCHOPE et al., 2002). For these reasons, it is preferable to use degradation rates and adsorption coefficients determined directly on a specific soil rather than literature values.

Adsorption and degradation in soil samples collected near the experimental site have been studied in two research works. ZHANG (2003) determined atrazine sorption and degradation parameters from batch experiments carried out on more than 50 soil samples collected in the vadose zone and in disturbed and undisturbed soil column experiments. She found that up to a concentration of $20 \, mg \, l^{-1}$ batch atrazine adsorption can be described by a linear isotherm with an average distribution coefficient of $0.325 \, l \, kg^{-1}$ (Tab. 5). The distribution coefficient obtained from the column experiments was similar ($0.30 \, l \, kg^{-1}$, Tab. 5). ZHANG (2003) found a great spatial variability of the K_d-values and suggested that representative results could only arise from a large number of samples. The K_d-values correlated well with the soil organic matter content ($r^2 = 0.83$, $K_{oc} = 40 \, l \, kg^{-1}$). CLAUSEN et al. (2002) carried out batch experiments on a few anaerobic soil samples from the saturated zone (2.5-3. m depth). They found a distribution coefficient of $0.65 \, l \, kg^{-1}$ for atrazine and of $1.75 \, l \, kg^{-1}$ for isoproturon (Tab. 5).

Table 5: Distribution coefficients, K_d, and first order degradation constants, λ

Herbicide	$K_d \, [l \, kg^{-1}]$		$\lambda \, [d^{-1}]$	
(Reference)	Batch	Column	Batch	Column
Atrazine (ZHANG, 2003)	0.325 ± 0.14	0.30	0.0027 (0.001; 0.0039)[a]	0.0050 (0.002; 0.0087)
Atrazine (CLAUSEN et al., 2002)	0.65 ± 0.21	-	no degradation observed	-
Isoproturon (CLAUSEN et al., 2002)	1.75 ±0.23	-	no degradation observed	-

a. minimum and maximum values

There are larger differences in the degradation constants of both studies. ZHANG (2003) found first order degradation constants of $0.0027 \, d^{-1}$ and $0.005 \, d^{-1}$ for atrazine in aerobic conditions (Tab. 5); CLAUSEN et al. (2002) did not observe any degradation, neither for atrazine nor for isoproturon in anaerobic environments.

Compared to literature values, the atrazine K_{oc} determined by ZHANG (2003) is relatively low, indicating a weak adsorption capacity. The degradation rates (Tab. 5) lead to atrazine half-lives of 139-257 days which is in the mid-range of the literature values (13-402 days). No degradation of isoproturon was observed in soil samples collected in the saturated zone. Literature values indicate short half-lives (6.5-30 d) for isoproturon in the unsaturated zone (WALKER et al., 2001) and slower degradation in saturated soil samples and groundwater under aerobic conditions (60-1312 d and 55 d, respectively; JOHNSON et al., 1998).

Chapter 4

Results and Discussion

The herbicides atrazine and isoproturon were applied together with an inert tracer in May 2001 and 2002 (Ch. 3, 3.5). After the application the water flow was monitored by measuring the water content and the soil water pressure head; the chemical transport was studied through soil solution and groundwater samples. The results are presented in this chapter. The description focuses on plots 3 and 4 to which the chemicals were applied in both years and where groundwater samples were available. The observations of plot 1 and 2 in 2001 will only be mentioned if they show a deviating behaviour. The results of the mass balance calculation are presented afterwards. Because the observations and the mass balance indicate some unexpected behaviour of the chemicals, a staining experiment was performed, that is discussed in this chapter. Some curiosities of the electrical conductivity in the soil solution are described. Finally, the results are critically discussed.

1.   Water Flow

1.1.   Soil Hydraulic Properties

The water movement in the unsaturated zone depends on two fundamental soil hydraulic properties: the soil water retention function, $h(\theta)$, and the unsaturated hydraulic conductivity function, $K(\theta)$. While $h(\theta)$ was directly estimated from the measured state variables h and θ, the function $K(\theta)$ was assessed using the internal drainage method.

1.1.1.   Soil Water Retention Function

The soil water retention function, $h(\theta)$, describes the relationship between the soil water pressure head and the soil water content. The $h(\theta)$-relation depends on the soil properties and can be subject to hysteresis.

Figure 4 presents the observed data for plot 3 and the fitted soil water retention function using the VAN GENUCHTEN model; the data on plot 4 are similar (Appendix 4.2). The couples of h- and θ-values measured at different depths spread in a relatively wide cloud, even though doubtful measurements were not taken into account. In order to detect changes of the $h(\theta)$ function as a response to structural or textural effects, the points were grouped according to the measurement depth. At 70 and 100 cm the soil water content varies only little (between 0.39 and 0.43) and the small range of the $h(\theta)$ points does not allow to define a reliable retention function. Therefore, no significant differences in the soil water retention could be detected and one single retention function is assumed.
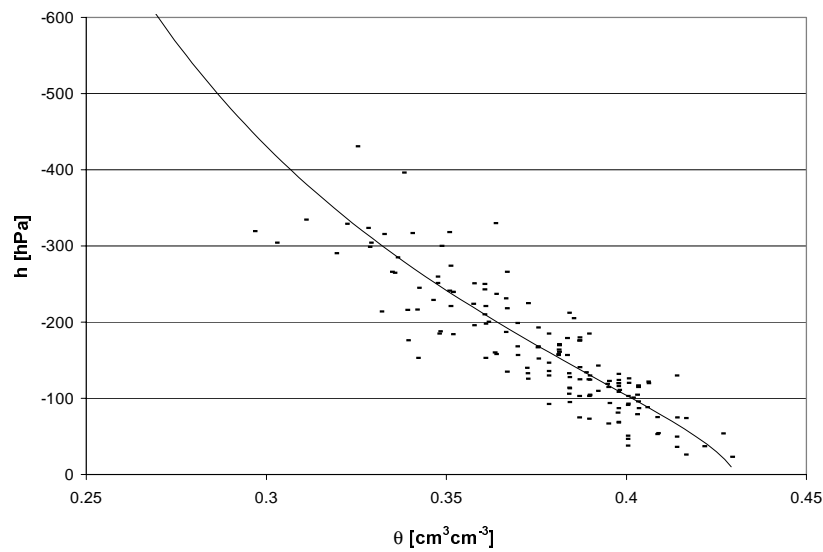
Figure 4: Measured h and θ and fitted retention function using the VAN GENUCHTEN model (plot 3)

In order to detect a possible hysteretic behaviour, the measured h(θ) couples were sorted according to dry and humid periods. On plot 3, the few available h(θ) couples corresponding to wetting cycles lie in the lower part of the data cloud indicating a slight hysteretic behaviour (Fig. 5). On plot 4, on the other hand, no hysteretic effect could be detected. Therefore, a unique soil water retention function was supposed.
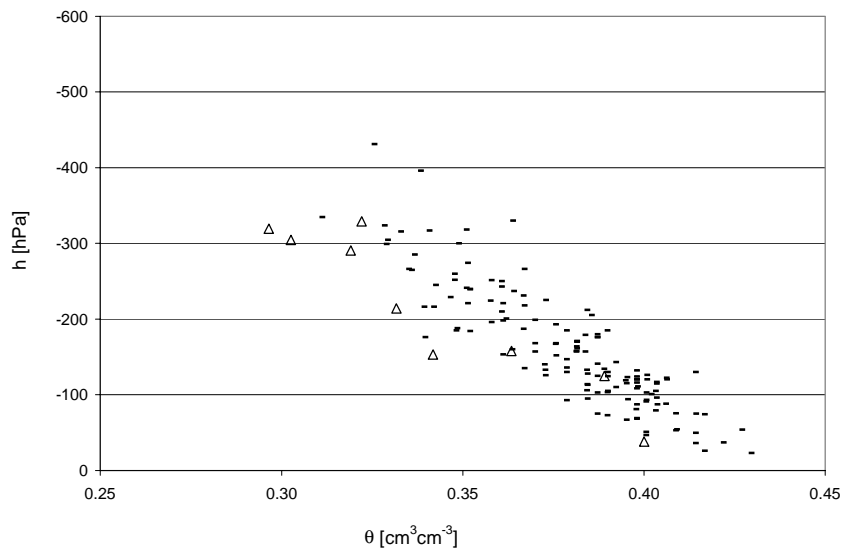
Figure 5: Sorted h(θ) points, drying (dots) and wetting (triangles) cycles (plot 3)

The computer code RETC (VAN GENUCHTEN et al., 1994) allows to analyse the soil water retention and hydraulic conductivity functions of unsaturated soils by adjusting analytical solutions to measured data. The VAN GENUCHTEN model (1980, equation 2.3) of the soil water retention function was fitted to the measured data on the plots 3 (Fig. 4) and 4 (Appendix 4.2).

The residual and saturated water contents, θ_r and θ_s, were set to fixed values, while the parameters α and n were adjusted (Tab. 6).

Table 6: Parameters of the soil water retention function (VAN GENUCHTEN, 1980). α and n were adjusted to the data sets, $m=1-n^{-1}$.

Data Set	θ_r [cm^{3}cm^{-3}]	θ_s [cm^{3}cm^{-3}]	α [cm^{-1}]	n [-]	m [-]
Plot 3	0.07	0.43	0.0042 (0.004-0.005)[a]	1.554 (1.459-1.649)	0.356
Plot 4	0.07	0.42	0.0034 (0.003-0.004)	1.655 (1.457-1.853)	0.396

a. 95% confidence intervals

The ROSETTA code (SCHAAP, 1999) predicts the soil hydraulic properties using a hierarchical set of pedotransfer functions and literature values. The parameters of Tab. 6 correspond to values reported for silty loam soils. Similarly, when using the mean grain size distribution and bulk density values measured on samples between 0.90 and 1.30 m depth (Tab. 3), the pedotransfer functions implemented in ROSETTA lead to similar values as listed in Tab. 6.

In conclusion, the observed soil water retention functions are consistent with the mean soil texture between the surface and 1.30 m depth. No significant change of the retention characteristics with depth could be detected from the h(θ) data.

1.1.2.   Unsaturated Hydraulic Conductivity

The internal drainage method allows to determine the unsaturated hydraulic conductivity function through changes of the state variables θ and h. It consists of flooding a soil surface and observing the water redistribution in the profile (VACHAUD et al., 1978). After the water has infiltrated into the soil, the surface is covered to prevent evaporation. Profiles of the soil water pressure head and the soil water content are measured regularly while the water moves through the unsaturated zone. According to the principle of mass conservation, the changes in water content at the times t and t´ correspond to the volume of water drained from the profile, S_z. The hydraulic gradient at the bottom of the profile, z, can be determined from the pressure head measurements. The unsaturated hydraulic conductivity, K(θ) [L T^{-1}] is then given by Darcy's law as

$$K(\theta) = \frac{dS_z}{dt \cdot \frac{dH}{dz}} \qquad (4.1)$$

where dS_z [L] is the loss of water from the profile during $dt = t - t´$

A more detailed description of the method is given in VACHAUD et al. (1978). Even under natural conditions it is possible to calculate the unsaturated hydraulic conductivity, if a zero flux level appears in two successive hydraulic charge profiles.

A few values of the unsaturated hydraulic conductivity as a function of water content could be deduced from an internal drainage experiment and from natural hydraulic charge profiles. The unsaturated hydraulic conductivity function was adjusted to the field data with the computer code RETC using the equation of VAN GENUCHTEN (1980) based on the statistical pore-size distribution model of MUALEM (1976, equation 2.4). The parameters of the hydraulic conductivity function are θ_r, θ_s, n, the pore connectivity parameter, l, and the saturated hydraulic conductivity, K_s. By using the soil water retention parameters given in Tab. 6 and setting l to 0.5 (Ch. 2, 1.2), the values obtained for K_s were 1.4 mm h^{-1} and 0.7 mm h^{-1} on plot 3 and 4, respectively. Yet, the fit of the conductivity function to the field data was relatively poor and the K_s values must be considered as an order of magnitude. Saturated hydraulic conductivity values given in the ROSETTA code for silt loams or similar soil textures are about 5 to 20 times higher than those obtained from the field data.

1.2.   Time-space Evolution of the Water Content and Pressure Head

The water content and pressure head profiles were measured at each sampling of the suction cups during the two years of the field study. After important rainfall the soil becomes wet over the entire profile. Near the surface, however, the water content decreases quickly due to strong evaporation. As an example, Fig. 6 shows typical water content and hydraulic charge profiles observed during a dry period (October 11, 2001) and subsequent to 16 mm of rain (May 18, 2001). In the absence of rainfall, the soil water content is lowest near the soil surface and increases with depth. But even during long dry periods the soil stays considerably humid near the surface, indicating that water rises from the shallow groundwater table due to capillary forces. During the study, the θ-values were never inferior to 0.28 cm^3 cm^{-3}.
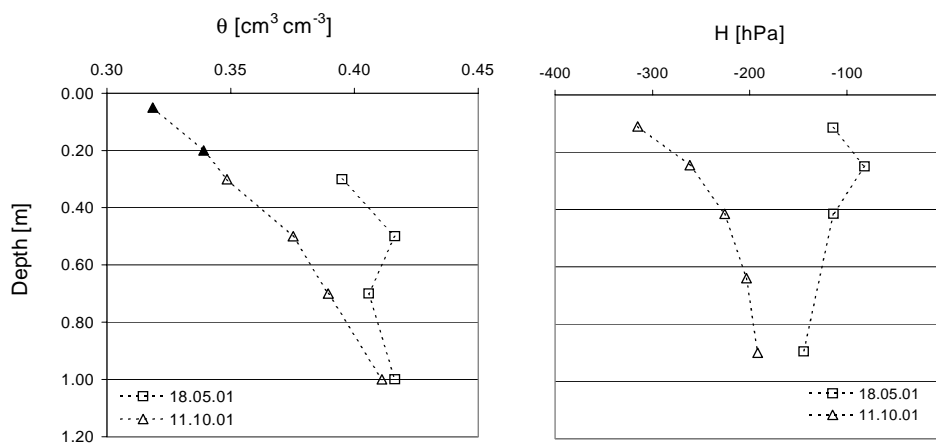
Figure 6: Profiles of water content and hydraulic charge during a dry period (Oct. 11, 2001) and after rainfall (May 18, 2001). Filled points: gravimetrically measured water contents

Some problems appeared with the TDR probes installed at shallow depth, especially on plot 3 where the TDR probe at 10 cm depth measured systematically higher water contents than at 30 cm. This is in contrast to gravimetrically measured values and suggests problems with the TDR method. TDR measurement errors may arise from various sources, among them high salinity and high temperatures. NADLER et al. (1999) observed an influence of high electrical conductivities on the dielectric number in a loamy soil. They concluded that TDR can be safely used to a soil water electrical conductivity of 16 dS m^{-1}. TOPP et al. (2000), on the other hand, sur-

mised that although the calibration curve may not necessarily show deviations from equation 3.1, high salt contents can induce important errors, especially at high water contents when using long TDR probes. At the Martigny site, the soil water electrical conductivity near the surface reached values of 25 dS m^{-1} after heavy rainfall (Fig. 19, p. 52). This could explain doubtful measurements at 10 cm depth; the values were not taken into account for the interpretation.

The hydraulic charge profiles react similarly to climatic conditions. During dry periods, a water flow from the groundwater towards the soil surface is observed, while during and after rainfall events the water flow is directed towards the groundwater table (Fig. 6). Regular h and θ measurements made in the summer 2002 give information about the reaction time of the profile to precipitation. On June 24, 2002, for example, the wetting front had reached 60 cm depth only two hours after a rainfall event (15 mm within 3 hours) indicating that water may infiltrate quickly to considerable depth.

1.3.   Quantification of Water Flow

Between mid May and June 2002, pressure head profiles were determined every afternoon (Appendix 4.1) and water content profiles at regular intervals varying between 1 and 10 days. A positive hydraulic gradient indicates that water moves towards the soil surface, while a negative gradient signifies a downward flux. The measurements show that high positive hydraulic gradients appear at 75 cm depth during dry periods (Fig. 7), but the flow direction changes quickly as a response to precipitation.
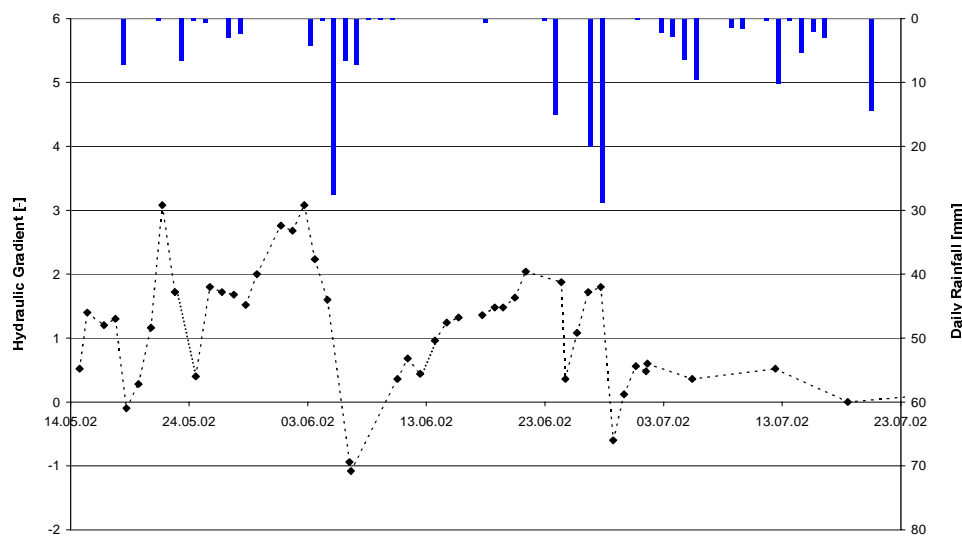
Figure 7: Hydraulic gradient observed at 75 cm depth during May and June 2002 and daily rainfall (secondary axis)

A water balance was calculated for the soil profile between 30 and 75 cm depth: daily water contents were estimated by interpolating between two measurements; fluxes were calculated based on the daily measured hydraulic charge and the soil hydraulic properties from Tab. 6; the changes of water volume within the profile were compared to the sum of fluxes at 30 and 75 cm depth.

The water volume changes correspond approximately to the sum of fluxes during wetting cycles when negative gradients appeared at 75 cm depth. During dry periods, however, the water volume in the profile decreased, although the sum of fluxes indicate a gain of water. The measured hydraulic gradients and water contents are punctual values at the time of the measurement, and therefore, a water balance can only represent a rough estimate. The discrepancy between fluxes and water volume changes during dry periods shows that the evaporative flux near the soil surface is essentially underestimated when based on measurements in the afternoon. Obviously, the hydraulic charge at 30 cm depth changes significantly during the day with maximum fluxes appearing around noon. A precise quantification of the water flow would have required permanent measurement of the pressure head. The rapid and important changes of hydraulic gradients show the influence of the strong evaporation and the shallow groundwater table.

2.   Solute Concentrations

The herbicides atrazine and isoproturon and a tracer were applied to the instrumented plots in May 2001 and 2002. The transport of the chemicals 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 made in 2001, a more efficient sampling scheme was implemented in 2002. Accordingly, the interpretation will focus on observations made in the second year, and 2001's data will serve to confirm the analysis.

2.1.   Soil Solution Concentration in the Unsaturated Zone

Soil solution samples taken before the chemical's application in May 2002 contained no iodide and only traces of the herbicides applied in 2001. Iodide, atrazine, and isoproturon were applied on plots 3 and 4 on May 24, 2002.
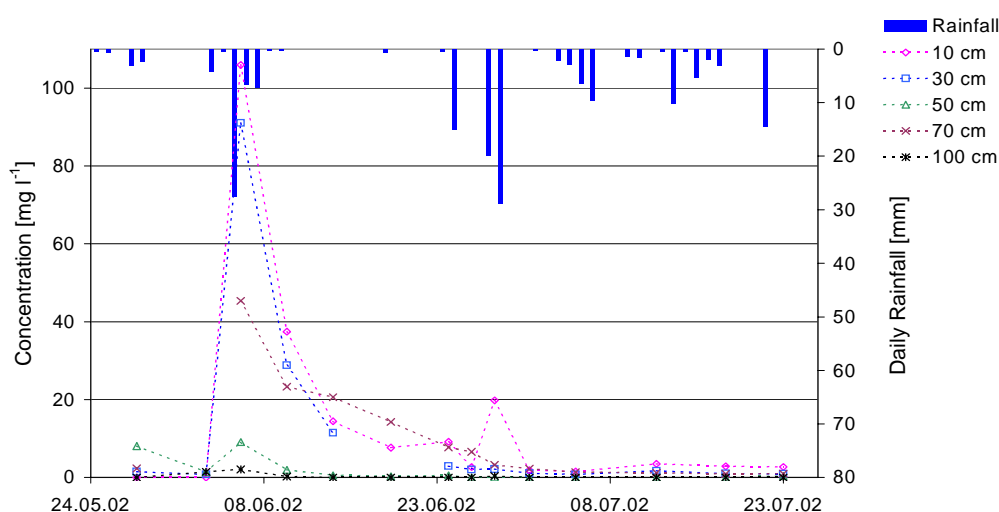
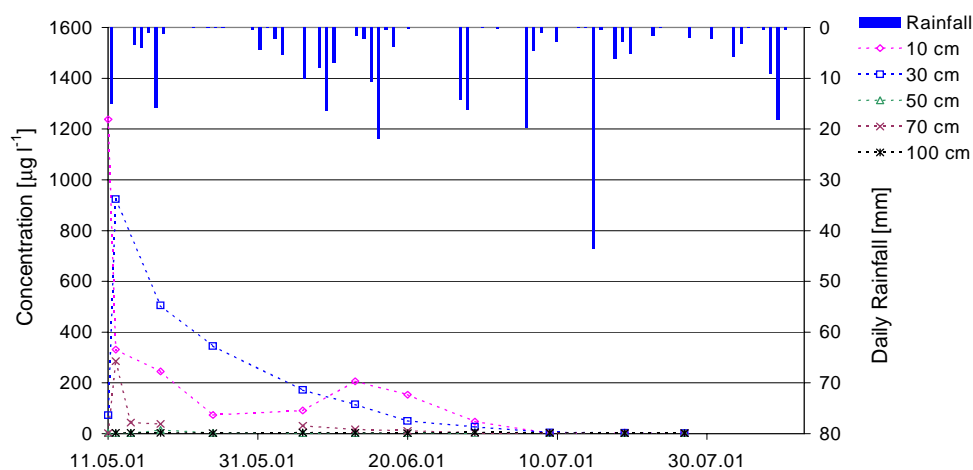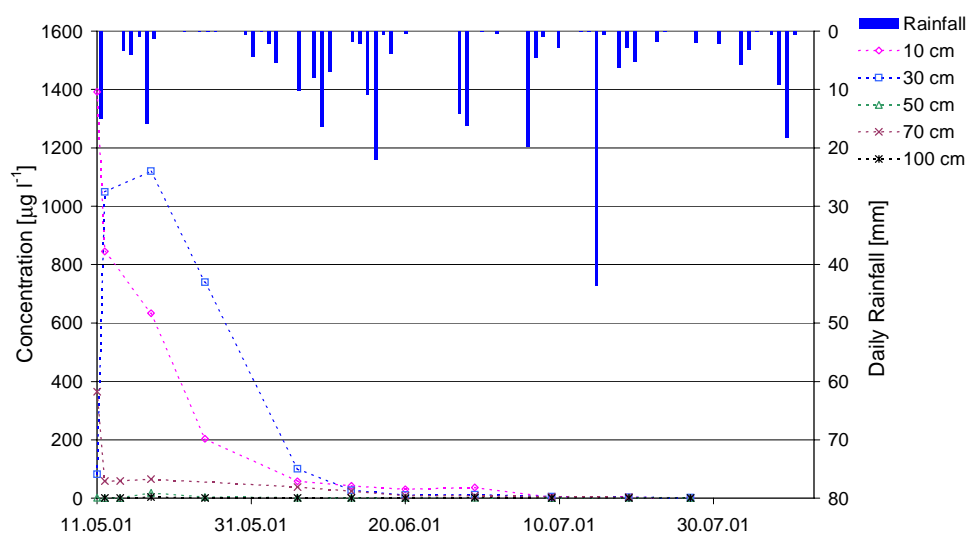**Figure 8:** Iodide concentration in the suction cups at different depths on plot 4 in 2002 and daily rainfall (secondary axis)

Figure 8 shows the temporal concentration changes of iodide measured in the suction cups at different depths. During two weeks without rainfall following to the application, the concentra-

tions in the unsaturated zone remained low. After the first important rainfall event on June 5, high iodide concentrations appeared at 10, 30, and 70 cm depth. Surprisingly, the iodide content remained low at 50 cm depth 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 (49 mm on June 27/28). From July on, the iodide concentration remained low over the whole profile.
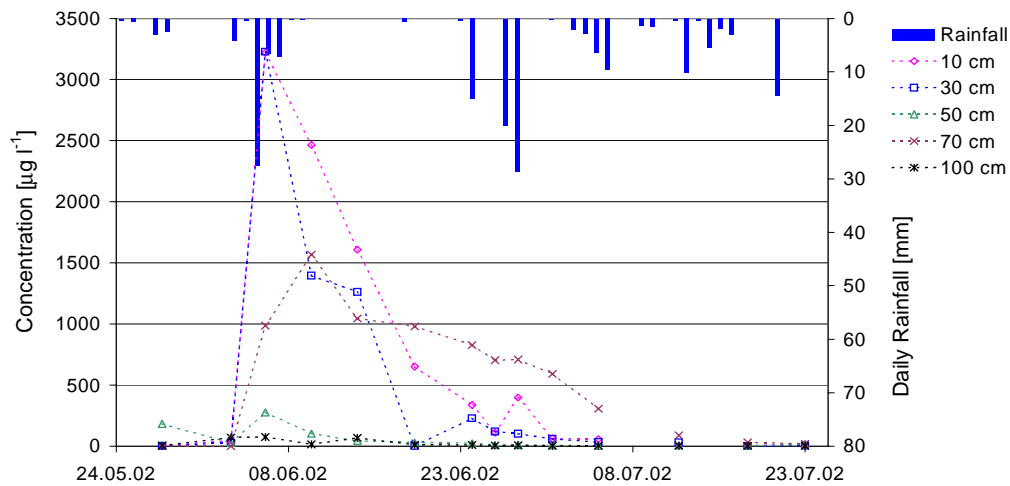
Figure 9: Isoproturon concentration in the suction cups at different depths on plot 4 in 2002 and daily rainfall (secondary axis)
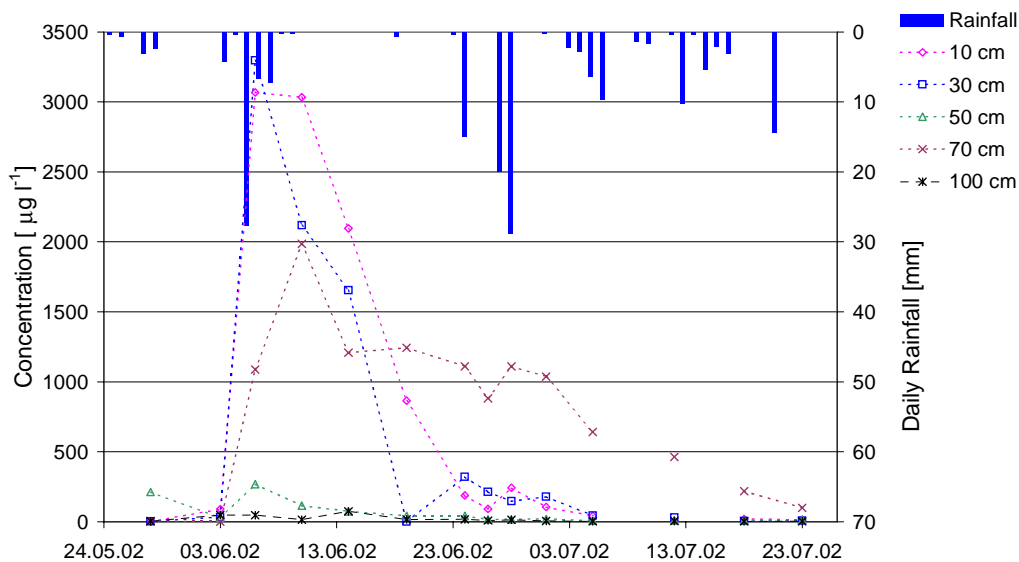
Figure 10: Atrazine concentration in the suction cups at different depths on plot 4 in 2002 and daily rainfall (secondary axis)

The herbicide concentrations show a similar development (Fig. 9 and 10): the concentrations remained low over the entire profile during the two weeks following the application, and max-

imum concentrations appeared immediately after the rainfall of June 5. At the 50 cm suction cup, the herbicides were hardly detected although considerable concentrations were measured at 70 cm depth. This was observed in both years, even though in 2002 the suction cups were sealed with bentonite to prevent water flow and solute transport along the instruments. The herbicide concentrations decreased slower than the salt concentration (Fig. 8), especially at the 70 cm suction cup. The behaviour of the two herbicides was very similar; both reached a concentration of nearly 3300 µg l^{-1} near the surface. At 70 cm, however, atrazine was measured at a slightly higher concentration than isoproturon. A similar temporal development of the concentration was observed on plot 3 (Appendix 4.4).

Figure 11: Isoproturon concentration in the suction cups at different depths on plot 4 in 2001 and daily rainfall (secondary axis)

Figure 12: Atrazine concentration in the suction cups at different depths on plot 4 in 2001 and daily rainfall (secondary axis)

In 2001, plots 3 and 4 had been irrigated with 15 mm of water subsequent to the chemical's application (May 11). Consequently, high herbicide concentrations were already measured at 10 cm depth only 8 hours after the application (Fig. 11 and 12). On the following day, maximum concentrations were observed at 30 cm and the herbicides had already reached the 70 cm suction cup although they were not detected at 50 cm. The first rainfall on May 17 caused an increase of the atrazine content at 30 cm depth, but in general the concentrations decreased from the day of application on. Subsequent to a humid period at the beginning of June, a slight increase of the isoproturon concentration was recorded at the 10 cm suction cup. On plot 3 much higher concentrations were observed, although the same concentrations had been applied. The temporal development, however, was similar (Appendix 4.3)

On plots 1 and 2 (Appendix 4.3), that were not irrigated, the first soil solution samples were taken subsequent to the rainfall event on May 17, 2001. The herbicide concentrations showed a similar development as on plots 3 and 4: high concentrations were measured right after the rainfall and decreased quickly. The second concentration rise in mid June was more significant than on the irrigated plots. Peaks were observed at deep suction cups (70 and 100 cm), although the herbicide contents remained low at some shallower instruments. Temporal changes of the bromide concentration in 2001 are also given in appendix 4.3.

The principal observations in the unsaturated zone are

- the solutes remain at or near to the soil surface as long as no water is applied.

- the solute transport in the unsaturated zone is closely linked to precipitation or irrigation. High chemical concentrations in the unsaturated zone appear almost immediately after irrigation or the first heavy rainfall event following to the application.

- the concentrations decrease steadily during dry periods and further attenuated peaks are observed near the soil surface after important rainfall.

- one and a half month after the application, the chemical concentrations are relatively low again in the upper meter of the profile (< 1 % of the maximum observed).

- the herbicides show basically the same behaviour as the tracer suggesting that adsorption is not a predominant process in the soil of the experimental site.

2.2.   Soil Sample Concentration

Soil samples were collected using hand augers on plot 4 on June 10, 2002, when the first herbicide peak occurred in the soil solution (Fig. 9). They consisted of solid material taken between 0-30, 30-60 and 60-90 cm depth. The samples were oven dried at 30 °C and analysed at the BRGM laboratory (Orléans/France); the detection limit for both herbicides was 10 µg kg^{-1}.

Fig. 13 shows the herbicide concentration measured in soil solution samples and in soil samples on June 10, 2002. Even though solution and soil sample concentrations cannot be compared directly, the concentration profiles are similar. Only in the lowest soil sample (60-90 cm), small concentrations were measured, although high concentrations appeared in the solution at 70 cm. It has to be kept in mind, however, that the soil samples were mixtures of material collected over a 30 cm depth range and that the resulting concentration represents an average.
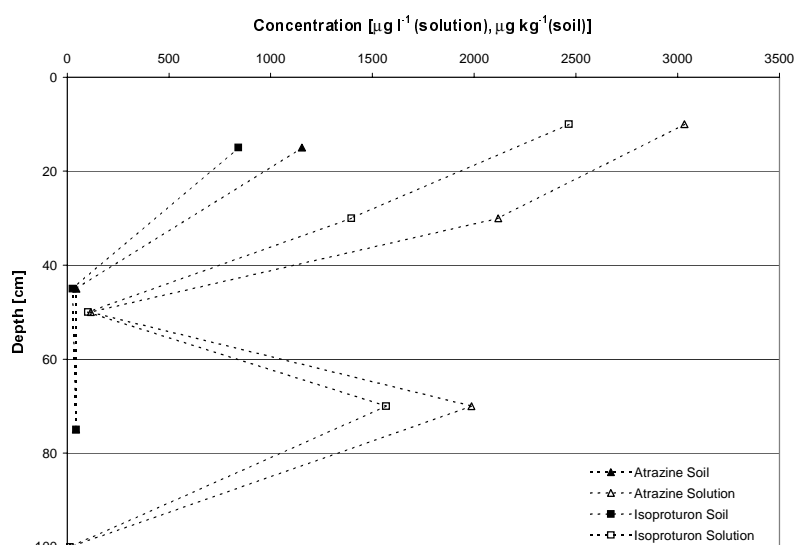
Figure 13: Herbicide concentration in soil solution samples [μg l^{-1}] and soil samples [μg kg^{-1}] on June 10, 2002

Iodide concentrations were measured on soil samples collected at the depth of the suction cups in June and July 2002. A suspension of 150 ml of water and 50 g of dry soil was shaken for 1 hour and the supernatant solution was filtered before analysis of the salt concentration. Here again, the results indicate high chemical contents in the upper part of the soil profile and lower concentrations in the deeper part.

In conclusion, the soil sample analyses confirm the high chemical concentrations measured in the shallow suction cups. At greater depth, herbicides were detected in the soil samples, but at low concentrations. It demonstrates that some herbicides have been transported deep into the vadose zone by the rainfall in early June 2002. Though, the soil sample analyses do not confirm the high concentration measured in the suction cup at 70 cm, suggesting that high chemical contents may appear locally.

2.3.   Concentration in the Saturated Zone

Figure 14 presents the herbicide concentration in the groundwater on plot 4 in 2002 together with the GW table depth. The temporal changes of the chemical concentration are remarkably similar to the fluctuations of the groundwater table. The GW depth is very sensitive to climatic conditions; during dry periods the water table decreases steadily, while important rainfall events cause an almost immediate rise.

In 2002, the plots were not irrigated subsequent to the chemical application; hardly any chemicals were found in the GW during the first two weeks after the application without any rainfall (Fig. 14). Like in the unsaturated zone, a sudden high peak appeared in the GW as a consequence of the precipitation (28 mm) on June 5. The concentrations decreased during the following weeks and a second concentration peak appeared after the heavy rainfall of June 27/28 (49 mm). Interestingly, the 15 mm precipitation on June 24 caused a slight rise of the GW table, but not of the herbicide concentration (Fig. 14). A major difference between the rainfall events on

June 24 and June 27/28 (other than the water quantities) was their intensity: the mean rate on June 24 was 5 mm h^{-1} (maximum of 12 mm in 30 minutes), while on June 27/28 a lower rate of 2.7 mm h^{-1} (maximum of 7.4 mm in 40 minutes) was recorded. Apparently high rainfall quantities with a low intensity favor the herbicide leaching (see section 6).

A third attenuated concentration peak was observed in mid July. The concentration evolution of the different herbicides is very similar, with the second concentration peak being slightly higher for atrazine than for isoproturon. On plot 3, on the other hand, the atrazine concentration in the GW was constantly higher than the isoproturon concentration (~40%, appendix 4.6).
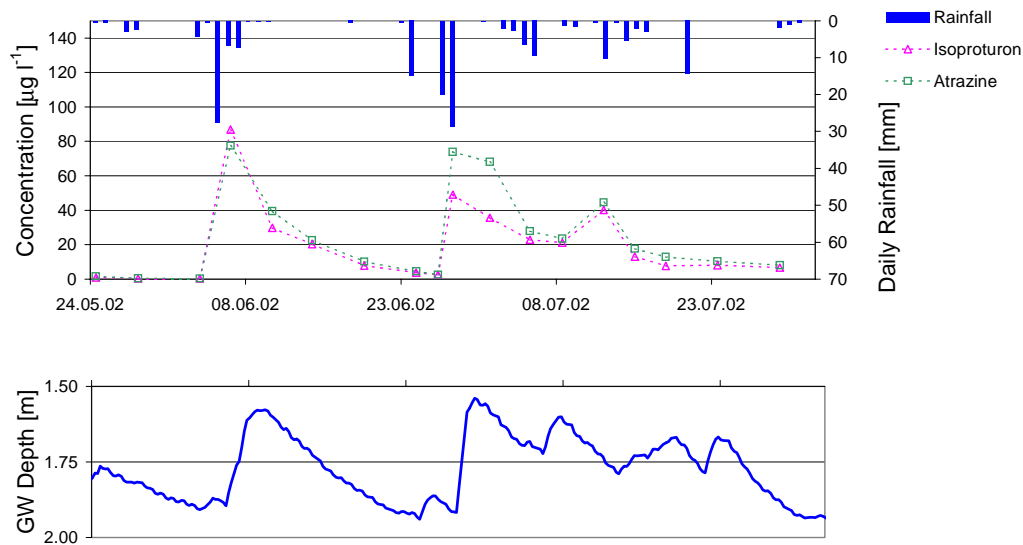
Figure 14: Herbicide concentration in the groundwater on plot 4 in 2002 (daily rainfall on secondary axis) and depth of the groundwater table
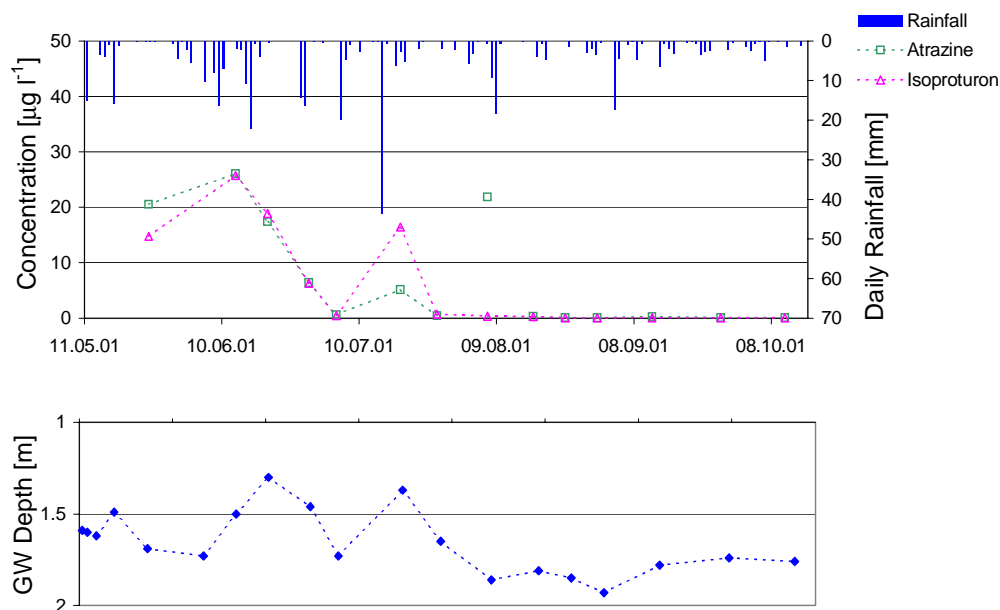
Figure 15: Herbicide concentration in the groundwater on plot 4 in 2001 (daily rainfall on secondary axis) and depth of the groundwater table at the sampling times

In 2001, the depth of the GW table was measured less frequently. Consequently, the link between the level changes and the climatic conditions is less evident. The plots were irrigated with 15 mm of water after the application. When the first GW sampling took place two weeks later, high chemical concentrations had already reached the GW (Fig. 15, see Appendix 4.5 for plot 3). A peak was observed in mid-June after several consecutive rainfall events. During the subsequent dry period the GW concentrations decreased quickly and another peak was recorded in mid July following to heavy rainfall on July 15. The concentration magnitudes on plot 4 were significantly lower in 2001 compared to 2002 although identical herbicide masses were applied. It is likely that in 2001 the maximum concentration occurred right after the irrigation and/or the following first precipitation, and that a first, early peak was not detected because the sampling took place only two weeks later.

In summary, the concentration in the saturated zone correlates well with the observations from the vadose zone and shows that

- the chemical transport is closely related to precipitation. Important rainfall events (>15 mm) following the application can cause considerable leaching.

- water and chemicals move rapidly through the unsaturated zone and reach the GW in a very short time (less than a day).

- the GW concentrations decrease steadily during dry periods. The concentration and the GW depth change in a very similar way.

- both herbicides are present at similar concentrations. Nevertheless, isoproturon tends to remain longer in the unsaturated soil, while atrazine appears at slightly higher concentrations in the saturated zone.

- a few months after the application, the GW concentration is relatively low.

3.   Mass Balances

Mass balance calculations are useful to identify transport or reaction processes in an experiment. A mass balance was calculated by integrating the mass of solutes present at the measurement depths over the soil profile (Appendices 4.7 and 4.8). For example, it was supposed that the water and herbicide content measured at 10 cm depth were representative for the soil compartment between the surface and 20 cm depth. Between 80 cm and the GW table, constant water content and solute concentration, identical to the values measured at the deepest instruments (1 m) were assumed. Whenever measurements of the water content were missing, interpolated values were used. In the saturated zone, the concentrations were related to a saturated water content of 0.45 cm^3 cm^{-3}. As the GW sampling was not depth specific (Ch. 3, 3.4), the measured concentration was integrated over the whole water column (from the water table to a depth of 2.50 m corresponding to the lower end of the piezometers). Only herbicides present in the liquid phase were considered. Due to the numerous simplifying assumptions, the mass balance can only give a rough estimate of the recovered herbicide mass.
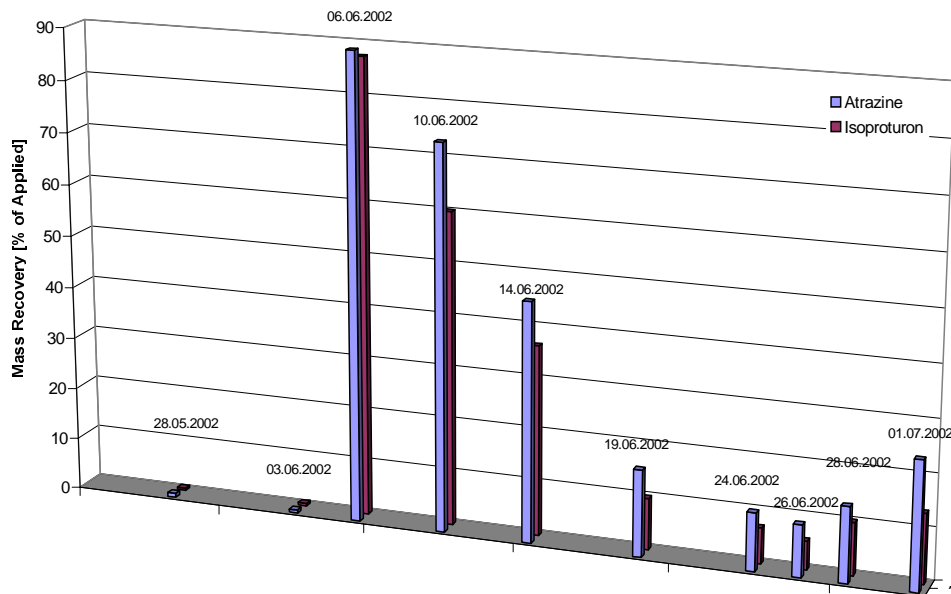
Figure 16: Mass Balance on plot 3 in 2002

On both plots the mass recovery was very low until the first precipitation, indicating that most of the applied substances remained at or near the soil surface. On plot 3, the herbicide mass recovery reached its maximum (89 %) after the first rainfall following to the application (June 6, Fig. 16). The mass recovery then decreased progressively to less than 10 % on June 26. Subsequent to the second heavy rainfall (27/28 June), the total recovered mass increased slightly. It is possible that during dry phases part of the herbicides have persisted at locations that are not accessible with the sampling devices (e.g., between the GW table and the deepest suction cup or in immobile water zones).

On plot 4 the temporal development was similar, but the maximum mass recovery reached nearly 200 % on June 6 (Appendix 4.8). This overestimation must be attributed to the simplifying assumptions in the mass balance calculation. One major simplification is that the measured GW concentrations are integrated over the whole water column. Integrating the concentration value over just the upper 10 cm of the GW column, however, barely influences the mass recovery. Another assumption is that the chemicals advance homogeneously through the soil profile. Nevertheless, if heterogeneous, two-regional transport occurred, this assumption would not be correct. The solution in the suction cups could then stem from easily accessible mobile water with higher chemical concentrations as in the immobile zones. In such a case, the integration of the high chemical contents over the whole pore space could lead to an overestimation in the mass recovery.
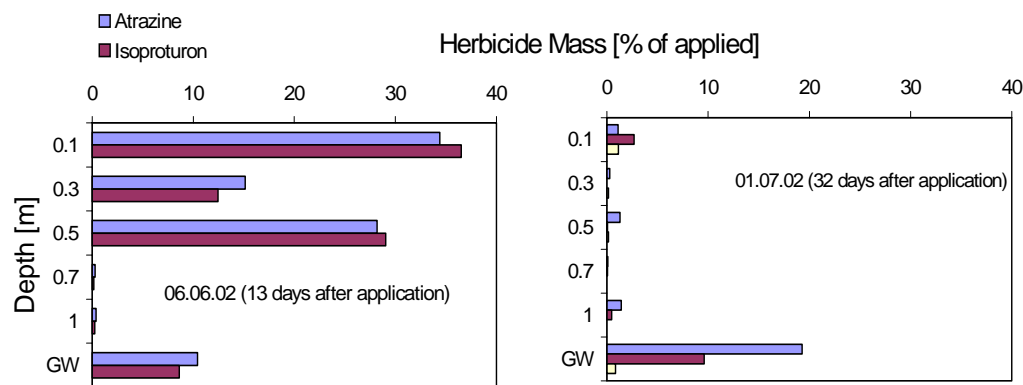
Figure 17: Mass Balance in different segments of the soil profile on plot 3 on June 6 and July 1

The mass balance was also calculated for different depth segments at various sampling times. On June 6, it clearly shows high recovery rates in the upper 50 cm of the soil, low rates in the deeper part of the unsaturated zone, and again a rather high recovery rate in the groundwater (Fig. 17). On July 1, the center of mass was located in the groundwater and hardly any herbicides were left in the unsaturated zone. Consequently, subsequent to the first important rainfall after the application, a large part of the pesticides remained in the upper soil layer and another part was quickly transported to the GW table. After the second important rainfall event, hardly any herbicides remained in the unsaturated zone; they had almost completely been transported to the deeper soil layers and the GW.

In 2001, the mass recovery on plot 3 exceeded 180 % after the application and irrigation, while on plot 4 the maximum did not reach 50 % (Appendix 4.7). The recovered herbicide mass then decreased steadily on both plots.

In conclusion, the mass balance shows that

- the recovered masses vary considerably between the plots although the same concentrations have been applied.

- integrating the concentrations measured in the soil solution samplers over the whole soil profile may lead to considerable overestimations in the mass balance.

- after the first heavy rainfall subsequent to the chemical application, high recovery rates were observed in the upper 50 cm of the soil and in the GW simultaneously.

4.   Dye-Tracing Experiment

Because the sampling techniques cannot detect heterogeneous spatial flow patterns in soils, non-equilibrium flow can hardly be proven through usual tracer studies. Coloured dyes, on the other hand, provide the means for a direct observation of the spatial structure of water and solute flow in an entire section of a soil profile.

The dye tracer Brilliant Blue FCF ($C_{37}H_{34}N_2Na_2O_9$-S_3) has been used in recent studies to stain the flow paths of water in field experiments (FLURY et al., 1994). The dye has an extremely low toxicity, is well visible in soil material, and adsorbs only weakly on soils (FLURY & FLÜHLER, 1994). A staining experiment was carried out on pot 1 on July 2, 2002. The soil was irrigated with 20 mm of Brilliant Blue solution at a concentration of 4 kg m^{-3}. The solution was applied in 6 doses within 7 hours which corresponds to a moderate rainfall event. The soil was not covered and the potential evaporation during the experiment reached 3.7 mm. Therefore, the amount of infiltrated solution was approximately 16.3 mm. A pit was opened the next morning.

At this time, the bulk of the dye had reached a homogeneous depth of approximately 6 cm, but at some locations stains were visible down to more than 50 cm (Fig. 18). The thin lines of infiltrations clearly represent accelerated flow pathways (N. JARVIS, personal communication). In spite of the small amount of applied dye solution, the penetration depth is considerable at some locations.
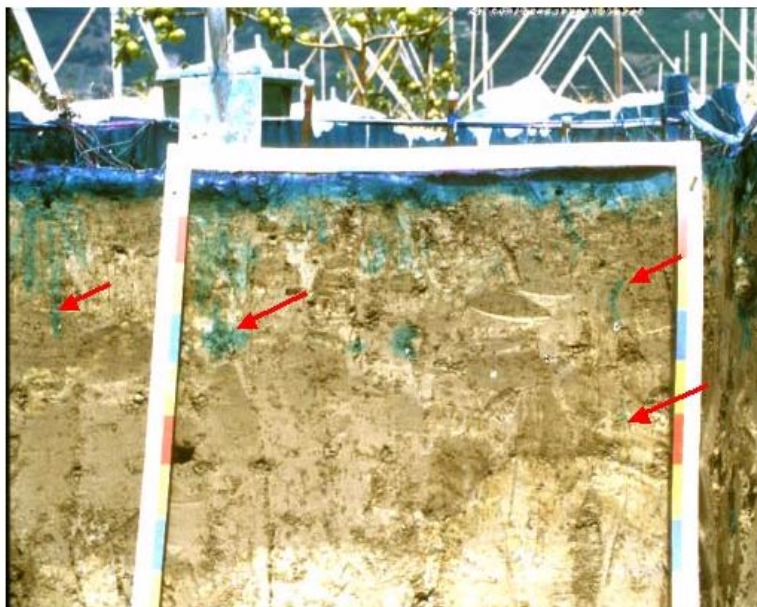
Figure 18: Stained soil profile, colours on frame indicate 10 cm intervals. Red pointers = stained surfaces.

The soil is an unstructured silty loam with some layers made up of slightly finer or coarser sediment (Ch. 3, 2.1) in which macropores like worm channels or big root holes were not observed. The deep penetration of the dye at some places, however, suggests that part of the soil water moves quickly whereas the other part contributes only little to the transport. Consequently, the concept of mobile and immobile water (VAN GENUCHTEN & WIERENGA, 1976) seems suitable to describe the water and solute transport.

5.   Electrical Conductivity in the Unsaturated Zone

The salt concentration in a soil solution can be described by its electrical conductivity (EC). In 2002, the EC of the solution in the upper 50 cm of the soil profile varied between 7.3 and 25 dS m^{-1} (Fig. 19). The changes correlate well with the climatic conditions: high values appear after heavy rainfall while during dry periods the salt content decreases. At greater depth, on the other

hand, the EC remains quite constant at 5 dS m^{-1} (Fig. 19). The changes in EC are due to salts that are naturally present in the soil; the applied iodide can only play a negligible role. A possible mechanism to explain this is a transport of salt ions towards the soil surface with the upward water flux during dry periods. Subsequent to precipitation the salts are carried down again into the soil with the infiltrating water. Another possible mechanism is the existence of mobile and immobile water and the diffusion of the ions into the immobile phase during dry periods.
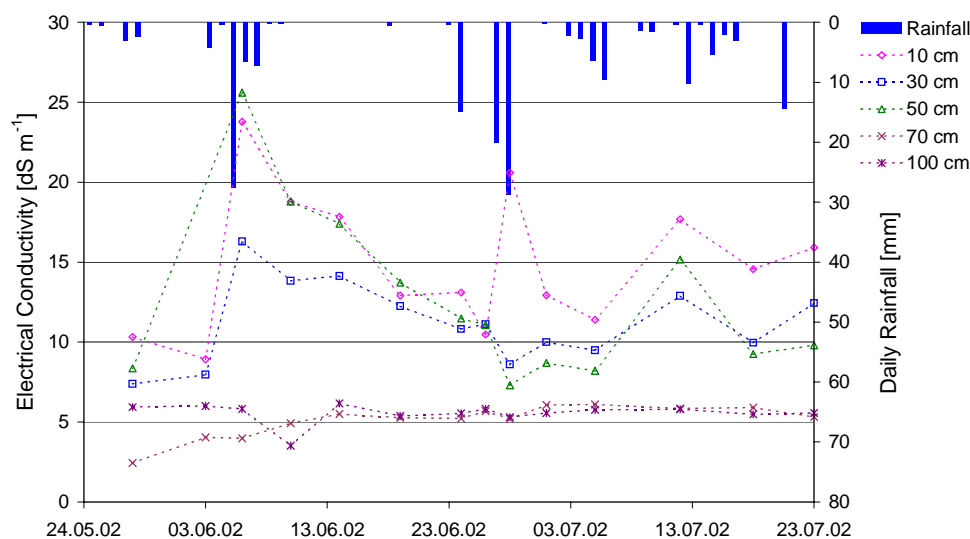
Figure 19: Electrical Conductivity in the soil moisture samples on plot 3 in 2002 and daily rainfall (secondary axis)

6.   Summary and Discussion

The soil of the experimental plots is a relatively homogeneous silty loam. The observed retention curve is characteristic of silty loam soils, but the hydraulic conductivity as estimated from the internal drainage test is much lower than expected. The high evaporation and the shallow depth of the GW table lead to high positive hydraulic gradients and a strong capillary rise during dry periods. As a consequence of rainfall, however, the positive hydraulic gradients in the soil profile change rapidly and negative gradients are observed. This is not consistent with the above mentioned low hydraulic conductivity and suggests that water flows down quickly through only a small portion of the soil and much slower in the matrix.

The solute transport is closely linked to precipitation. In both experimental years, the herbicides were rapidly transported to the GW after the irrigation or the first heavy rainfall subsequent to the application. The rapidity of the transport suggests that the herbicides are not effectively retained by adsorption and that non-equilibrium processes occur at the experimental plots. This assumption is supported by various observations:

- The concentrations measured on the plots varied considerably although the same amounts of chemicals were applied. Additionally, high chemical concentrations were detected in some deep suction cups, while in others at shallower locations hardly any herbicides were observed. The low concentrations measured at some suction cups may

be related to bypassing of the samplers.

- The first concentration peak appeared in the GW and in the unsaturated zone simultaneously, showing that part of the solutes is transported rapidly towards the GW. Further peaks were observed in the GW later on, while only low concentrations prevailed in the unsaturated zone, indicating that some solutes are transported slower towards the GW.

- The dye tracing experiment clearly displays that the water infiltrates deeper at some distinct locations than in the major part of the soil matrix.

The concentration in the GW decreased as the water level declined. The chemicals may either have been removed laterally with the GW flow or they were transported upward with the capillary rise. In the unsaturated zone, the initially high concentrations decreased slower during the dry period in mid June 2002. The solutes cannot have been transported downwards with the water flow, because upward fluxes were observed in the soil profile. Adsorption and degradation cannot be responsible for the reducing concentrations either, because the tracer contents showed the same temporal development as the herbicides and the distribution coefficient and degradation constant measured in the laboratory are only low (ZHANG, 2003). Two other mechanisms may explain the decreasing concentrations in the unsaturated zone:

- The solutes may have been transported towards the soil surface with the upward water flux. White powder observed at the soil surface suggests accumulation and precipitation of salts from the soil solution. In this case, the concentration in the soil profile should increase after successive heavy rainfalls. An increase, however, was only observed at 10 cm depth after the precipitation in late June 2002 and it was very attenuated; the explanation is therefore not very reasonable.

- The soil may be divided into regions containing mobile and immobile water with diffusion of chemicals between the two. During dry periods, diffusive exchanges might have taken place between the mobile and the immobile phases thus reducing the solute concentration in the soil water samples extracted with the suction cups (predominantly composed of easily extractable water). Subsequent to precipitation, part of the solutes would diffuse slowly from the immobile to the mobile region and cause an increase of the concentration. Though, as mentioned above, an increase of the herbicide concentration in the upper vadose zone was hardly observed.

Although neither of the mechanisms can explain the observations in a completely satisfactory way, the assumption of mobile and immobile water seems more likely. No leaching to the GW was detected after short, high intensity rainfall, whereas leaching was observed after long rainfall with low intensity; such an observation suggests that, in the latter case, time was sufficient to allow diffusive exchanges of solutes between the immobile and mobile regions. Nevertheless, even with low intensity rainfall the downward flow is rather quick and the subsequent GW level rise quite fast compared to the time-scale of diffusion processes.

The recovered herbicide masses on the plots decreased quickly in both years and approximately 2 months after the application, only relatively low chemical contents were observed, even after heavy rainfall. While in the GW, the removal of the chemicals can be attributed to the lateral groundwater flow, this cannot be the case in the unsaturated zone. Degradation can hardly be the cause for the apparent disappearance, because only low degradation rates have been measured in the laboratory. Another mechanism could be the formation of bound residues. Bound

residues may form when a pesticide is covalently bound to the soil organic matter or through sequestration (complexation) of the molecules (LOISEAU & BARRIUSO, 2002). According to BARRIUSO & KOSKINEN (1996), the formation of bound residues is a rapid process; they observed significant residue formation during the first few months following to the atrazine application. The capacity to form bound residues depends on the nature of the soil organic matter (BARRIUSO & KOSKINEN, 1996). In a laboratory study, LOISEAU & BARRIUSO (2002) observed important residue formation in a soil with an organic carbon content as low as 1.2 %.

Since the herbicides were transported as quickly as the tracer, adsorption does not seem to play a predominant role in the soil at the experimental site. This is consistent with the studies of ZHANG (2003) and CLAUSEN et al. (2002) that report low atrazine adsorption coefficients. Nevertheless, a slightly different behaviour was observed for the two herbicides. Isoproturon persisted at slightly higher concentrations near the soil surface, whereas atrazine leached quicker and at higher concentrations indicating a stronger adsorption of isoproturon as supposed by CLAUSEN et al. (2002).

Chapter 5

Numerical Modeling

Modeling has become a major tool to simulate the transport and the persistence of pollutants in the vadose zone and the groundwater. Mathematical models represent the behaviour of a system by a set of equations. In the case of simplified transport conditions, e.g., steady state conditions in homogeneous and isotropic aquifers, the equations can be solved analytically; for more complex situations, such as for transient water flow or non-equilibrium solute transport with nonlinear reactions, however, numerical solutions have to be employed.

1.   Theoretical Considerations

1.1.   Model Classification

Considerable progress has been made in the conceptual understanding and mathematical description of water flow and solute transport through the unsaturated zone in the past decades. Models represent schematic views of a complex physical reality, they are based on the following principle (CLARKE, 1973)

$$f(y_t, x_t; y_{t-1}, x_{t-1}; y_{t-2}, x_{t-2}, \ldots; a_1, a_2 \ldots) + E_t = 0 \qquad (5.1)$$

where y_t and x_t are output and input variables at time t, respectively, a_n are system parameters, E_t is the residual error at time t, and f is the functional form of the model. Models differ according to the nature and precision of the functional form and the parameters.

Depending on the functional form, a model is called

- conceptual, if it is based on the consideration of physical, chemical, and biological processes.

- empirical, if it is based on observations made in the laboratory or in field experiments, and it does not explicitly follow physical, chemical, and biological laws.

- mechanistic, if it incorporates the fundamental flow and transport mechanisms currently known using physical, chemical, and biological laws.

- functional, if it incorporates only simplified treatments of solute and water flow processes (ADDISCOTT & WAGENET, 1985).

The variables (y_t and x_t), the system parameters (a_n) and the residual error (E_t) can

- have one unique value and be viewed free from random variations. The model is then

called deterministic.

- be described by probability distributions, in which case the output is expressed as a probability density function and the model is called stochastic (VANCLOOSTER et al., 2000a).

1.2.   Modeling Strategies

1.2.1.   Inverse and Direct Problems

The use of a model requires knowledge of the parameters that control water flow and solute transport. These parameters can be determined experimentally and be introduced into the model (direct problem). In many cases, however, some parameters are not known and thus, have to be evaluated. An input-output relationship is then supplied to the model resulting in an estimation of the parameters (inverse problem). In an inverse simulation, the problem is solved with an arbitrary chosen parameter set and the system response is calculated. The system response is then compared to the output data set, and the parameters are adjusted until deviations between observed and simulated responses are minimized. The most common approach is to determine as many parameters as possible by laboratory or field experiments and to find the remaining parameters by inverse modeling. A high number of estimated parameters may result in a non-uniqueness of the model and thus highly uncertain predictions. The importance of each model component (and thus, the effect of an error in the parameters) can be evaluated in a sensitivity analysis.

1.2.2.   Calibration and Validation

Before a model can be used to predict the solute transport, it has to be calibrated and validated. During the calibration process the parameters are gradually changed until the model prediction matches a measured data set sufficiently well. Most often, models are calibrated using a trial and error method that is naturally subjective, influenced by the perception of the researcher. Therefore, automatic calibration methods have been proposed (VANCLOOSTER et al., 2000a) that use well defined statistical optimization algorithms to adjust the simulation output. The degree of correspondence between model output and measured data can be analysed graphically in time series plots or scatter plots. Additionally, statistical criteria can be used as model deviation indicators (VANCLOOSTER et al., 2000a), the most simple being the arithmetic difference between the measured and calculated output. The calibrated model has to be validated by simulating the water flow and/or solute transport for a different time period and comparing the results to the corresponding data set. The model may be considered validated if the level of performance is the same for both time periods. If during the second simulation the parameters have to be readjusted, the procedure cannot be considered a validation, but only a recalibration (LOAGUE & GREEN, 1991) and other time periods are needed to validate the model.

For a coupled problem of water flow and solute transport processes, the common procedure is to first calibrate the hydraulic component of the model using water content and hydraulic head measurements. The water flow model is then used together with measured concentration profiles to estimate the transport parameters (sequential inversion method; MISHRA & PARKER, 1989). A model that is calibrated and validated can be used to predict solute transport.

1.3.   Model Errors

Three types of errors exist that evolve from different sources: model errors, input errors, and parameter errors (LOAGUE & GREEN, 1991). Model errors occur when the model does not include all the processes necessary to explain the observed system behaviour. As a result the model will not be able to simulate the observations even if input data and parameter estimation are correct; e.g., if hysteretic hydraulic processes are to be predicted using a non-hysteretic hydraulic model (MISHRA & PARKER, 1989). Input errors arise from noisy data sets due to measurement errors. Parameter errors may appear because the value of a parameter is determined on the basis of only a limited number of local measurements that might not be exact. An inverse solution may bear parameter errors if the model parameters are highly interdependent or non-unique (LOAGUE & GREEN, 1991). Generally, it is impossible to devide the model deviation in components originating from model error, input error, and parameter error. The sum of the three errors is the total simulation error that can propagate between model components (e.g., from the water flow component to the transport simulation), thus complicating the simulations.

2.   Simulation of the Local Transport Experiments

The principal objective of the simulations in this study was to test whether a numerical model can reproduce the experimental observations and to better understand the processes involved in the pesticide transport under the specific conditions of the experimental site: i) high evaporation rates and important upward fluxes with high water contents over the whole profile, ii) an apparently homogeneous loamy soil with a low hydraulic conductivity, but an extremely rapid transport. These contrasting characteristics suggest that physical non-equilibrium conditions influence the solute transport on the plots.

2.1.   Tool Selection

Within the last decades several computer models have been developed to simulate the water flow and solute transport in agricultural environments (WAUCHOPE et al., 2003) , some of them account for physical non-equilibrium processes (JARVIS, 1998; SIMUNEK, 2003).

The various models differ in terms of their underlying assumptions and complexity. The purpose of this section is not to give an exhaustive review of available pesticide leaching models or to give a detailed description of the tools. Our intension is to explain why the HYDRUS-1D model was chosen for the simulations. For detailed descriptions and model comparisons, the interested reader is referred to review papers and databases such as presented by WAUCHOPE et al. (2003), SIMUNEK et al. (2003), BEULKE et al. (2001), GARRATT et al. (2002), VANCLOOSTER et al. (2000a), VANCLOOSTER et al. (2000b), ARMSTRONG et al. (2000).

Simple functional models have been developed in recent years that include treatment of physical non-equilibrium conditions (JARVIS, 1998). An example of such a model is the Pesticide Leaching Model (HALL, 1993; HALL & WEBSTER, 1993). It is a capacity type model in which water moves down the profile in a "tipping-bucket" fashion. The soil solution is divided into mobile and immobile phases with only the mobile phase being displaced during drainage. As the model assumes that water outflow from each layer is zero until filled to field capacity, rapid and deep penetrating bypass flow in a soil cannot be simulated (JARVIS, 1998). Upward fluxes due to evaporation cannot be simulated either with the tipping bucket approach. In this study,

however, important upward fluxes and significant GW table changes have been observed that are likely to play a role for the chemical transport. Furthermore, the usual time step in these functional models is one day, yet time scales appropriate to characterize non-equilibrium flow would be hours or even minutes (JARVIS, 1998).

Mechanistic models that account for physical non-equilibrium have recently been divided into two groups: dual-porosity and dual-permeability models (SIMUNEK et al., 2003). Both groups divide the soil into two separate pore domains. While dual-porosity models assume that water in the matrix domain is stagnant, dual-permeability models allow for water flow in both, the macropores and the micro (matrix) pores (SIMUNEK et al., 2003). The model MACRO (JARVIS, 1994) is an example of a dual-permeability model. In the micropores, water flow and solute transport are calculated using Richard's equation and the convection-dispersion equation (CDE), respectively, while in the macropores, water flow and solute transport are gravity driven and described by a simplified capacitance-type approach. An exchange between the two pore regions is calculated as a function of an effective aggregate half-width. Dual-permeability models like MACRO are frequently used to describe flow and transport in fractured or structured media displaying shrinkage cracks, earthworm channels, root cracks, or heterogeneous soil textures (e.g., LARSSON & JARVIS, 1999).

In dual-porosity models the water flow is restricted to one flow domain (inter-aggregate pores), while the matrix domain (intra-aggregate pores) retains and stores water, but does not permit convective flow. The HYDRUS-1D model, for example, includes provisions for dual-porosity calculations. It uses Richard's equation for water flow and the mobile-immobile CDE for the solute transport in the mobile region. An exchange between the pore regions is described as a first-order process (VAN GENUCHTEN & WIERENGA, 1976, see Chapter 2). The mobile-immobile water concept is often used to describe solute transport processes in aggregated porous media (VANDERBORGHT et al., 1997).

The soil at the experimental site is a rather homogeneous silt loam. Pits have been dug at several occasions (TDR installation, dye tracing experiment), but no macropores like cracks, worm channels, and root holes have been observed. The soil texture varies only little from silt loam to sandy loam. Therefore, the MIM concept implemented in the HYDRUS-1D model seems appropriate for simulating the accelerated solute transport on the experimental plots. Moreover, HYDRUS-1D permits to specify atmospheric boundary conditions at an hourly time. As evaporation in the valley is strong and varies considerably within a day, an hourly time step is important for the simulation of the strong capillary rise and the quick flux changes derived from the experiment.

2.2.   Model Implementation

The HYDRUS-1D model (SIMUNEK et al., 1998) is a Microsoft Windows based modeling environment for simulating water flow and solute transport in variably saturated media, its operating equations are given in Chapter 2.

2.2.1.   Space and Time Discretisation

The model domain consists of a one dimensional column stretching from the soil surface to a depth of 2500 mm. The grid is composed of 251 equally spaced nodes. The upper part of the

soil profile is unsaturated and the lower part is water saturated. The Galerkin formulation was selected for the spatial discretisation in the transport simulations (SIMUNEK et al., 1998).

The time discretisation was optimized during the simulation using five parameters: an initial time step of 0.01 hour, a maximum and a minimum time step of 1 and 10^{-4} hour, respectively, as well as two time step multiplication factors [-] (upper value = 1.3, lower value = 0.7, see manual for more precise informations). In the transport simulations, a Crank-Nicholson scheme was used for the time discretisation (SIMUNEK et al., 1998).

2.2.2.   Initial and Boundary Conditions

At the beginning of each simulation, the pressure head distribution has to be specified over the whole profile. The lower part of the soil profile was water saturated and the pressure head at the bottom node was specified as the height of the water column. From the water table to the soil surface the profile was supposed to be at equilibrium. The initial solute concentration was set to zero, because no herbicides were detected in the soil and the groundwater before the application in 2001 and only traces had persisted in May 2002.

At the upper boundary, atmospheric conditions with possible surface ponding were imposed. Hourly potential evapotranspiration rates (Penman-Monteith) were calculated based on data from nearby weather stations (Ch. 6, 1.4) and specified together with hourly measured rainfall as a time variable boundary condition. The amount of irrigation water applied in 2001 was added to the rainfall. Solutes were introduced by adding the chemical concentration to the first rainfall subsequent to the application in 2002 and to the irrigation in 2001 (Concentration Flux Boundary Condition).

For the lower boundary condition of the hydraulic model, two basically different assumptions were considered: i) the GW table depth is influenced by lateral water supplies from the river, the canal, the slope, etc., or ii) the groundwater table depth changes as a consequence of evaporation and rainfall, only. Consequently, two different lower boundary conditions were studied and are discussed in this chapter:

- a variable pressure head boundary condition (approach 1): With this boundary condition, the groundwater level is specified as pressure head on the bottom node (Dirichelet Type) at an hourly time step. Thus, the groundwater level is prescribed and not calculated by the model. Water is allowed to enter and leave the profile through the lower boundary.

- a zero flux boundary condition (approach 2, Neumann Type): No water can enter or leave the profile at the lower boundary. The groundwater level changes are used as calibration data for the inverse solution.

For the transport simulations, a concentration flux condition was imposed at the lower boundary when using approach 1. The concentration of the water entering the profile was supposed to be zero. For the impermeable boundary condition, a zero gradient was assumed.

2.3.   Water Flow Simulations

For the water flow simulations, the soil water retention parameters obtained from the field experiments were used. The hydraulic conductivity function, on the other hand, was assessed by inverse modeling. To this end, the data collected during the two years were split into two sets, one including the measurements of 2001 and the other one made up of the larger data set collected in 2002. The hydraulic conductivity function was calibrated on the more detailed data set from 2002, and the data from 2001 was used for the second simulation (validation).

2.3.1.   Parametrisation and Inverse Modeling

The calibration period started at the end of March 2002, roughly two months before the chemical application, and ended in mid August 2002.

The soil profile was assumed to consist of one uniform soil layer to which the parameters of the soil water retention function (θ_r, θ_s, α, n) estimated from the field measurements were attributed (Tab. 6). The parameters of the hydraulic conductivity function (K_s, l) were determined by inverse modeling on pressure heads and/or on GW levels measured in 2002 (Tab. 7). The measured pressure head values were used for the calibration because they are more precise and reliable than the TDR measurements (Ch. 4, 1.2). Table 7 gives an overview of the inverse simulations carried out for plots 3 and 4 with the two modeling approaches. In order to implement the mobile-immobile water concept (MIM), a value of the immobile water fraction had to be defined. The model considers that immobile water cannot evaporate. As the soil water content measured during both seasons always exceeded 0.28, this value was taken as the immobile water content.

Table 7: Inverse simulations for both modeling approaches on the two plots

	Approach 1 Variable Pressure	Approach 2 No Flux
Calibrated Parameters	K_s[a], l	K_s, l
Calibration Data	h[b]	h and GW level
Results Plot 3	$K_s = 0.93$ [0.58-1.28][c] $l = 0.004$ [-0.63-0.64]	$K_s = 1.595$ [1.59-1.60] $l = 8.86$ [8.80-8.92]
Plot 4	$K_s = 0.92$ [0.78-1.07] $l = 0.074$ [-1.29-1.43]	$K_s = 0.98$ [0.90-1.06] $l = 9.75$ [9.52-9.98]

a. Saturated hydraulic conductivity in mm h^{-1}
b. Pressure head measured in the vadose zone
c. 95% confidence intervals

The calibrated hydraulic conductivity values obtained with the two approaches are similar; values are slightly higher on plot 3 compared to plot 4 (Tab. 7). The calibrated pore connectivity parameter, l, is different from the value of 0.5 estimated by MUALEM (1976): it is very low in approach 1 and considerably higher in approach 2. At low values (<0.5), the parameter l has

hardly any influence on the course of the K(h)-curve, explaining the large confidence intervals obtained in approach 1 (Tab. 7). The high value of l in approach 2, on the other hand, results in a quicker decrease of the hydraulic conductivity as the soil becomes unsaturated (at θ-values between 0.41 and 0.36). At low water contents, however, the parameter hardly influences the hydraulic conductivity.

The calibration results can be evaluated by analysing mathematically or graphically the difference between observed and predicted values. The residual errors were analysed for both approaches on the two plots by calculating the Maximum Error (ME), the Root Mean Square Error (RMSE), the Coefficient of Determination (CD), the Modeling Efficiency (EF), and the Coefficient of Residual Mass (CRM) (LOAGUE & GREEN, 1991; Appendix 5.1). Table 8 lists the values of the Root Mean Square Error corresponding to the different simulation approaches (A1, A2) on both plots for the groundwater as well as the pressure heads and the water contents at 10 and 85 cm depth.

Table 8: Root Mean Square Error (RMSE) for the inverse simulations

RMSE	Plot 3					Plot 4				
	h 10 cm	h 85 cm	θ 10 cm	θ 85 cm	GW	h 10 cm	h 85 cm	θ 10 cm	θ 85 cm	GW
A 1	-40.90	-39.07	5.47	1.75		-35.78	-18.46	10.89	3.28	
A 2	-72.38	-46.54	6.76	3.20	14.66	-41.00	-24.03	13.55	1.48	17.57

The smallest residual errors were obtained for the first approach which is not surprising as the GW level was imposed and only h and θ had to be calculated. In the second approach where the groundwater level changes had to be calculated, the soil water pressure head and the water content present larger residual errors. The model preferably fitted the GW level, because data describing the GW level position were much more numerous in the inverse simulation (the groundwater level was measured automatically every 6 hours, the pressure head once a day or less).
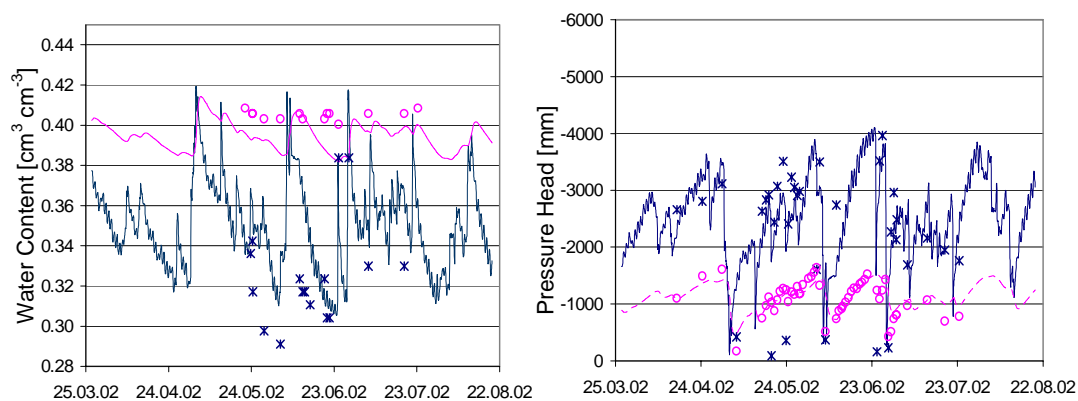
Figure 20: Observed and simulated water contents and pressure heads (plot 4, 2002) using approach 1: observed values at 10 cm (crosses), at 85 cm (circles), and simulated values (lines)
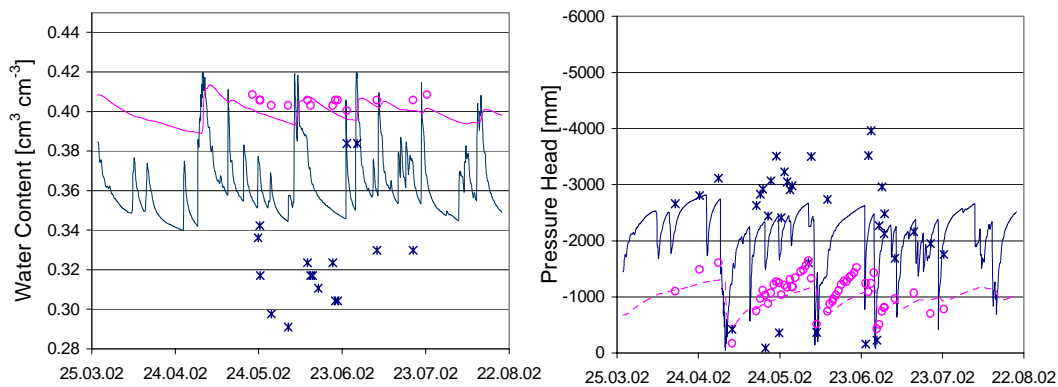
Figure 21: Observed and simulated water contents and pressure heads (plot 4, 2002) using approach 2: observed values at 10 cm (crosses), at 85 cm (circles), and simulated values (lines)

Figures 20 and 21 show the graphical analysis of the calibration results on plot 4 for the two approaches (see Appendix 5.2 for plot 3). The simulation started in late March, and data are available since late April. A good fit between observed and simulated pressure heads and water contents is achieved, when the GW level is imposed as a variable pressure boundary condition (approach 1, Fig. 20). The water contents are slightly overestimated near the soil surface and underestimated at 85 cm depth. The pressure heads are well reproduced, except for some values close to zero subsequent to precipitation.

Approach 2 matches the observed pressure heads and water contents less well (Fig. 21). The water content near the soil surface is systematically overestimated and the soil suction is underestimated. At 85 cm depth, however, the measured data are well reproduced by the model. The GW level changes are relatively well predicted (Fig. 22); the simulations slightly overestimate the depth of the GW table, especially during dry periods.
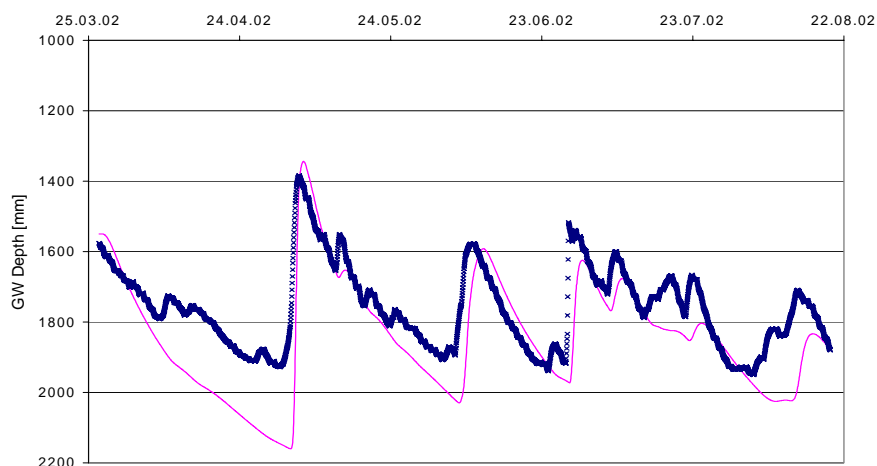
Figure 22: Observed (crosses) and simulated (line) groundwater level changes (plot 4, 2002) using approach 2

In summary, approach 1 leads to a fairly good reproduction of the observed data. Approach 2 does not match satisfactorily the observed water contents and pressure heads near the soil surface, but it allows to simulate the GW table depth.

2.3.2.   Validation

A second simulation was carried out using the data measured between April and September 2001. The simulation started on April 24 at 3 a.m. The water flow was simulated with both approaches and the Root Mean Square Error was calculated (Tab. 9). Figures 23 and 24 show the observed and simulated pressure heads and water contents on plot 4 using approaches 1 and 2, respectively.

Table 9: Root Mean Square Error (RMSE) for the validation period

RMSE	Plot 3					Plot 4				
	h 10 cm	h 85 cm	θ 10 cm	θ 85 cm	GW	h 10 cm	h 85 cm	θ 10 cm	θ 85 cm	GW
A 1	-42.14	-24.88	3.56	1.92		-44.62	-24.09	4.80	2.08	
A 2	-50.57	-33.98	4.93	2.76	11.95	-45.61	-41.03	4.97	1.44	18.26

Again, the best fit was obtained when imposing the GW level changes as lower boundary condition (Tab. 9, Fig. 23). The simulated pressure heads deviate significantly from the measured values during the first month of the validation period (Fig. 23). This can be attributed to the initial condition that assumes hydraulic equilibrium which is not in agreement with the natural conditions. Obviously, some time is needed before the effect of the initial condition is no longer perceptible. During the calibration, such a poor initial fit was not observed, because the simulations started one month earlier than the field measurements.
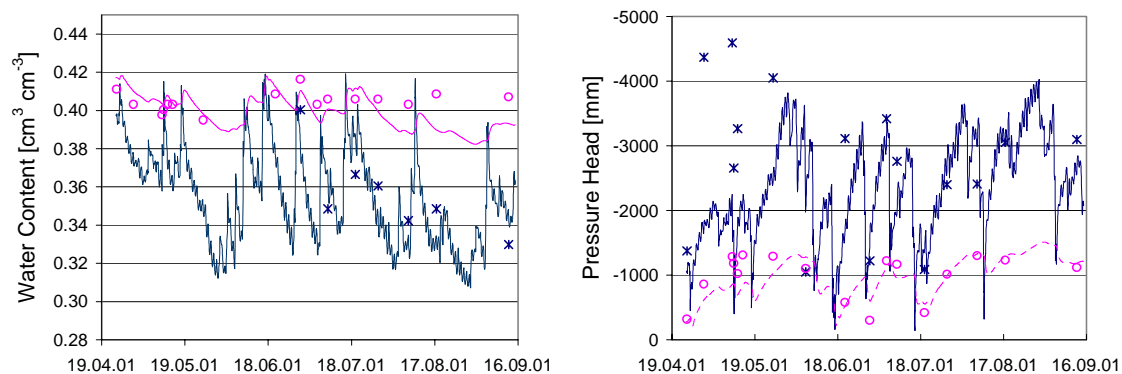
Figure 23: Observed and simulated water contents and pressure heads (plot 4, 2001) using approach 1: observed values at 10 cm (crosses), at 85 cm (circles), and simulated values (lines)

When using approach 2, the observed data are less well matched (Tab. 9, Fig. 24). The soil suction near the surface is again underestimated, even after the initial simulation phase. The water contents, however, are better matched than for the calibration period (Tab. 8, Tab. 9). The meas-

ured water contents in 2001 were generally higher than in 2002 which may be the reason for the better fit as the model has difficulties in fitting low water contents. The depth of the GW table is poorly reproduced at the beginning of the simulation (Fig. 25). From June on, however, the model matches well the variation of the GW table as a consequence of precipitation and evaporation.
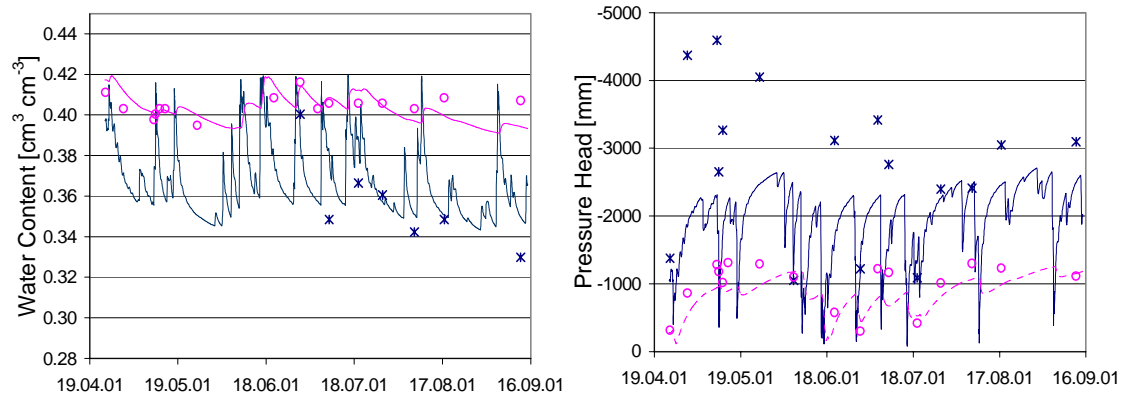
Figure 24: Observed and simulated water contents and pressure heads (plot 4, 2001) using approach 2: observed values at 10 cm (crosses), at 85 cm (circles), and simulated values (lines)
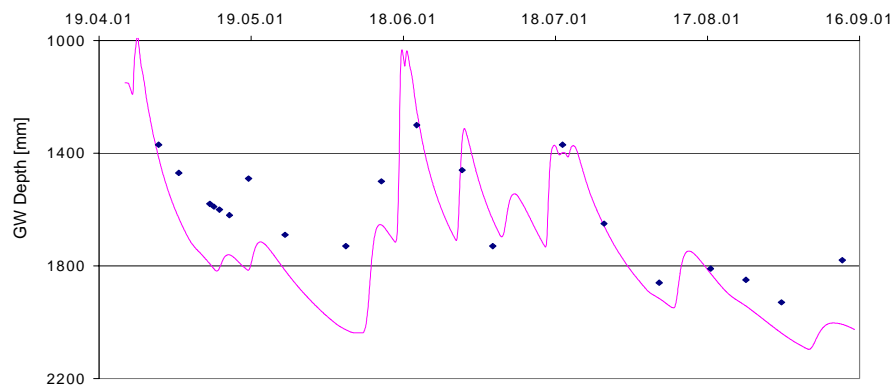
Figure 25: Observed (points) and simulated (line) groundwater level (plot 4, 2001) using approach 2

The validation process shows that the model is able to fit the observations reasonably well when using approach 1. It could therefore in principle be used to predict the pressure heads and water contents in the soil profile. Nevertheless, approach 1 requires knowledge of the GW level which is not known for future situations. With approach 2, the pressure heads and water contents in the deep vadose zone as well as the groundwater level can be relatively well predicted. Near the soil surface, however, the model results are not satisfactory.

2.3.3.   Water Fluxes

At the surface water enters or leaves the soil as a consequence of rainfall and evaporation. The Reference Evapotranspiration (further on called potential evapotranspiration), ET_0, was calculated according to the formula of Penman-Monteith. ET_0 is defined as evapotranspiration through a soil surface covered with gras when the water supply is not limited; it depends on climatic conditions only. Actual evapotranspiration, on the other hand, depends on hydrogeological and soil physical conditions, particularly on the soil water availability. With a shallow groundwater table, it can be expected that due to capillary rise the actual evapotranspiration is close to ET_0. On the experimental site, this is confirmed by the continuously high water content observed in the soil profile. Because the soil surface is horizontal, rainwater is hardly removed by runoff but accumulates as ponded water. As a consequence, an important part of the precipitation (potential infiltration) percolates into the soil (actual infiltration).

The water fluxes at the bottom of the profile differ according to the lower boundary condition (see 2.2.2): approach 1 allows fluxes in both directions at any rate and approach 2 does not allow for any flow through the lower boundary. In this section, the boundary fluxes for the different boundary conditions will be analysed.

Figure 26 shows the cumulative boundary fluxes simulated with approach 1 on plot 4 (positive values indicate upward fluxes). The actual infiltration represents 87.9 % of the potential infiltration showing that most of the rainfall infiltrates into the soil profile. The actual evaporation attains 87.6 % of the potential evapotranspiration suggesting that evaporation is not significantly limited by the soil water system. At the bottom, water enters the profile most of the time indicating that the GW level is not regulated by percolating rainwater and evaporation only. The total inflow of 248 mm at the lower boundary accounts for 42 % of the potential evapotranspiration. Only 2.6 mm of water leave the profile through the lower boundary during the simulation period.
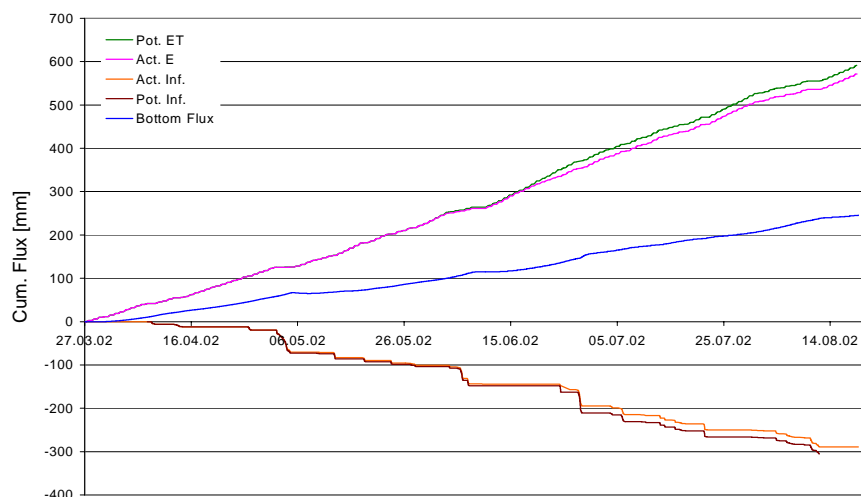
Figure 26: Cumulative Fluxes [mm] at the upper and lower boundary (approach 1, plot 4, 2002)
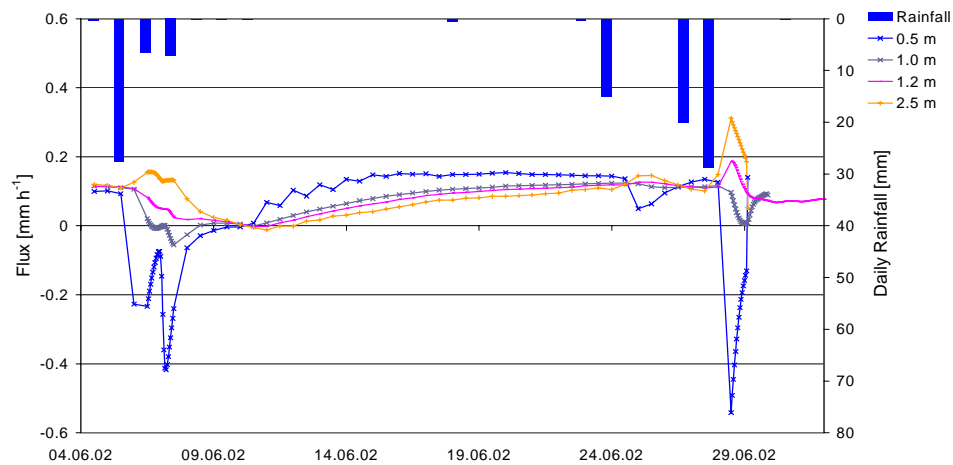
Figure 27: Fluxes [mm h^{-1}] at 0.5, 1.0, 1.2, and 2.5 m depth (lower boundary) using approach 1 (plot 4)

Average hourly water fluxes [mm h^{-1}] at different depths were calculated for June 2002 (Fig. 27). The fluxes were calculated at 12 a.m. and 12 p.m. each day and every hour on the days following to rainfall events (June 5, June 28). In early June, the model indicates upward fluxes from the bottom of the profile towards the surface (positive values, Fig. 27). Subsequent to the precipitation on June 5, water enters the soil profile through the two boundaries simultaneously: Rainwater enters the profile from the soil surface down to 1 m depth (negative fluxes, Fig. 27). At 1.2 m the flux remains positive suggesting that the zero flux level is located between 1 m and 1.2 m depth. Nevertheless, the groundwater table rose to a depth of only 1.40 m on June 6 which is below the zero flux level. Similarly, subsequent to rainfall on June 27/28, the zero flux level is located at about 1 m depth, while the groundwater level rises to a depth of 1.50 m. Therefore, in the simulations the groundwater table rise is entirely due to the inflow of water through the lower boundary and not to the drainage of rainwater. An inflow of water through the lower boundary could be caused by the drainage of water at the regional boundaries (e.g., river or slopes). This, however, should happen gradually as a retarded response to precipitation, but not simultaneously.
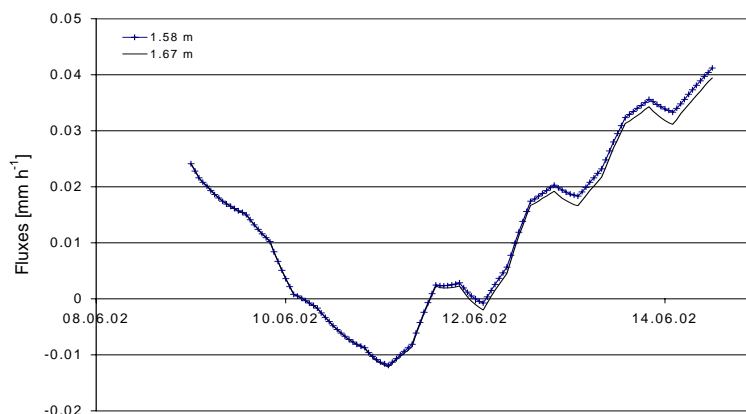
Figure 28: Average hourly fluxes above the falling GW table (1.58-1.67 m depth) between June 9 and 15, 2002.

Between June 10 and 12, the soil profile is nearly at an equilibrium state (Fig. 27). During this period, the GW level decreases (from 1.58 to 1.67 m depth), positive fluxes at the surface indicate that evaporation takes place and negative fluxes at the lower boundary suggest that water flows out at the same time. The simulated fluxes above the GW table indicate a slight drainage of rainwater between June 10 and 12 (<0.013 mm h^{-1} during 36 hours, Fig. 28). Such a little drainage (less than 0.5 mm) is not plausible, because the chemicals that were applied to the soil surface reached the groundwater right after the rainfall, suggesting that a much larger amount of rainwater must have drained into the groundwater.
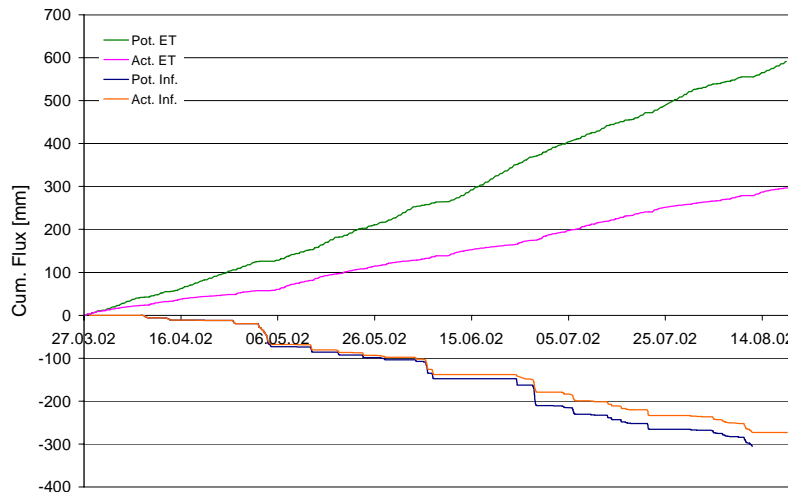
Figure 29: Cumulative Fluxes at the upper boundary (approach 2, plot 4, 2002)
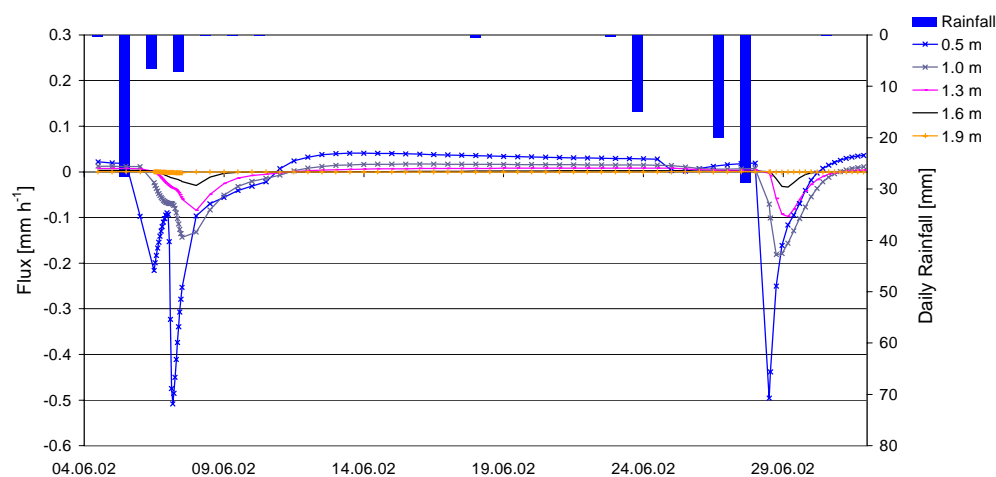
Figure 30: Fluxes [mm h^{-1}] at 0.5, 1, 1.3, 1.6, 1.9 m depth using approach 2 (plot 4)

When using approach 2, the actual infiltration reaches 272 mm corresponding to 89.5 % of the potential infiltration. No water enters the soil column at the lower boundary. Consequently, the actual evaporation is only 296 mm or 50.1 % of the potential evapotranspiration (Fig. 29). During the dry period in mid June, positive fluxes indicate an upward flow from the groundwater towards the soil surface (Fig. 30). The magnitude of the flux is lower compared to approach 1,

which is in agreement with the lower cumulative evaporation (Fig. 29). After the precipitation on June 6 and on June 27/28, the fluxes are negative down to about 1900 mm depth indicating that the GW level rise is caused by the percolation of rainwater. At greater depth, the water flow fades and becomes zero at the bottom node where the zero flux boundary condition is imposed (Fig. 30).

In conclusion, approach 1 shows very little or even no drainage to the GW after rainfall events and the GW level rise is entirely due to an inflow of water through the bottom boundary. This is not consistent with the observations, because solutes that had been applied to the soil surface appeared in the GW quickly after rainfall. In approach 2, the pressure heads and water contents near the soil surface are not well reproduced and the actual evaporation is underestimated. Obviously, the amount of infiltrated rainwater is not sufficient to sustain the important evaporation and to reproduce the high position of the GW table.

2.3.4.   Sensitivity Analysis of the Immobile Water Content

The hydraulic parameters were derived from the field measurements or from inverse modeling. The immobile water content, θ_{im}, however, was neither directly measured nor calibrated. A maximum possible θ_{im} was chosen with respect to the lowest measured water content during the study period. Consequently, a sensitivity analysis was realized to evaluate the influence of this parameter.

The most widely used technique is the 1-D sensitivity analysis (VANCLOOSTER, 1995) or the "one at the time" method (SOUTTER & MUSY, 1999), where one input parameter is gradually changed keeping the other parameters constant. The corresponding change of an objective function characterises the absolute sensitivity of the input parameter. Here, the objective functions were the cumulative actual infiltration and evaporation between late March and August 2002 (calibration period). Additionally, for approach 1, the cumulative inflow of water through the lower boundary and for approach 2, the mean GW level were defined as objective functions. The optimal value (value used for the simulations) of the immobile water content was the maximum possible (0.28, 2.3.1); therefore only lower values were considered.

When using approach 1, a small reduction of θ_{im} leads to an increase in actual evaporation, actual infiltration, and water inflow at the lower boundary (Fig. 31). The increased evaporation is related to the higher fraction of accessible soil water, as the model considers that only mobile water can evaporate. The higher evaporation is sustained by a stronger infiltration and an increased inflow of water through the lower boundary. When θ_{im} is further reduced, the model becomes less sensitive because the potential evapotranspiration is reached and no further increase is possible. The changes of θ_{im} lead to a slight gradual worsening of the h and θ prediction in the unsaturated zone.
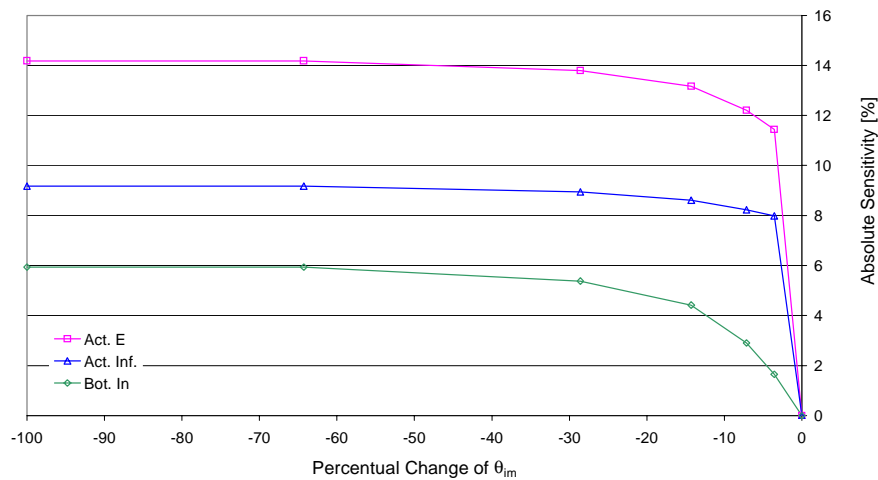
Figure 31: Influence of the parameter θ_{im} on the cumulative actual infiltration (Act. Inf.), the cumulative actual evaporation (Act. E), and the cumulative inflow of water at the lower boundary (Bot. In) for approach 1 (optimal value of $\theta_{im} = 0.28$).
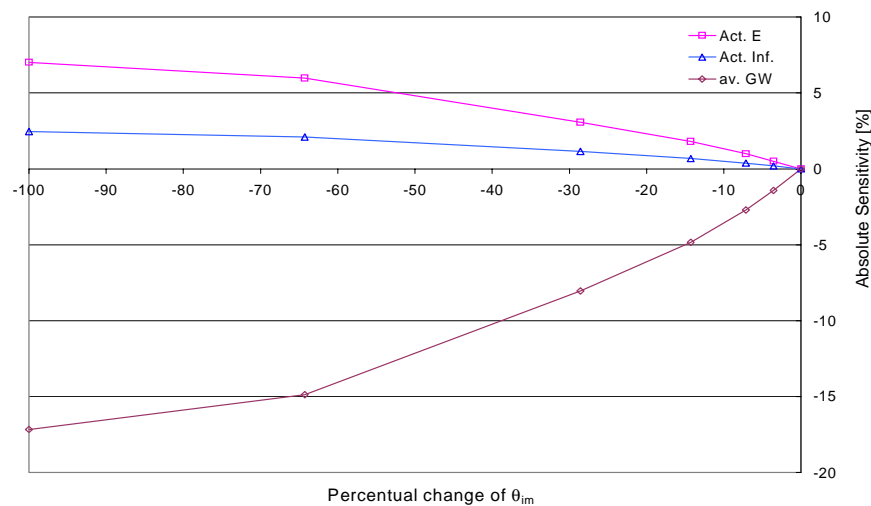
Figure 32: Influence of the parameter θ_{im} on the cumulative actual infiltration (Act. Inf.), the cumulative evaporation (Act. E), and the average groundwater table depth (av. GW) for approach 2 (optimal value of $\theta_{im} = 0.28$).

With approach 2, the surface fluxes are less sensitive to changes in θ_{im} (Fig. 32). The gradual increase of evaporation is sustained by a slightly higher infiltration and even more by a stronger capillary rise: The decrease of θ_{im} results in a considerable lowering of the GW table (av. GW, Fig. 32). Additionally, the lowering of the immobile water content causes a deterioration of the fit between observed and simulated h and θ values.

In conclusion, the absolute sensitivity of the θ_{im} value is limited to less than 20 % for the chosen objective functions. Concerning the model accuracy (e.g., the reproduction of observed h and θ values), approach 1 is less sensitive to a change in θ_{im}, because it can adjust by increasing the inflow of water through the lower boundary. In approach 2, lower immobile water contents lead

to a worse prediction of the GW level. The value of 0.28 chosen in the model leads to the best simulation results.

2.4.   Transport Simulations

In the unsaturated zone, low (or even zero) chemical concentrations were observed at some shallow suction cups, while high concentrations appeared at deeper instruments (Fig. 9, Fig. 10). These observations may be related to non-equilibrium flow, bypassing of suction cups, bad functioning of the soil water samplers, etc. and cannot be reproduced by the model.

In the GW, the chemicals are subject to 3-dimensional processes (e.g., lateral transport), whereas the model is exclusively 1-dimensional. Moreover, the GW samples could not be taken at a specific depth, but they represent unknown mixtures of the water column between the GW table and lower end of the piezometer (2.5 m; see sampling method, Ch. 3, 3.4). As a consequence, the absolute values of observed and simulated GW concentrations cannot be compared, but only the general tendencies of the concentration changes can be considered.

For the same reasons, a calibration of the transport parameters is difficult. Hence, they were either directly measured in the laboratory (distribution coefficient, degradation constant) or assessed by roughly adjusting the simulations to the available concentration data (dispersivity, mass transfer coefficient, fraction of adsorption sites in contact with the mobile liquid).

In order to reproduce the quick transfer of the solutes through the vadose zone, a high dispersivity (1000 mm) had to be assumed. This value is clearly exaggerated and must be considered as a lumped parameter accounting for even faster transport than calculated with the MIM concept. A mass transfer coefficient, α, of 10^{-4} h^{-1} was assumed, which is in the range of the values found by VANCLOOSTER et al. (1993) in undisturbed sandy soil columns. The distribution coefficient and the degradation constant were chosen according to the column experiments of ZHANG (2003, Tab. 5). It was presumed that adsorption takes place in the immobile phase only (fraction of adsorption sites in contact with the mobile liquid, $f = 0$), an assumption considered appropriate for worst case estimations (JARVIS, 1998). The transport of atrazine and isoproturon and their concentration in the GW was very similar (Fig. 14). Consequently, the simulations were realized for atrazine only.

2.4.1.   Simulated Concentrations in the Saturated Zone

The transport was simulated for plot 3 and 4 using both approaches. The chemicals were introduced with the first rainfall subsequent to the application (on June 3 at 2 p.m.). Figures 33 and 34 show the observed and simulated atrazine concentration in the GW on plot 4 using approach 1 and 2, respectively (see Appendix 5.3 for plot 3). The simulated GW concentrations were calculated as an average over the water column.
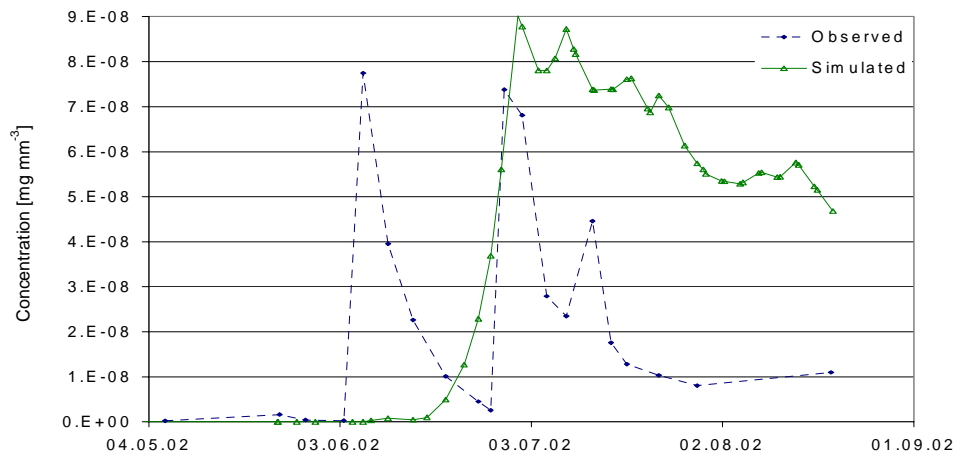
Figure 33: Observed and simulated atrazine concentration in the groundwater using approach 1
(plot 4, 2002).
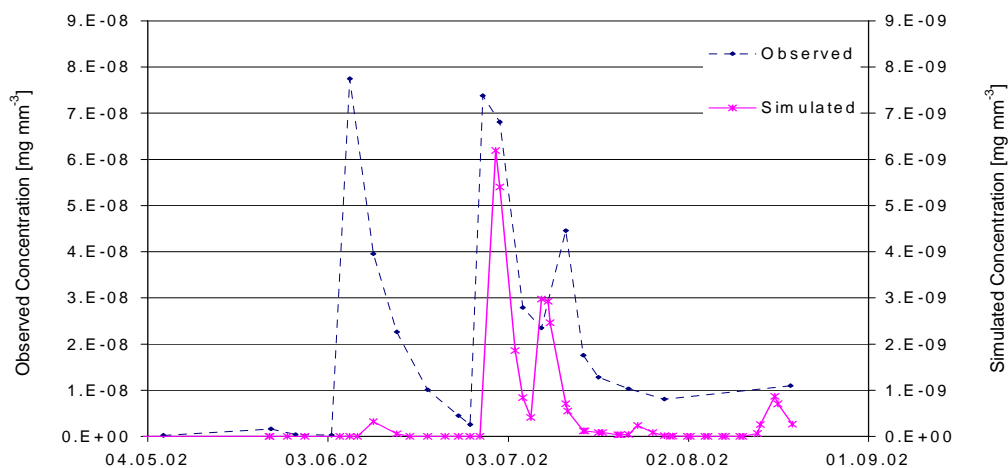
Figure 34: Observed and simulated atrazine concentration in the groundwater using approach 2
(plot 4, 2002).

Approach 1 predicts quite few herbicides in the groundwater in early June, when the first peak
was observed. The second peak is well matched, although the simulated concentration starts to
rise earlier than observed in the field. After the maximum, a concentration decrease is indicated
by the model, but the simulated concentrations decrease slower than observed on the plots (Fig.
33).

With approach 2, a relatively higher first herbicide peak is predicted in early June. The shape of
the second and third concentration peaks are well reproduced, although the third concentration
maximum occurs slightly earlier than observed. In contrast to approach 1, the concentrations re-
main low from mid July on. Another attenuated concentration maximum is predicted in mid Au-
gust that cannot be confirmed due to a lack of data.

In summary, the relative magnitude of the chemical peak observed after the first rainfall subse-
quent to the application is significantly underestimated by the model. The second concentration

rise is well reproduced with both approaches, but approach 1 does not reproduce the rapid concentration decrease afterwards. The order of magnitude of the simulated concentrations is quite different with the two approaches.

2.4.2.   Simulated Concentrations in the Unsaturated Zone

Figures 35 and 36 show the observed and simulated atrazine concentration at 10 and 30 cm depth on plot 4 for approach 1 and 2, respectively (see Appendix 5.4 for plot 3).
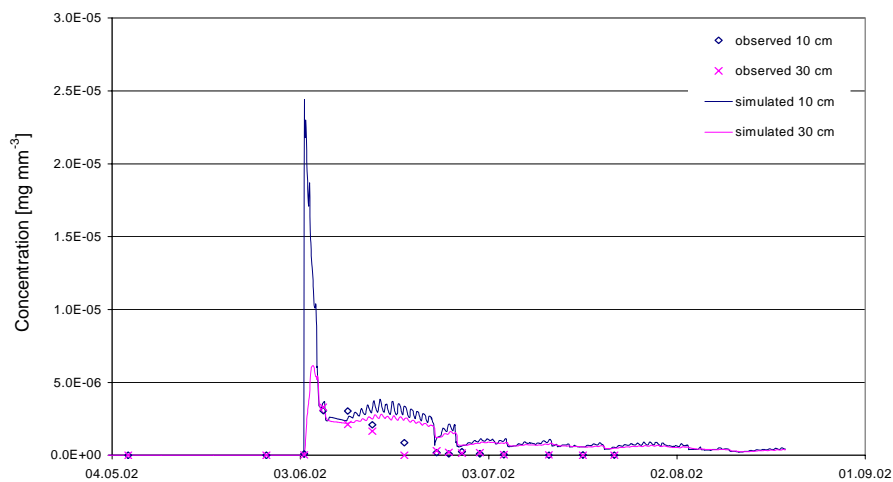
Figure 35: Observed and simulated atrazine concentration in the mobile water at 10 and 30 cm depth (plot 4, 2002) using approach 1
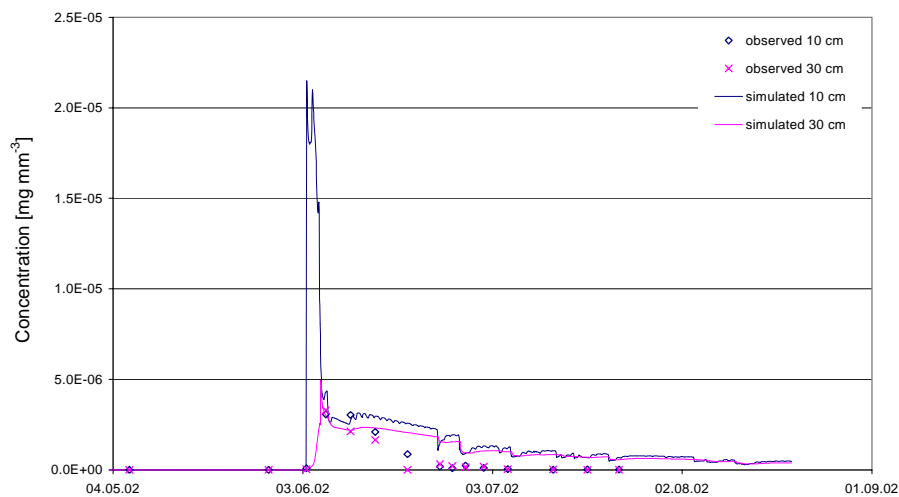
Figure 36: Observed and simulated atrazine concentration in the mobile water at 10 and 30 cm depth (plot 4, 2002) using approach 2

Here, the concentration magnitude and the temporal development is very similar for both approaches. As a consequence of the high dispersivity and the large immobile water content, the simulations indicate a huge concentration peak near the surface just after the beginning of the

rainfall. No measurements of the concentration in the soil solution are available at that time and therefore, the simulated high peak at 10 cm depth cannot be confirmed. At 30 cm depth, the simulated peak is considerably attenuated (Fig. 35 and 36). Both approaches simulate the concentration decrease fairly well even though the simulated values remain slightly higher than observed.

2.4.3.   Simulated Concentration-Depth Profiles

Concentration-depth profiles on plot 4 were calculated at different times for both modeling approaches (Fig. 37).

In approach 1, the chemical reaches a considerable depth only one day after the first heavy rainfall subsequent to the application (06.06.02, Fig. 37). This is not surprising regarding the high dispersivity of 1000 mm and the important immobile water content. During the following days and with further rainfall on June 6 and 7, the solute infiltrates deeper into the soil profile reaching a depth of 1.20 m (Fig. 37, A1). The dry period in mid June is characterized by strong evaporation and upward water fluxes over the whole profile (Fig. 27, p. 66). In spite of this, a considerable amount of chemicals is transported deeper into the profile (24.06.02, Fig. 37) explaining why the simulated concentration rises even before the rainfall at the end of June (Fig. 33). A downward transport of solutes during a dry period with upward fluxes has been described as "flow against dispersion" by ELRICK et al. (1994). The chemicals are transported downward by the dispersive flux against the evaporative water flow. This clearly mathematical phenomenon is caused by the exaggerated dispersivity and intensified by the high immobile water content.
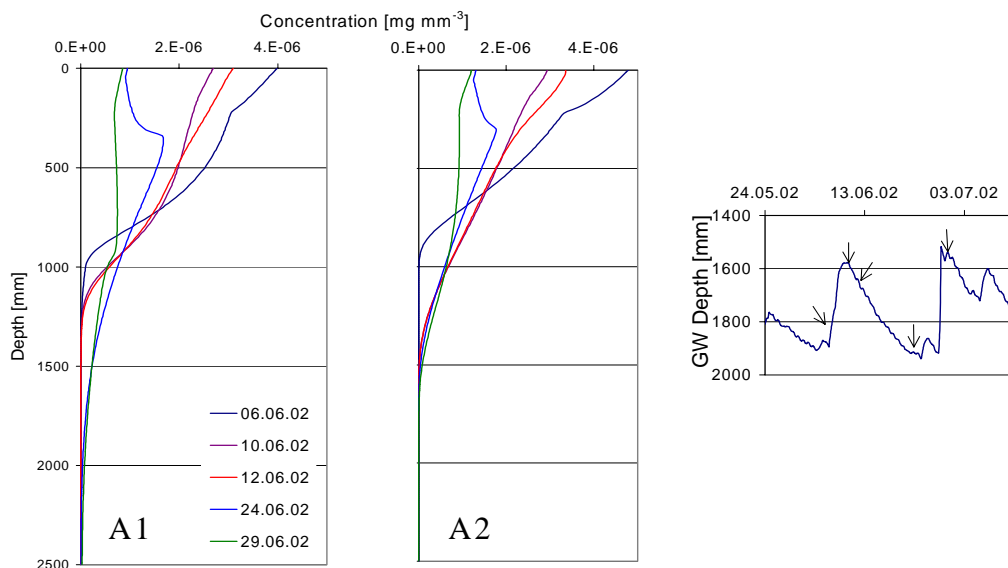
Figure 37: Simulated concentration-depth profiles on plot 4 at different times (for approach 1 and 2) and groundwater table depth (pointers indicate the time corresponding to the concentration profiles).

When using approach 2, the chemical reaches a depth of 1.50 m subsequent to the rainfall in early June (10.06.02, Fig. 37, A2). During the rest of the simulation period, only few solutes are transported to greater depths and no chemicals reach the bottom of the profile. The downward transport against the water flow discussed above does also occur when using approach 2, but as

the evaporation is much lower, its effect is far less important. This explains why in approach 2 the magnitude of the simulated concentrations are lower compared to approach 1.

When using approach 2, hardly any chemicals are predicted in the groundwater as long as the groundwater level falls. Only after the rainfall on June 27/28 and the quick rise of the GW table, a peak appears in the saturated zone (Fig. 34). This concentration maximum is to a great extend caused by the GW table rise and the solution of chemicals from the deep vadose zone. Each new rise of the groundwater table during the following simulation leads to a further concentration peak. The influence of the rising GW table is also visible in approach 1 where small temporal peaks are visible on the slowly decreasing concentration (Fig. 33).

2.4.4.   Sensitivity Analysis of the Immobile Water Content and the Dispersivity

For the transport model, a sensitivity analysis was realized in order to assess the influence of the immobile water content on the herbicide concentration in the GW. Moreover, the high dispersivity chosen in the model causes a significant downward flux against the evaporative water flow when using approach 1 (2.4.3.). Therefore, the effect of a reduction of this parameter was also evaluated in a sensitivity analysis.

Again, the "one at the time" method was used (2.3.4.) and one of the parameters (dispersivity or immobile water content), was gradually changed in two subsequent analyses. The objective function was the mean atrazine concentration in the GW during the calibration period. Figure 38 shows the absolute sensitivity of the GW concentration for both parameters when using approach 1 (A1) and approach 2 (A2).
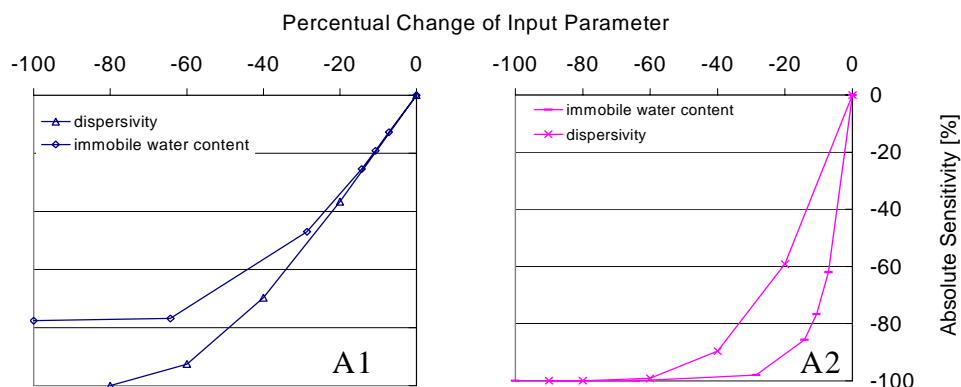
Figure 38: Influence of the immobile water content and the dispersivity on the mean herbicide concentration in the GW for approach 1 (A1) and approach 2 (A2). The optimal values are 0.28 cm^3 cm^{-3} and 1000 mm for the immobile water content and the dispersivity, respectively.

Both approaches are sensitive to a change of the transport parameters; a reduction of the parameters leads to a reduction of the herbicide concentration in the GW.

Approach 2 is significantly more sensitive than approach 1; a decrease of the transport parameters reduces considerably the depth of the sharp solute front in approach 2. Consequently, the

rising GW level after a rainfall event hardly reaches the chemicals in the deep vadose zone anymore, thus leading to an important reduction of the GW concentration.

With approach 1, the influence of the dispersivity is greater than the influence of the immobile water content, contrary to what is observed with approach 2. This confirms that in approach 1 the artificial transport against the evaporative water flow caused principally by the high dispersivity value is an important component of the solute movement. In approach 2, on the other hand, this effect is less perceptible and therefore influences the GW concentration less.

Finally, the sensitivity analysis shows that both, the immobile water content and the dispersivity, have a considerable influence on the herbicide transport in the soil and consequently, on the concentrations in the GW. Since the simulations underestimate the concentration observed in the GW, choosing lower parameter values would still worsen the simulation results.

2.5.   Discussion

The model HYDRUS-1D was used for simulating water flow and solute transport on the experimental plots assuming a high degree of physical non-equilibrium (MIM concept).

For the hydraulic simulations, two different lower boundary conditions were considered leading to two modeling approaches:

- When assuming a variable pressure head lower boundary condition (A1), the model fits well the observed pressure heads and water contents. The strong evaporation is well reproduced. Subsequent to precipitation, however, the simulations indicate only few drainage to the GW; the observed GW level rise is not a consequence of percolating rainwater, but it is due to an inflow of water through the lower boundary. This is not consistent with the observation that high herbicide concentrations appear in the GW quickly after rainfall subsequent to the application.

- When no inflow of water is assumed at the bottom boundary (A 2), the groundwater level changes are well predicted as a consequence of precipitation and evaporation. Notwithstanding, the model cannot reproduce satisfactorily the pressure head and the water contents near the soil surface, and the high evapotranspiration occurring in the region is significantly underestimated.

It must be concluded that the lower boundary condition cannot be exactly defined. Either the model is too unrestricted resulting in unreasonable water fluxes at the bottom node or the soil column is considered isolated and excluded from the regional water flow. A correct approach has to limit the availability of water to realistic times and amounts.

The transport of the chemicals as observed in the field experiment was extremely quick. In order to account for this rapidity, a high dispersivity value (1000 mm) together with a great immobile water content were assumed. The simulations still do not reproduce satisfactorily the high concentrations observed after the first rainfall in June 2002. The high concentrations occurring in late June and July 2002, on the other hand, are indicated by the model and are a consequence not only of the solute transport towards the deep vadose zone, but also of the substantial groundwater level rise subsequent to rainfall events and the dissolution of the chemicals from the deep vadose zone.

In conclusion, the model HYDRUS-1D is not adapted for the use as a predictive tool because two principal problems turned up during the simulations:

- In the specific context of the observation area, where the shallow GW influences considerably the water conditions in the unsaturated zone, a correct simulation of the water flow depends to a great extend on a realistic definition of the lower boundary condition. When using a one-dimensional model, however, the boundary conditions cannot be correctly defined. The problem could probably be solved by using a three-dimensional global (saturated-unsaturated) model or, probably, an unsaturated 1-D model coupled to a 3-D saturated model.

- Even with the MIM concept, it is difficult to reproduce the extremely rapid transport observed after rainfall events. Dual-permeability models, where water flow in the matrix is possible as well, are often used to simulate transport in macropores or interaggregate pores (SIMUNEK et al., 2003). Such a model would probably better reproduce the observed rapid transport.

REGIONAL OBSERVATIONS

Chapter 6

Monitoring of the Groundwater

The regional study is the main contribution of the HYDRAM laboratory to the European project PEGASE. The objective is to create a data set including information about herbicide contaminations in an alluvial aquifer with a shallow GW table. The data will further be used by other partners of the project to develop and test modeling tools that allow to simulate the fate of herbicides in GW systems. In this study, the observations are complementary to the local experiments and help to evaluate the contamination risks of the GW.

The surveyed region (400 ha that we will call observation 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. 39). In this chapter some general characteristics of the Rhône River Valley are first presented and then, the method and the results of the monitoring are described.
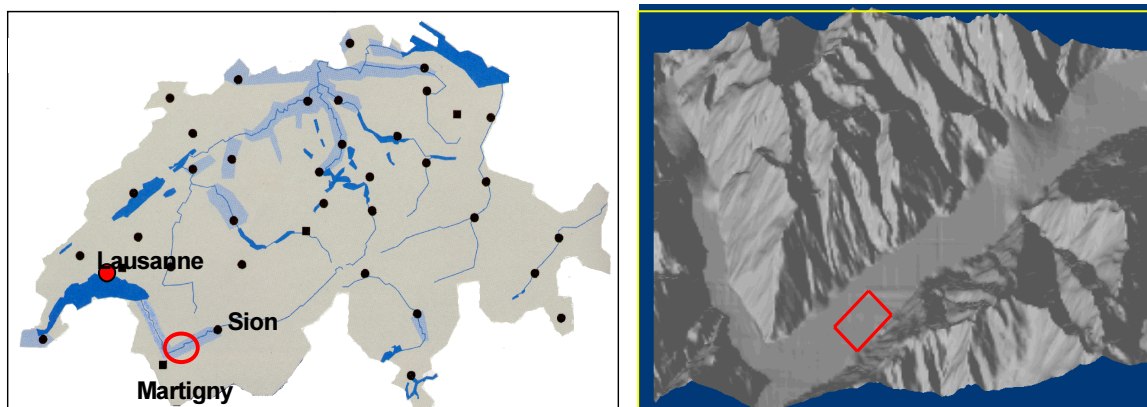
Figure 39: Map of Switzerland and 3D view of the Rhône River Valley. Rectangle: observation area.

1.   Characteristics of the Observation Area

1.1.   Geology and Morphology

Near Martigny, the Rhône River Valley is composed of two crystalline massifs: the "Massif de Mazembroz" on the right bank and the "Massif du Montblanc" on the left bank. The "Massif de Mazembroz" consists of precambrien and palaeozoic rocks like marble, amphibolites, migmatites, and granites formed during the caledonian and variscan orogeny. In the northeast they are overlain by the younger helvetics composed of metamorphic calcareous rocks of Triassic and Jurassic age. The centre of the "Massif du Montblanc" is made up of Variscan granitic rocks and permian rhyolite. At its eastern part, they are overlain by sedimentary rocks (schists, quartzites, dolomites, gypsum) of Triassic, Jurassic and Cretaceous age that formed in the helvetic and penninique basin.

The trough of the valley is filled with quaternary sediments deposited during a sequence of glacial and interglacial periods. According to seismic measurements performed by BESSON et al. (1993) the thickness of the loose sediments can reach 400-500 m. Since the fading of the glaciers, the Rhône River system deposited its alluvial sediments that were interrupted by lacustrine periods. On the left bank of the river, the zone between the slope and the main canal "Canal du Syndicat" (Fig. 42, p. 84) has long been marshland (GÉOVAL, 1984).

There is a sharp change in morphology between the slope and the plain; small debris fans are located at the bottom of the slope except for the region upstream of Charrat. Within the plain the slope is gentle (1 ‰, GÉOVAL, 1984). Natural boundaries of the observation area are the river in the northwest and the mountains in the southeast. Furthermore the "Canal du Syndicat" and a highway mark the landscape of the observation area (Fig. 42, p. 84).

1.2.   Soil Properties

In the 1980s, the construction of dams along the Rhône River was suggested for the production of hydraulic energy (HYDRO-RHÔNE project). Investigations dealing with the impact of the dams on agriculture and groundwater included many bore holes and drillings as well as the analysis of soil and water samples. Because the alluvial and lacustrine deposits are highly heterogeneous, a regionalization and generalization of the huge data sets was worked out in two research studies from which most of the following informations were taken (SOUTTER, 1996; DI GIOIA, 2002).

The surface soil consists mainly of loam and sand and has an average thickness of 3-4 m. Nevertheless, it may locally reach a thickness of 7-8 m or be completely absent (LANDRY, 1986). It is underlain by a 2.5 to 18 m thick sandy gravel layer that forms the generally unconfined upper aquifer. This aquifer can be further subdivided into coarser and finer horizons demonstrating the great spatial variability of alluvial deposits due to changes in the river's water power or inondations. Clay and loam of glacio-lacustrine origin separate the upper and the lower aquifer (LANDRY, 1986). The thickness of the lower aquifer is poorly known.

An attempt to regionalize and simplify the heterogeneous soil profile was undertaken by DI GIOIA (2002) using the REGIS method (developed by the Netherlands Institute of Applied Geoscience TNO, see www.nitg.tno.nl/ned/projects/regis/index.shtml for method description). He defined the following lithologic units:

- 0 - 3.4 m : upper loamy soil
- 3.4 - 11.8 m : upper gravel
- 11.8 - 17.5 m : lower loamy soil
- 17.5 - 25.5 m : lower gravel

The saturated hydraulic conductivity of the surface soil layer varies between 10^{-4} to 10^{-6} m s^{-1} (RÉGAMEY, 1988). The upper gravel layer locates the first generally unconfined aquifer and has a saturated hydraulic conductivity of $0.5 \cdot 10^{-4}$ and $2.5 \cdot 10^{-4}$ m s^{-1} (GÉOVAL, 1984).

The general properties of the surface soil are known from a statistical analysis of 511 samples taken in the Rhône River Valley in the 1980s (SOUTTER, 1996). The organic matter content varies between 0.5 and 1.5 % (95 % of samples), although maximum values of 10 % may appear near the soil surface (0 - 0.3 m). 80 % of the soil samples had clay contents lower than 15 %,

while the maximum observed clay content reached nearly 40 %. Consequently, the soil's Cation Exchange Capacity is generally less than 20 meq 100 g^{-1}. The pH of the soil is slightly alkaline varying between 7.5 and 8.5 for most samples. The electrical conductivity measured in soil-water suspensions with a pondered ratio dry soil to water of 1/5 was lower than 0.35 dS m^{-1} in 75 % of the samples; the maximum measured value was 2 dS m^{-1}. A former study realized near the observation area had shown that the soil was locally endangered by salinization due to a strong capillary rise of groundwater during summer (LAVANCHY, 1991).

1.3.   Groundwater Characteristics

The generally unconfined groundwater table has a shallow depth varying between 1 and 2 m. Due to the snow melt, the water level of the Rhône River is higher in summer causing an increase of the GW table. In general, maximum water levels appear in mid July and minimum levels in mid January. These seasonal changes of the GW level are more pronounced next to the river (up to 1.4 m) and less important within the plain (average of 0.4-0.6 m, DI GIOIA, 2002). Short term local variations of the GW level may superpose on the seasonal changes. According to LANDRY (1986), a heavy precipitation of 15-20 mm d^{-1} causes a noticeable water table rise. During dry times on the other hand, the strong capillary rise and upward fluxes due to evaporation may cause a decrease of the groundwater table.

Within the plain the GW flows mainly parallel to the Rhône River with an average gradient of 1 ‰ (RÉGAMEY, 1988). The water table contour lines (Appendix 6.2, DI GIOIA, 2002), however, show a significant inflow of water from the river and the slopes. During summer, hydraulic gradients next to the river may reach 5 ‰, while in winter they remain below 2.2 ‰. The region's principal canal "Canal du Syndicat" (Fig. 42, p. 84, further on called "main canal") serves as a drainage system, especially during high waters; its level is about 1 m lower than the GW (LANDRY, 1986). Near the slopes, water infiltrates into the aquifer causing a GW flow towards the northwest (Appendix 6.2).

The groundwater's average temperature is 9 °C (LANDRY, 1986). Since the river water is colder (5 °C), lower GW temperatures occur where river water infiltrates. Similarly, electrical conductivities of up to 2.3 dS m^{-1} were measured in the GW in July 1984, while the river water is less mineralized (0.1-0.3 dS m^{-1}). Thus, where river water infiltrates into the aquifer, electrical conductivities are generally low. The average sulfate and the chloride content of the groundwater are <100 mg l^{-1} and 20 mg l^{-1}, respectively, although higher concentrations may appear between the slopes and the canal due probably to inflow of greater concentrations from the hillside. The nitrate concentration is higher in summer than in winter revealing its agricultural origin; mean concentrations are 10 mg l^{-1}, but values as high as 120 mg l^{-1} were observed in the vicinity of a vineyard (LANDRY, 1986).

1.4.   Climate

Three meteorological stations, two of the Swiss Meteorological Service (Martigny and Sion) and one of the Valais canton (Saxon[2]) are located near the observation area (Fig. 39).

---

2.   located between Martigny and Sion

Due to the surrounding high mountain ranges (>3000 m), the climate in this part of the Rhône River Valley is very particular. Important solar radiation, high temperatures as well as strong winds, and often low relative humidities lead to high evaporation and recurrent water deficiencies in late summer (LAVANCHY, 1991).

Despite the small distance of less than 30 km between Martigny and Sion, there is a considerable upstream reduction of precipitation; the mean annual rainfall is 778 mm at Martigny and 600 mm at Sion representing a reduction of 22 % (SOUTTER, 1996). The average monthly precipitations display a slightly drier period during spring (March to May, Fig. 40). There may however be strong variations from one year to the other.
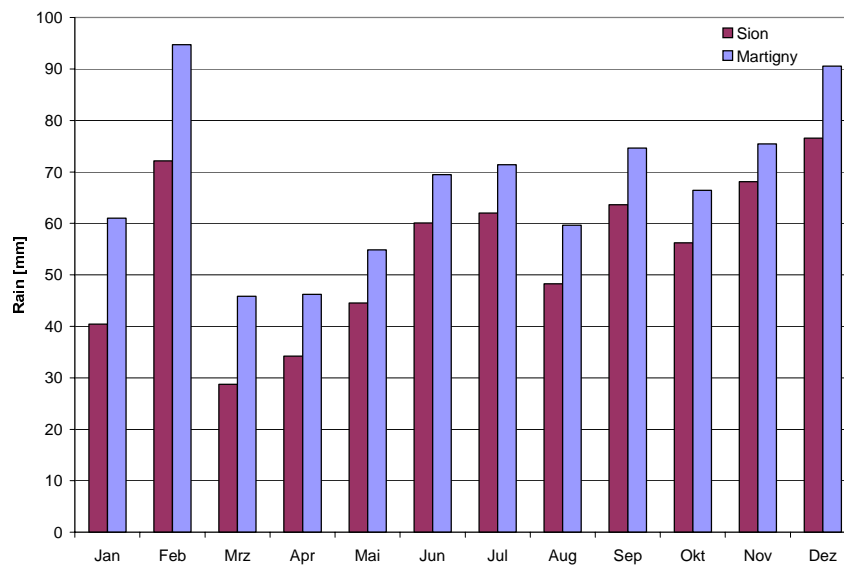
Figure 40: Average monthly rainfall in Martigny and Sion between 1990 and 1997
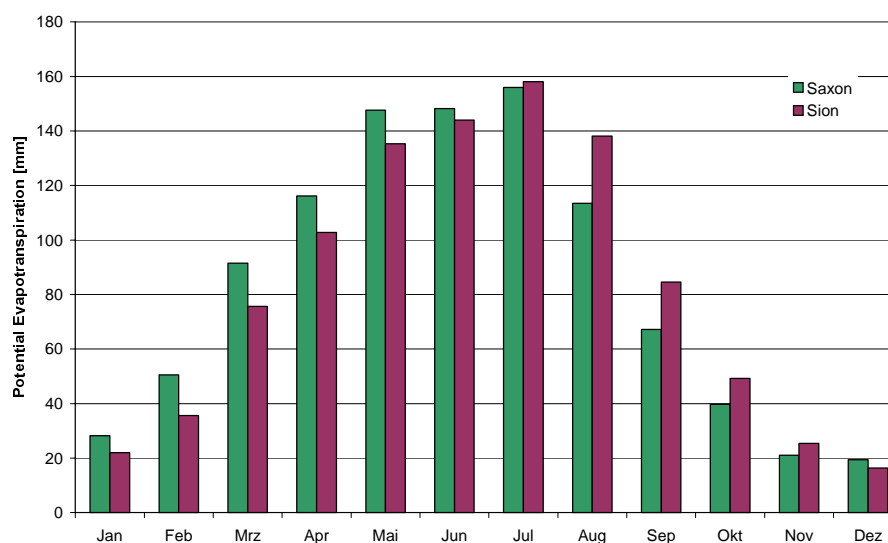
Figure 41: Average potential evapotranspiration in Saxon and Sion between 1990 and 1997

At the same time, there is an upstream increase in annual evapotranspiration. According to SOUTTER (1996), evapotranspiration may rise by 30 to 40 % between Martigny and Sion. The mean annual potential evapotranspiration in Sion is 650 mm y^{-1}. Monthly values from Saxon and Sion show that the potential evapotranspiration increases from February to July and decreases thereafter (Fig. 41). While from December to June evapotranspiration is lower at Sion than at Saxon, it gets superior at Sion in late summer and autumn.

The annual water balance is positive at Martigny and slightly negative at Sion. The monthly water balances, however, show negative values at both locations during summer (April to July at Martigny and April to September at Sion).

1.5.   Agriculture

The mild climate and the easy accessible water favour agriculture in the region. Fruit trees, vegetables, and corn cover most of the surface within the plain, while on the slopes vineyards predominate with some isolated apricot trees. The information in this section was obtained through interviews with the farmers of the region.

Most fields are equipped with a sprinkler irrigation system used primarily to protect fruit trees from frost during spring. During April and May, in case of frost threats, farmers irrigate their fields during the night and early morning. Rough estimates of the water supply during an irrigation are 10-40 l m^{-2}. The frequency of irrigation varies considerably from year to year. In 1998, anti-freezing irrigation took place approximately 10 times, while in the years 2000 to 2002 it was not necessary. The overall tendency is to minimize irrigation; some farmers even apply agrochemical substances that retard the fruit tree blossom to the time after freezing. In specially dry summers, irrigation may be necessary to overcome the lack of water, but in 2001 and 2002 this was hardly necessary either. The irrigation water is most often taken from the groundwater (agricultural wells are 13-16 m deep), sometimes also from canals or from the urban water supply.

Herbicides are applied to the fields once or twice a year. The moment of application is different according to the cultivation: vineyards are generally treated in March, fruit trees from late April to early May and if necessary again in late July or August, corn is typically treated in late June. On uncovered vegetable fields, herbicides are applied in April, while on covered fields they may be applied at nearly any time from January on. Farmers use different commercial herbicide products. The active ingredients are often simazine and diuron for vineyards, simazine, diuron, and terbutylazine for fruit trees, and atrazine for corn. Vegetables may be treated with simazine or terbutylazine, but many other substances are used for the various cultures. Most commercial products are liquids that have to be diluted with water and are sprayed over the fields from big tanks. A washing center with special discharge conduits exists in the village of Charrat to clean the tanks and other devices of pesticide application. As for the irrigation, it is extremely difficult to quantify the overall herbicide use. Generally, farmers apply the quantity indicated by the supplier of the commercial product, but many different products are used and some farmers even change the substance each year.

2.   Method

2.1.   Principle

As pesticide concentrations may change seasonally and locally over small distances, the GW has to be analysed over short time intervals at several specific sites. Piezometers had already been installed in the observation area during previous studies, but their properties (penetration depth, screening interval and length) were not precisely known. Therefore, 13 new piezometers have been installed in March 2001 near locations where the hydraulic head of the groundwater is surveyed twice a year by the Centre of Alpine Research (CREALP). The piezometers were arranged along four transects: two longitudinal transects in the direction of the groundwater flow (T1, T 2, Fig. 42) 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, they were screened over their entire length (0.5 mm slot width) except for the upper meter. The tubes were placed in hand-drilled holes (EIJKELKAMP drill-set) and the void around the tubing was sealed with bentonite mud. In order to sample the surface-near groundwater, the depth of the piezometers was less than 3.50 m. Consequently, according to the generalized soil profile (DI GIOIA, 2002; section 1.2), the pumped water stemmed from the upper loamy soil layer and not from the upper gravel layer defined as the first aquifer.
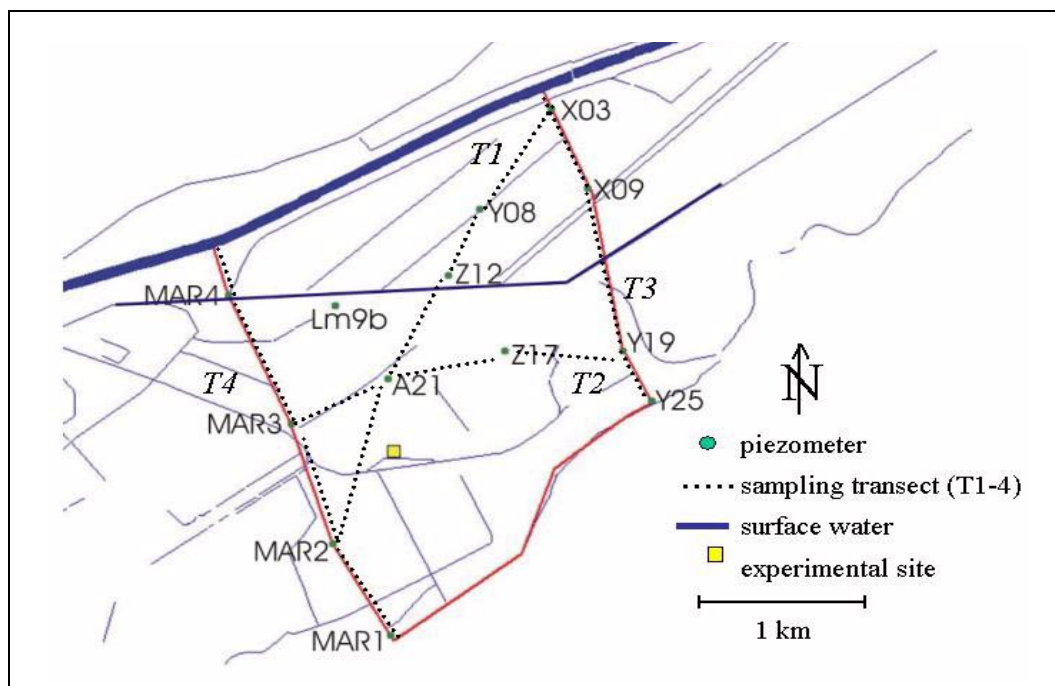
Figure 42: Observation area, location of the piezometers, and transects

Prior to the first sampling, the piezometers were purged by injection of compressed air in order to remove particles or dirt that might result from the installation. Groundwater samples were taken since the beginning of May 2001 approximately every 2 weeks until mid August, and during winter once a month. According to the findings of 2001, the sampling frequency was adjusted in 2002 and weekly samples were taken during June and July 2002. In the main canal, sampling took place once a month in the summer 2002.

The herbicides monitored within this study were selected in coordination with the other groups of the PEGASE project and according to former investigations:

Two measurement campaigns of pesticide concentration in the GW had been realized by the Office of Environmental Protection (SPE) of the Valais canton. A first sampling was carried out during summer at a high position of the water table (July 1997). In every piezometer of the Transect 4 (MAR1-MAR4, Fig. 42) pesticides were detected: atrazine in MAR1 (0.1 μg l^{-1}) and MAR4 (0.017 μg l^{-1}), isoproturon in MAR2 (0.42 μg l^{-1}) and terbutylazine in MAR3 (0.013 μg l^{-1}). The second campaign was performed in the winter (February 1998) at low groundwater levels; at that time, the concentrations measured in the piezometers of Transect 4 were below the detection limit.

Moreover, the CIPEL (Int. Commission for the Protection of the Leman Lake) had established a list of pesticides to be monitored in surface waters of the lemanic watershed (JOUANY, 1995) and did two measurement campaigns between 1995 and 1997. Three herbicides were detected in nearly all the samples: atrazine, simazine, and terbutylazine. In some places, isoproturon and diuron were also detected (CORVI & KHIM-HEANG, 1997). Even though the study concerned surface water, it gives some indications about the substances that are likely to appear in the GW.

Consequently, the herbicides analysed in the GW within this study were atrazine and its metabolite deethylatrazine, simazine, terbutylazine, diuron, and isoproturon.

2.2.   Sampling Procedure

The most important goal when sampling GW is to collect a representative and clean sample. Spatial variability and heterogeneities within the alluvial aquifer are facts, but representativeness has to be maximized by using accurate and reproducible techniques. Guidelines for GW sampling are described not only by national authorities (USEPA, PULS & BARCELONA, 1996), but also by researchers (CREASY & FLEGAL, 1999).

The GW was pumped using a peristaltic pump and high purity TYGON tubes (8 mm i. d.) generally used in the food industry. Preliminary tests confirmed that the groundwater chemistry was not modified by the sampling technique. The tubing of the peristaltic pump does not adsorb any pesticides, but some substances were released into the GW at the beginning. These chemicals did not interfere with the pesticide analysis and the leaching ceased quickly. After each sampling, the tubing was cleaned with at least one pump volume of a 20 % alcohol-water solution.

A piezometer has to be purged prior to sampling; preferably, this was done according to the low-flow purging technique (PULS & BARCELONA, 1996) where water is pumped at a low rate thus minimizing the drawdown in the piezometer. Flow rates were in the range of 0.1-0.5 l min^{-1}. The sampling tube was placed near the top of the water column in order to sample the upper part of the groundwater. The water was conducted in a Flow-Through Cell, where the pH, the temperature, and the electrical conductivity were measured. A sample was taken, when the physical parameters reached a constant value. At some piezometer locations, the hydraulic conductivity was too low to pump continuously. In these cases, the water volume of the piezometer was entirely removed twice before collection of the sample. When the water level had reached its initial position again, the pumping tube was positioned in the upper part of the water column and a sample was taken directly into a certified clean glass bottle.

The samples were stored at temperatures < 4°C. At the "Haute Ecole Valaisanne" (Sion), the herbicides were preconcentrated by Solid Phase Extraction (SPE) and analysed by HPLC-MS with a detection limit of 5 ng l^{-1} (except for diuron which had a detection limit of 15 ng l^{-1}).

3.   Results

3.1.   General Herbicide Observations

During the two years of the study, the GW was analysed for 6 herbicides: atrazine, deethylatra-zine, simazine, terbutylazine, isoproturon, and diuron. GW samples were taken throughout the whole study period.

Herbicides were detected in the groundwater at twelve of the thirteen 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 $0.1 \ \mu g \ l^{-1}$. In 2002, the same substances were detected, but at considerably lower concentrations.

As an example, the atrazine concentration in different piezometers of the observation area is shown in Figure 43. High concentrations appeared after heavy rainfall in mid June and especial-ly in late June 2001 that represented the first rainfall events subsequent to the herbicide appli-cation. In 2002, relatively strong precipitations were recorded already in early May and the highest concentrations were observed during the sampling campaign in mid May (Fig. 43). At this time, maximum concentrations were also measured in the main canal.

During the critical period in June 2001, atrazine was measured in several piezometers in the plain and near the slope at concentrations varying between 1.1 and $0.2 \ \mu g \ l^{-1}$ (MAR2 and Y19, respectively, Fig. 43). In the piezometers located near the river, the concentration also in-creased, but the magnitudes were lower (X03, X09, Fig. 43)
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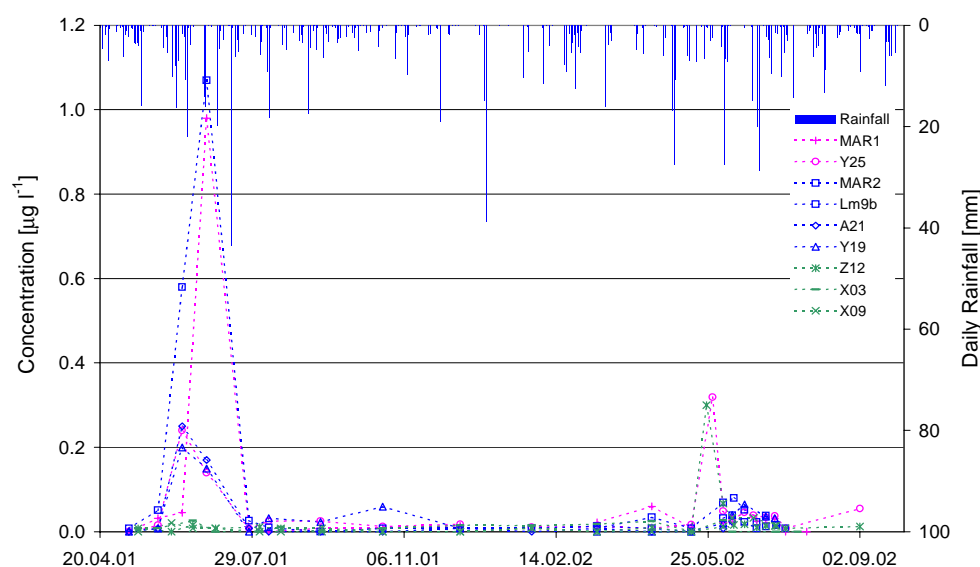
Figure 43: Atrazine concentration in different piezometers of the observation area

The highest concentration was measured in the piezometer MAR2 that is located on a corn field to which atrazine had been applied in June 2001 (Appendix 6.1). In 2002, when no herbicide had been applied to the field, the concentrations remained low. High concentrations were also observed at the piezometer MAR1 situated on a pasture close to the slope. At the piezometer Y25 also located near the hillside, a slight atrazine peak ($0.2-0.3 \ \mu g \ l^{-1}$) appeared in both years.

Other herbicides analysed within this study show similar patterns. The degradation product de-ethylatrazine, on the other hand, was never observed at concentrations exceeding 0.04 μg l^{-1}. In summary, the herbicide concentration measured in the different piezometers over the two year period shows that

- maximum concentrations are observed subsequent to precipitation during a short critical period in the summer.

- during the winter when no herbicides are applied only very low concentrations are detected.

- the concentration magnitude varies considerably between the different piezometers.

3.2.   Spatial Patterns of Herbicide Concentration and GW Characteristics

The spatial distribution of the herbicide concentrations in the observation area followed a general trend that is closely linked to the GW characteristics. Even without intensive hydrogeological examinations (that are beyond the intentions of this study), the influence of different external factors (e.g., boundary inflow, drainage) on the GW can be depicted. Close to the river, hydraulic gradients are comparably high (Appendix 6.2) and the electrical conductivity (EC) of the GW is low (Fig. 44). Near the slopes, the hydraulic gradients are moderate (Appendix 6.2); ECs measured in this area are low as well (Fig. 44). The region within the plain is characterized by low hydraulic gradients and highly mineralized GW (Appendix 6.2, Fig. 44). Consequently, three zones of different GW characteristics and herbicide concentrations appeared; they are presented in the following sections.
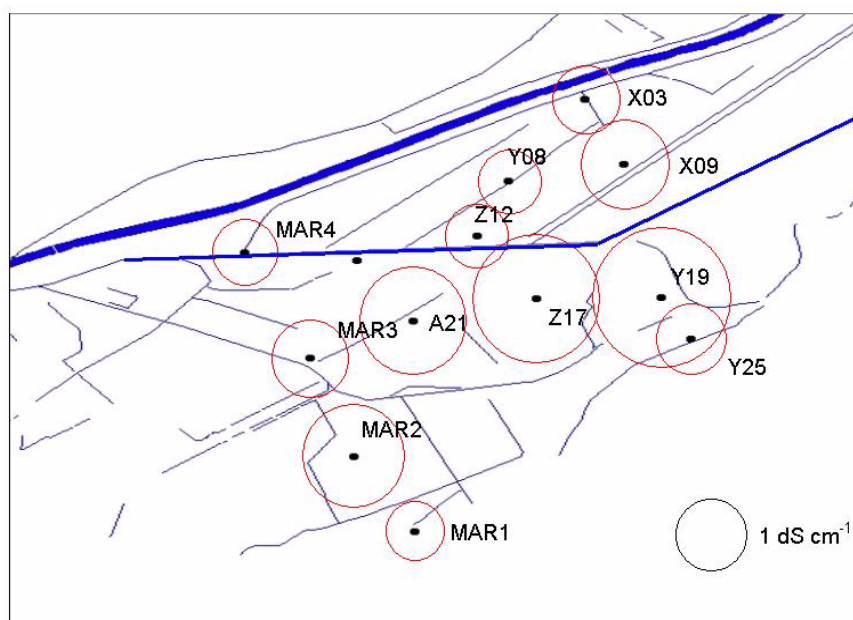
Figure 44: Electrical conductivity in the observation area in mid June, 2001

3.2.1.   River Influenced Zone

In the zone located between the river and the main canal, the GW is influenced by the river water. The water level in the river is higher than the GW table, while the canal serves as a drainage system (see 1.3). This causes an inflow of river water into the aquifer. The influence of the river is more pronounced in summer, when hydraulic gradients near the Rhône may reach 5 ‰ (Appendix 6.2).

Figure 45 shows the daily precipitations and the temporal changes of the water level in the 5 piezometers located between the Rhône River and the canal. The GW level in the piezometers is high in summer and low in winter as the water level in the river. At the piezometers located in immediate vicinity of the river (MAR4, X03) the effects of precipitation are hardly perceptible showing that they are influenced almost exclusively by the river. At larger distances (Z12, Y08), the effects of precipitation are more visible and superpose on the seasonal changes. (Irrigation cannot be the cause of the water level changes, because the fields at the piezometers have not been irrigated during the study period, Appendix 6.1).
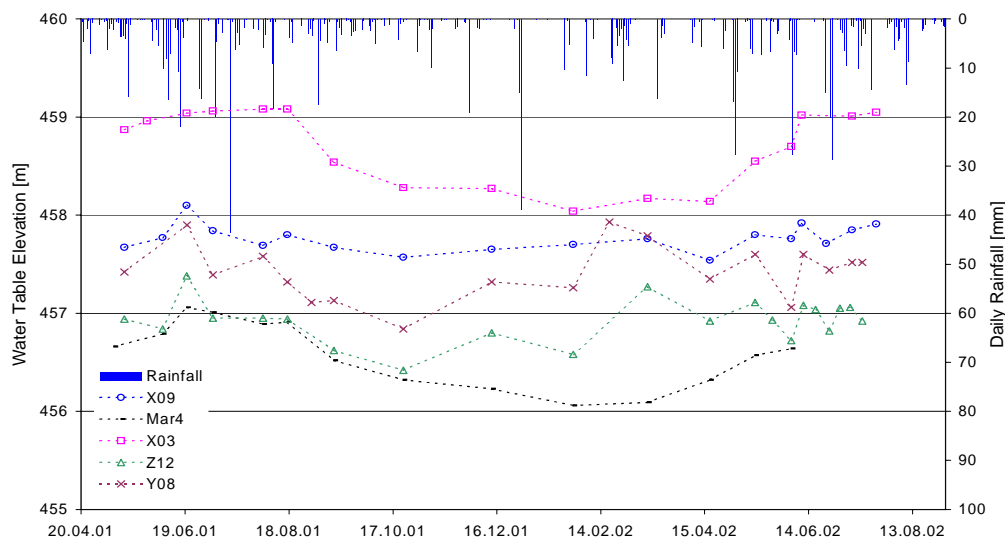
Figure 45: Water table elevation at the piezometers situated between the Rhône River and the main canal, daily rainfall on secondary axis

The EC of the river water is low, varying between 0.1 and 0.3 dS m^{-1}. Between the Rhône River and the main canal, the EC of the groundwater is relatively low (0.4-2.0 dS cm^{-1}, Appendix 6.4). The dilution of the GW by the slightly mineralized river water is most pronounced near the river and decreases with further distance from it: At the piezometer MAR4 situated close to the river, the electrical conductivity is 0.8 to 1 dS m^{-1} and varies only little in time (Appendix 6.4). At the piezometer Z12 close to the canal on the other hand, the EC may reach up to 2.1 dS m^{-1}. Lowest values (0.8 dS m^{-1}) were measured during the winter, while high values occurred in spring (Appendix 6.4). The electrical conductivity in the canal is higher than in the river (0.5-0.6 dS m^{-1}) indicating that the water is a mixture of draining GW and poorly mineralized surface water.

The herbicide concentrations observed at the piezometers MAR4, Z12, Y08, X03, and X09 located in this zone were relatively low. As an example, the concentrations in Z12 are discussed. The herbicide concentrations in the other piezometers are shown in Appendix 6.3.

The piezometer Z12 is situated on a field to which terbutylazine and diuron have been applied on May 14, 2001 and on April 29, 2002. Both substances were among the herbicides observed in this piezometer (Fig. 46).
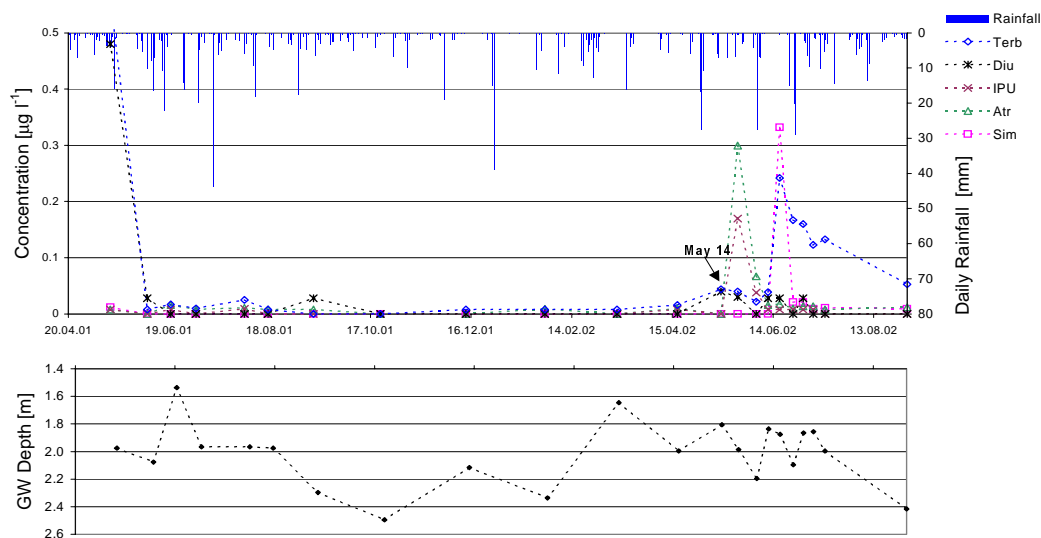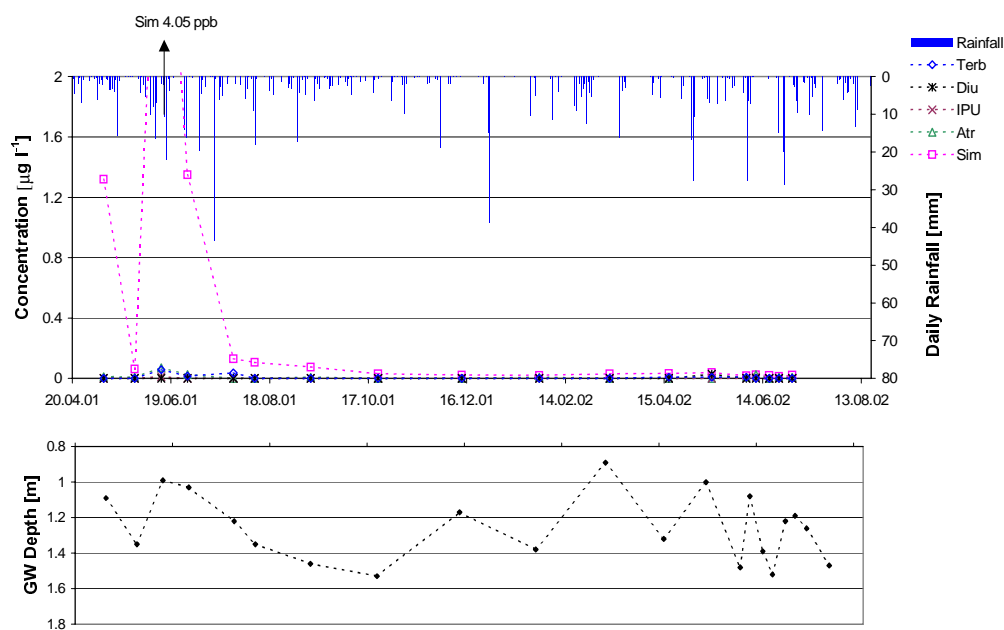

Figure 46: Herbicide concentration[a] and GW depth in the piezometer Z12 in 2001 and 2002. Daily rainfall on secondary axis.
a. Terb: terbutylazine; Diu: diuron; IPU: isoproturon; Atr: atrazine; Sim: simazine

The maximum concentration in this piezometer (0.5 µg l^{-1}) was observed on May 15, 2001, one day after the herbicide application, indicating that the transport through the unsaturated zone was fast. The concentration decreased quickly; two weeks later, only very low concentrations had persisted.

In 2002, (herbicide application on April 29) both substances were detected at low concentrations in the samples taken on May 14 (0.04 µg l^{-1}). A higher terbutylazine peak of 0.24 µg l^{-1} was observed on June 18 and the concentrations remained relatively high until mid July as did the GW level. Additionally to the herbicide applied on the field, peaks of atrazine and isoproturon were detected on May 24, and of simazine in mid June.

As described before, the hydraulic gradients in the area near the river are rather high. Solutes that reach the GW may therefore be transported quickly towards the canal explaining the rapid decrease of the concentration observed in 2001. In 2002, the first heavy rainfall after the application was recorded on May 3 (28 mm, Fig. 46) and the subsequent sampling took place 11 days later (May 14). It is possible that the relatively strong GW flow in this area has prevented the detection of higher concentrations. In the same way, some herbicides that were not applied to the field at piezometer Z12 have been transported towards the piezometer by the advective groundwater flow (atrazine, isoproturon, simazine).

Accordingly, the terbutylazine peak in mid June would represent a second concentration maximum. The terbutylazine concentration remained high until mid July as did the groundwater level (Fig. 46); the peak of simazine detected at the same time declined faster. This may be related to the different origins: the leaching of terbutylazine from the above located field and its solu-

tion in the GW on the one hand, and the relatively quick convective transport of simazine on the other hand. Nevertheless, for diuron that had also been applied to the field, the concentrations remained low.

In conclusion, the herbicide concentrations are rather low in the area between the river and the main canal. The relatively high hydraulic gradients in this zone suggest that herbicides reaching the GW are quickly diluted. Therefore, only small peaks of substances applied to the field around a piezometer are observed. Peaks of other substances than those applied in the direct vicinity may be transported towards a piezometer by the advective groundwater flow.

3.2.2.   Slope-Influenced Zone

Close to the hillside in the south of the observation area, the GW is influenced predominantly by water infiltrating from the slope. Hydraulic gradients observed between the piezometers Y25 and Y19 in 2001/2002 were 2.4 ‰ in late June 2001 and reduced to 0.6 ‰ in December (Appendix 6.7).

Figure 47 shows daily precipitations and the periodic changes of the water level in the piezometers located closest to the slope (MAR1, Y25) and at further distance (MAR2, Y19). Again, the seasonal changes can be observed with generally lower water levels between September and January. The water level at the piezometers located near the tilt (MAR1, Y25) develops similarly with a difference of 1 m between the lowest and the highest position. At their neighboured piezometers MAR2 and Y19 located at greater distance from the slope, the GW is lower (except for a short period in February and March 2002) and the variations between summer and winter are slightly less pronounced.
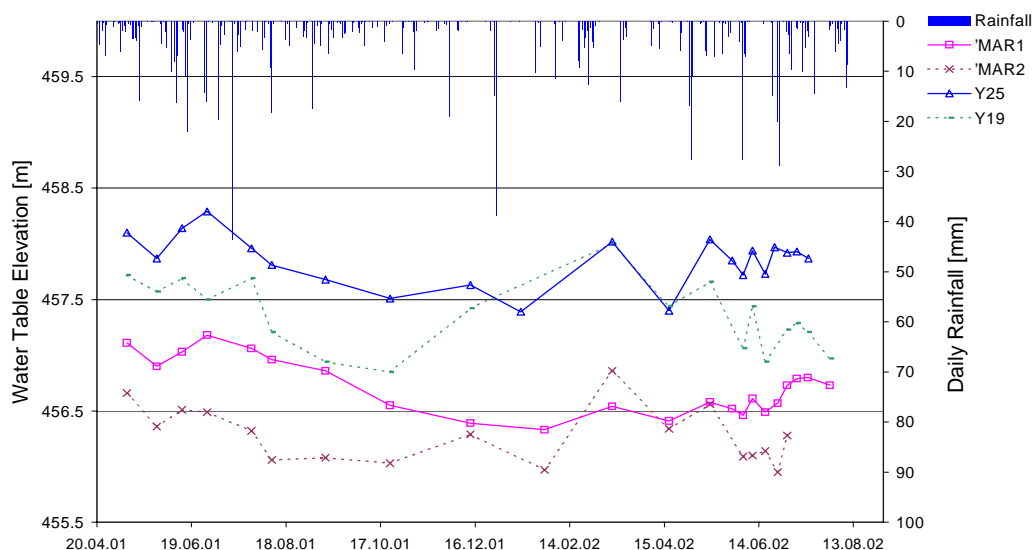
Figure 47: Water table elevation at the piezometers situated close to the slope (MAR1, Y25) and neighboured piezometers in the plain (MAR2, Y19), daily rainfall on secondary axis

The electrical conductivity in the piezometers located close to the slope (MAR1, Y25) is almost as low as along the river. At the piezometer Y25, the EC remains at 1 dS m^{-1} all over the year and at its downstream counterpart MAR1, it varies between 0.7 and 1.2 dS m^{-1} (Appendix 6.5).

The piezometers at greater distance from the slope show higher ECs varying between 1.35 and 2.2 dS m^{-1} at the piezometer MAR2 and between 2 and 4.4 dS m^{-1} at Y19. Therefore, the low EC near the tilt can be attributed to a lateral infiltration of less mineralized water.

At the piezometers MAR1 and Y25 situated close to the slope, high herbicide concentrations were measured during the critical period in 2001. Figure 48 shows the concentrations observed in Y25.
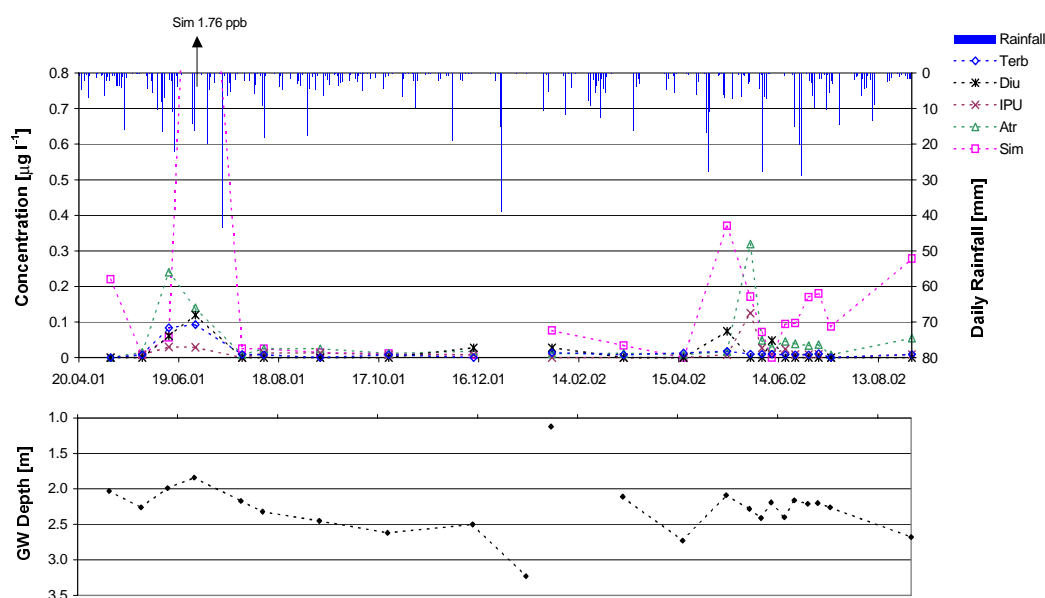
Figure 48: Herbicide concentration and groundwater depth in the piezometer Y25 in 2001 and 2002. Daily rainfall on secondary axis.

The piezometer is located on a pasture and no herbicides have been applied (Appendix 6.1). Notwithstanding, peaks of simazine and atrazine were detected in the piezometer in both years (Fig. 48). In 2001, simazine was detected at a concentration of 1.76 µg l^{-1} subsequent to precipitation at the end of June. In 2002, a maximum concentration of 0.37 µg l^{-1} was measured on May 14. A second attenuated peak was observed in early July after heavy rainfall at the end of June (49 mm on June 27/28). Atrazine was observed at lower concentrations that decreased somewhat quicker.

As no herbicides had been applied to the field above the piezometer Y25, the solutes have been transported towards the piezometer by the infiltrating water from the nearby slopes where vineyards grow. The herbicide concentrations in piezometer MAR1 show similar traits (Appendices 6.1 and 6.3). Consequently, in the zone close to the slope, the occurrence of high herbicide concentrations in the GW is related to the inflow of contaminated water from the hillside.

3.2.3.   Zone within the Plain

Within the plain, between the two areas presented above, the influence of the river or the slope is far less pronounced. According to the water level contour map of 1999 (Appendix 6.2), the average hydraulic gradient is only 0.5-1 ‰. Hydraulic gradients measured in 2001/2002 were even lower, ranging from 0.2-0.8 ‰ (Appendix 6.7).
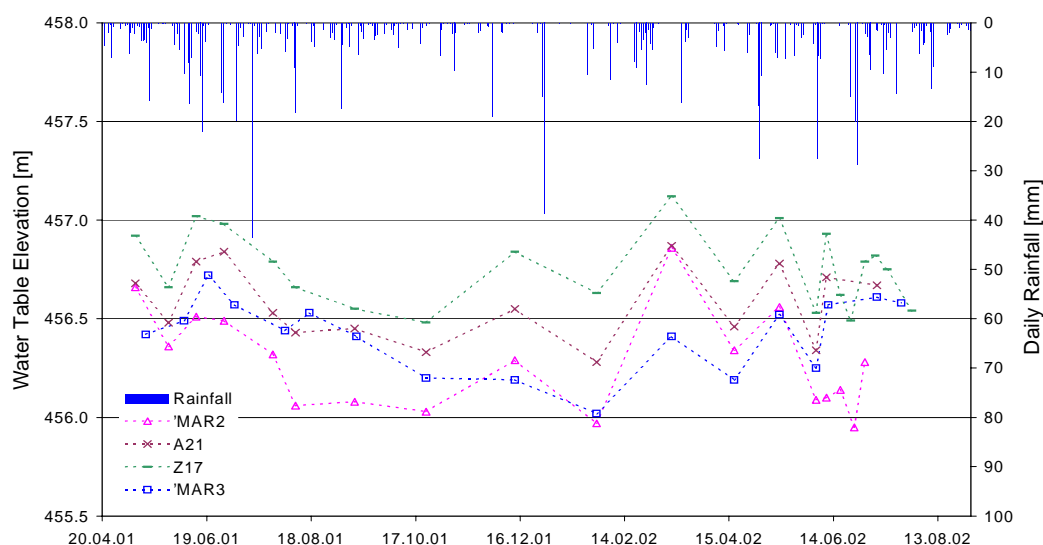
Figure 49: Water table elevation at the piezometers situated within the plain, daily rainfall on secondary axis

The piezometers located within this area have the lowest water levels. The GW level also changes seasonally, but short term changes show the growing influence of precipitation as a source of recharge (Fig. 49). The GW level falls during dry periods (April 2002, Fig. 49) and rises after precipitation (February and May 2002).

The GW is characterized by a high electrical conductivity, values vary between 2 and 4.5 dS m^{-1} (Appendix 6.6). Apparently, hardly any dilution with less mineralized water occurs in the centre of the plain.

The piezometers MAR2, MAR3, A21, Y19, Lm9b, and Z17 are located in this zone between the canal and the slope. High concentrations were observed in some of the piezometers (Appendix 6.3). The piezometer Z17 is situated on a pear tree field to which simazine has been applied in early May 2001 (Appendix 6.1). Figure 50 shows the herbicide concentrations measured during the two years.

High concentrations were measured in the groundwater in mid May 2001 and a peak of 4 µg l^{-1} was observed in mid June. By the end of June, the concentrations had decreased considerably (1.35 µg l^{-1} on June 29). The concentration development is similar to the GW level changes. In 2002 no herbicides were applied to the field and the concentrations remained low. High herbicide concentrations were measured in other piezometers located within the plain (Appendix 6.3) that could be related to an application on the field located above the piezometer.

Figure 50: Herbicide concentration and groundwater (GW) depth in the piezometer Z17 in 2001 and 2002. Daily rainfall on secondary axis

In the zone located within the plain, where the GW is hardly influenced by lateral inflow and where hydraulic gradients are low, high herbicide concentrations can be observed that originate from an application on the field located above a piezometer; in seasons when no herbicides are applied, the concentrations remain low. Other substances that have not been applied in the direct vicinity of a piezometer can also be detected, but at lower concentrations.

3.3.   Variations along the Transects

According to the direction of groundwater flow and the boundary influences, piezometer transects had been defined (Fig. 42, p. 84): two longitudinal transects, T1 and T 2, and two transversal transects (upper and lower boundaries). In this section, the concentrations and hydraulic gradients along two transects during the critical period in June 2001 are presented.

The transect at the upper boundary of the observation area is transversal to the groundwater flow direction (T4, Fig. 42). The hydraulic gradient is highest near the river (~13 ‰) illustrating the accelerated GW flow between the river and the canal; it is lower near the slope (2.4 ‰) and still lower in the middle of the plain (Fig. 51). During the peak period (late June 2001), the herbicide concentrations were very low between the river and the canal, slightly higher in the canal, and they largely exceeded the drinking water limit next to the slope (Fig. 51).
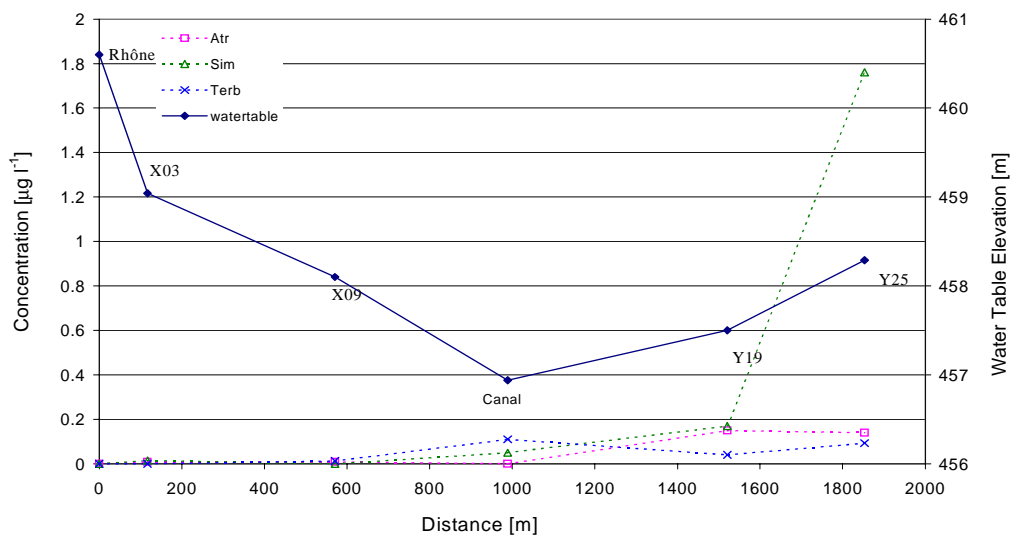
Figure 51: Herbicide concentration and water table elevation along the upper boundary transect in late June, 2001
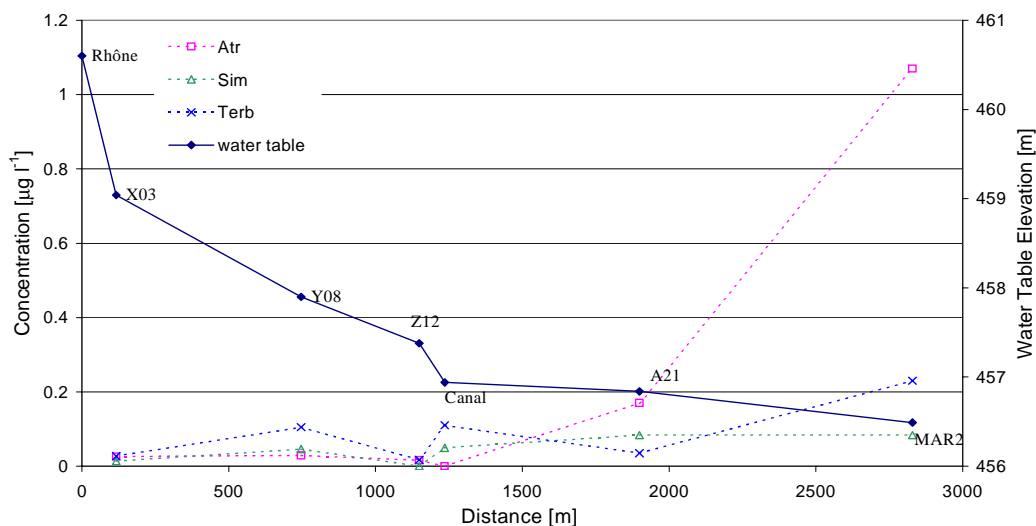
Figure 52: Herbicide concentration and water table elevation along transect 1 in late June 2001.

The same is observed for the transect 1 (situated within the direction of GW flow, Fig. 42). The hydraulic gradient is high close to the river (Fig. 52). No herbicides were detected in the river and the piezometers located between the river and the canal (X03, Y08, and Z12) had the lowest herbicide concentrations in the region. In the canal, that serves as a drainage system, concentrations of up to 0.11 µg l^{-1} were measured although a strong dilution can be expected. Within the plain, hydraulic gradients are low and an important peak was observed at the piezometer MAR2 (Fig. 52).

Consequently, high herbicide concentrations were measured at some piezometers, but the transects do not show evidence for a spatial continuity of the contaminations (Fig. 51 and 52). High concentrations appear only locally near the slope or within the plain. A transport of herbicides from one piezometer to another cannot be determined even if cross-checking transects for

successive sampling campaigns. Therefore, it can be concluded that the contaminations are confined in space and time, at least at the available (space and time) scales.

4.   Conclusion

Herbicides were detected in 12 of the 13 piezometers. Important concentrations exceeding by far the drinking water limit (0.1 µg l^{-1}) appeared locally during a short period of time (mid May to mid July) as a consequence of heavy rainfall subsequent to the application. Throughout the rest of the year, the concentrations remained below the drinking water limit.

In the observation area, three zones of different GW characteristics and herbicide concentrations could be determined:

- Between the Rhône and the main canal, the GW is largely influenced by infiltration of river water; consequently, high hydraulic gradients, low electrical conductivities, and low herbicide concentrations are observed. Apparently, water infiltrating from the river causes a quick dilution and transport of chemicals that reach the GW.

- Along the hillside, water coming from the slopes infiltrates into the aquifer. Hydraulic gradients are moderate, the GW's electrical conductivity is low, and solutes coming from the slope may be transported towards a piezometer causing temporarily high herbicide concentrations.

- Within the plain, the GW is little influenced by lateral inflow. Accordingly, hydraulic gradients are low and the water is highly mineralized; high concentrations of herbicides that had previously been applied to the above located fields can be observed.

An important factor controlling the occurrence of herbicides in the groundwater is precipitation. It can be stated that

- high concentrations appear after heavy rainfall subsequent to the herbicide's application, especially after the first important precipitation.

- observed travel times through the unsaturated zone are short (within one day).

- high concentrations observed in the GW decrease quickly (~2 weeks).

- several concentration maxima of the same herbicide may be observed that coincide with high GW levels.

The observed contaminations are limited in time and space and different substances are detected from one piezometer to another. This lack of continuity in the observed pesticide concentrations complicates the prediction of the fate of solutes in the GW. A very precise knowledge of pesticides use, both in space and time, is required.

The water samples were taken exclusively near the surface of the GW table located in the upper loamy soil layer. It is not possible to draw any conclusions about the contamination risks of the underlying more permeable aquifer layers. In these deeper layers, the concentrations might be

lower due to the faster water flow and a stronger dilution. This, however, should be examined in a complementary study by taking depth specific GW samples in deep piezometers.

CONCLUSION

The major purposes of the present study were to analyse in detail the transport of two selected herbicides from the soil surface to the groundwater and to evaluate the contamination risk of the alluvial aquifer in the Rhône River Valley between Martigny and Charrat. In this area, the low clay and organic matter content, the intensive agricultural use, and the low depth of the groundwater table lead to an assumed high vulnerability of the groundwater to contamination.

Furthermore, the complete data set collected during this study should allow other partners of the PEGASE project to assess the performance of modeling tools that predict the fate of pesticides in the soil and the groundwater.

The investigations are carried out at two different scales: a detailed study of the transport processes in the unsaturated zone at local scale field sites and a systematic monitoring of the groundwater quality at a regional scale (about 400 ha).

Intensive measurements during two years on the experimental plots have shown that the water flow in the unsaturated zone is strongly influenced by climatic factors:

- During dry periods, the shallow GW and the strong evaporation lead to positive hydraulic gradients over the whole soil profile and an important capillary rise. The water contents remain quite high, even near the soil surface.

- Subsequent to precipitation, negative gradients in the vadose zone indicate downward fluxes and, after important rainfall, drainage of the rainwater into the aquifer occurs; the groundwater level rises within only few hours.

The chemical transport is also closely linked to the climatic conditions:

- As long as no water is applied to the soil (precipitation or irrigation), the chemicals remain near the soil surface. After the first rainfall event following to the application, however, part of the herbicides are 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 suggest bypassing of part of the soil matrix. A dye tracing experiment suggests that some kind of non-equilibrium flow occurs.

- During dry periods, the initially high concentrations in the unsaturated zone and in the GW decrease steadily.

- After further important rainfall, supplementary concentration peaks appear in the groundwater.

- Approximately 2.5 months after the application, the concentrations are relatively low again and no further concentration peaks are observed.

- The rapidity of the transport and the high concentrations occurring in the GW indicate that adsorption does not play an important role.

The experimental results have been used to calibrate a mechanistic deterministic model (HYD-RUS-1D). The numerical simulations should help to analyse the processes involved in pesticide transport and, if possible, to predict the fate of chemicals applied to the soil surface. The MIM (mobile-immobile water) concept was used in order to account for the observed rapid transport.

In the study area, the shallow GW and the high evaporation influence considerably the water conditions in the unsaturated zone. The simulations show that in such cases the use of a one-dimensional model to simulate the water flow and the chemical transport in the vadose zone is hindered due to difficulties in defining the lower boundary condition. Two types of lower boundary conditions were examined: a variable pressure head boundary condition and a zero flux condition.

None of the two conditions was completely satisfactory. The first indicates a disproportionate inflow of water through the lower boundary and hardly any drainage of rainwater into the aquifer, the second does not reproduce pressure heads and water contents near the soil surface and underestimates the evaporation.

In fact, the flow of the GW is typically three-dimensional and a global (saturated - unsaturated) 3-D model or the coupling of an unsaturated 1-D model to a 3-D saturated model would be more appropriate to simulate precisely the water flow and solute transport in both, saturated and unsaturated zones.

Nevertheless, the model HYDRUS-1D allowed to describe qualitatively the observed herbicide transport. The MIM concept and a very high dispersivity value were used to account for the rapid transport and the quick arrival of the chemicals in the groundwater. Still, the model cannot reproduce the high concentrations occurring right after the first rainfall event, indicating that the MIM concept is not sufficient to describe the accelerated transport in the apparently homogeneous loamy soil. The concentration peaks observed in the groundwater after further heavy rainfall are reproduced in the simulations. They are a consequence of a slow downward movement of the chemicals in the unsaturated zone together with the groundwater level rise after heavy rainfall.

At the regional scale, herbicides were detected in 12 out of 13 piezometers, in some cases at high 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 regional observations are in good agreement with the conclusions of the local experiments and confirm that:

- the solutes are rapidly transported towards the GW with the first rainfall subsequent to the application. Observed travel times through the unsaturated zone are short (a few hours or days).

- high concentrations in the GW decrease quickly during dry periods (~2 weeks).

- additional peaks may appear in the groundwater that coincide with high water levels.

- during the winter, when no herbicides are applied, the concentrations remain low.

Both, the local and the regional study suggest that in many cases the pesticides detected in the groundwater come from the above-located fields. Nevertheless, the regional characteristics of the groundwater play an important role for the observation of herbicides:

- Near the Rhône river, high hydraulic gradients quickly dilute concentrations of chemicals that were applied to the above fields and transported to the groundwater; herbicides originating from more distant fields may also be detected.

- Near the slope, an inflow of contaminated water from the hillside (vineyards) can contribute significantly to the GW contamination

- Within the plain, high concentrations of herbicides applied to the above-located fields can be temporarily observed.

In summary, contaminations are confined in time and space and different substances are detected from one piezometer to another. This lack of continuity in the observed pesticide concentrations will complicate the prediction of the fate of solutes in the GW. A precise knowledge of the pesticide use, both in space and time, is required.

It can be concluded that in spite of the assumed high vulnerability of the aquifer, no systematic regional herbicide contamination could be observed. Nevertheless, high herbicide concentrations may appear locally during the summer months that are related to a large extend to climatic conditions. The river has a beneficial effect on the GW, because infiltration into the aquifer contributes to the dilution and transport of the pesticides reaching the GW. The inflow of polluted water from the slopes, on the other hand, may contaminate the GW. Consequently, the contamination risk is especially high near the slope and under the fields treated with herbicides, after heavy rainfall or floods during the weeks following the application, and in years with unusually high groundwater levels. It is much smaller during long dry periods, and at locations near the river. Furthermore, the contamination is confined in time and space; it is therefore not surprising that the scarce isolated measurement campaigns performed previously have not detected herbicides or only limited concentrations in the groundwater.

Further research should focus on:

- depth-specific measurement of the herbicide concentration in the groundwater and on the concentrations in the upper gravel layer

- the evaluation of the water and solute fluxes at the regional boundaries

- determination of the herbicide concentration in the whole profile from the soil surface to the GW table, especially during dry periods when GW concentrations decrease

- include simulations with a 3-D global (saturated-unsaturated) model or a 1-D root zone model (accounting for non-equilibrium flow) coupled to a 3-D saturated model.

The coupling of root zone models with groundwater models is one of the tasks of the ongoing PEGASE project that various partners are working on. Hopefully, the data base collected during the present study can contribute to the success of the modeling part of the project.

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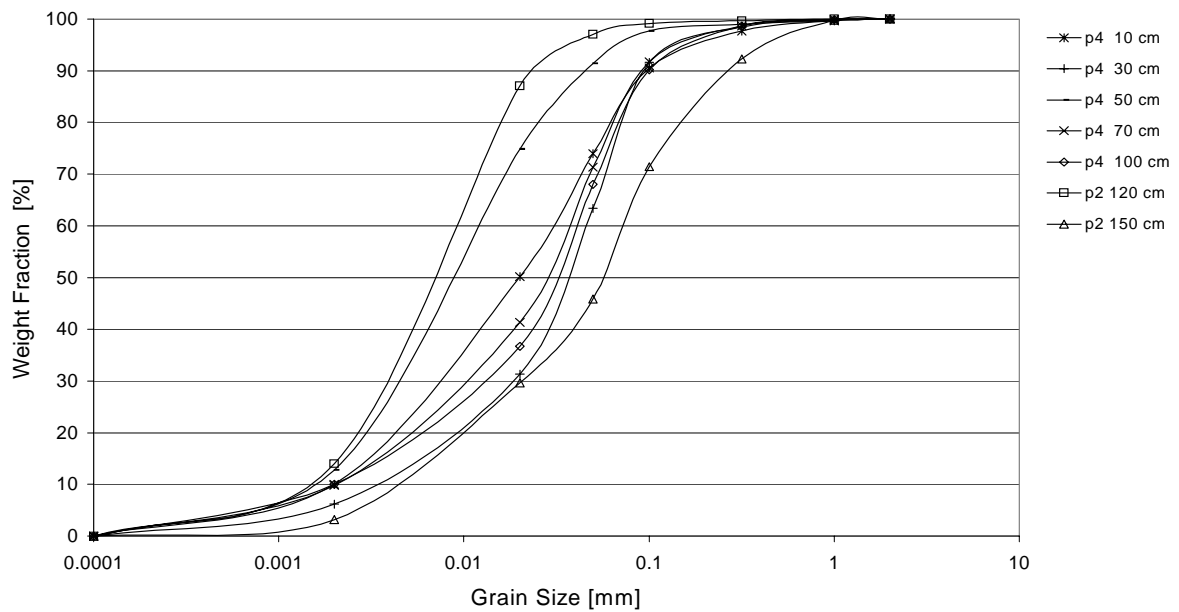
6.6. EC within the Plain

6.7. Hydraulic Gradients and Herbicide Concentration along Transects in 2001

3.1. Grain Size Distribution

On plot 1 at different depths

On plot 2 (p2) and 4 (p4) at different depths

Plot	Depth [m]	Clay	Silt		Sand				USDA classification
		<2 µm	2-20 µm	20-50 µm	0.05-0.1 mm	0.1-0.316 mm	0.316-1 mm	1-2 mm	
1	0.10	0.10	0.40	0.24	0.15	0.07	0.02	0.01	Silt Loam
1	0.30	0.07	0.29	0.33	0.24	0.05	0.01	0.00	Silt Loam
1	0.50	0.09	0.35	0.26	0.19	0.09	0.01	0.00	Silt Loam
1	0.70	0.08	0.28	0.29	0.23	0.11	0.01	0.00	Silt Loam
1	1.00	0.11	0.64	0.16	0.06	0.02	0.00	0.00	Silt
1	1.20	0.11	0.77	0.08	0.03	0.01	0.00	0.00	Silt
1	1.50	0.01	0.20	0.33	0.37	0.08	0.00	0.00	Silt Loam/Sandy Loam
4	0.10	0.10	0.40	0.24	0.16	0.07	0.02	0.00	Silt Loam
4	0.30	0.06	0.25	0.32	0.28	0.07	0.01	0.00	Silt Loam
4	0.50	0.13	0.62	0.17	0.06	0.01	0.01	0.00	Silt Loam
4	0.70	0.10	0.32	0.30	0.20	0.07	0.01	0.00	Silt Loam
4	1.00	0.10	0.27	0.31	0.22	0.08	0.01	0.00	Silt Loam
2	1.20	0.14	0.73	0.10	0.02	0.01	0.00	0.00	Silt Loam
2	1.50	0.03	0.27	0.16	0.26	0.21	0.07	0.00	Sandy Loam

3.2. Density and Porosity

Measured on undisturbed soil samples from different plots at different depths

Plot	Depth [m]	Density [g cm^{-3}]	Porosity [-]
1	0.10	1.50	0.48
1	0.10	1.46	0.50
1	0.10	1.43	0.51
2	0.10	1.50	0.47
2	0.10	1.52	0.48
2	0.10	1.52	0.45
3	0.10	1.54	0.47
3	0.10	1.47	0.47
3	0.10	1.49	0.46
4	0.10	1.51	0.46
4	0.10	1.51	0.45
4	0.10	1.42	0.48
1	0.30	1.53	0.51
1	0.30	1.48	0.53
1	0.30	1.54	0.48
2	0.30	1.47	0.46
2	0.30	1.54	0.46
2	0.30	1.50	0.49
3	0.30	1.46	0.47
3	0.30	1.47	0.47
3	0.30	1.40	0.48
4	0.30	1.44	0.49
4	0.30	1.49	0.48
4	0.30	1.50	0.49
1	0.50	1.49	0.48
1	0.50	1.49	0.50
1	0.50	1.50	0.50
2	0.50	1.45	0.49
2	0.50	1.45	0.49
2	0.50	1.44	0.45
3	0.50	1.44	0.49
3	0.50	1.50	0.47
3	0.50	1.39	0.49
4	0.50	1.50	0.49
4	0.50	1.47	0.50
4	0.50	1.49	0.50

Density and Porosity continuation

Plot	Depth [m]	Density [g cm^{-3}]	Porosity [-]
1	0.70	1.52	0.48
1	0.70	1.53	0.53
1	0.70	1.49	0.50
2	0.70	1.48	0.49
2	0.70	1.45	0.48
2	0.70	1.49	0.55
3	0.70	1.44	0.54
3	0.70	1.48	0.55
3	0.70	1.49	0.47
4	0.70	1.42	0.47
4	0.70	1.38	0.50
4	0.70	1.40	0.50
1	1.00	1.42	0.47
1	1.00	1.37	0.48
2	1.00	1.38	0.48
2	1.00	1.45	0.54
2	1.00	1.43	0.54
3	1.00	1.34	0.52
3	1.00	1.34	0.52
3	1.00	1.33	0.52
4	1.00	1.53	0.46
4	1.00	1.55	0.45
4	1.00	1.54	0.46

3.3. Method of Chemical Analysis for Herbicides

Preconcentration[3]

- conditioning of SPE[4] cartridges (3 ml C18 cartridge, SUPELCO, USA) with successively:
  2 ml dichloromethane
  2 ml methanol
  2 ml aceton
  twice 2 ml MilliQ water
- flow of the water sample through the conditioned SPE cartridge under a vacuum (max. 100 mbar, flow rate of 100 to 200 ml h^{-1}). Bottle of the sample is rinsed with MilliQ water that also passes through the cartridge
- cartridges are dried under pure nitrogen gas and a vacuum (400 mbar, 1 hour)
- herbicides are washed off the solid phase with twice 1.5 ml of methanol
- methanol is evaporated under nitrogen gas
- glas walls are rinsed with 500 µl of methanol, and methanol is evaporated until glas is completely dry
- herbicides are taken up in 200 µl of acetonitrile and 200 µl of MilliQ water

The preconcentration, P, of the sample is:

P = Volume of original water sample [ml] / Final volume of sample (0.4 ml)

HPLC Method

- Column: Vydac 201HS54, C18 Reversed Phase, 25 cm long
- Flow Rate/Time: 0.4 ml min^{-1}, 38 min
- Injection Volume: 100 µl
- Solvents: 0.05 vol % tetrafluoroacetic acid (TFA) and acetonitrile (ACN)
- Solvent Gradient:
0 min	70 % TFA, 30 % ACN
5 min	60 % TFA, 40 % ACN
20 min	50 % TFA, 50 % ACN
33 min	50 % TFA, 50 % ACN
38 min	70 % TFA, 30 % ACN
- UV-Detection, Wavelengths:
0 min	222 nm
20 min	235 nm
33 min	222 nm

---

3. modified after: "Dosage des pesticides par HPLC, Mode Opératoire Normalisé MO ME 020", Version 1, Service Cantonal pour la Protection de l'Environnement, République et Canton de Neuchâtel
4. Solid Phase Extraction

Appendix 3.3.

4.1. Hydraulic Charge in May/June 2002

On plot 3

Time	H [hPa] 10 cm Depth	H [hPa] 20 cm Depth	H [hPa] 40 cm Depth	H [hPa] 60 cm Depth	H [hPa] 85 cm Depth
14.05.02 18:00	-275.0	-237.0	-195.0	-161.0	-148.0
15.05.02 09:30	-283.0	-269.0	-216.0	-186.0	-151.0
16.05.02 19:30	-292.0	-288.0	-242.0	-200.0	-170.0
17.05.02 18:15	-307.0	-303.5	-253.0	-211.0	-178.5
18.05.02 16:45	-26.0	-98.5	-149.0	-180.0	-182.5
19.05.02 17:00	-295.0	-259.0	-215.0	-171.0	-164.0
20.05.02 18:15	-337.0	-324.0	-264.0	-208.0	-179.0
21.05.02 17:30	-337.0	-341.0	-271.0	-271.0	-194.0
22.05.02 19:00	-365.0	-358.0	-307.0	-242.0	-199.0
24.05.02 13:00	-321.0	-268.0	-231.0	-192.0	-182.0
25.05.02 18:00	-412.0	-381.0	-321.0	-242.0	-197.0
26.05.02 18:00				-245.0	-202.0
27.05.02 18:15	-346.0	-334.0	-306.0	-251.0	-209.0
28.05.02 18:15	-459.0	-409.0	-328.0	-235.0	-197.0
29.05.02 17:00		-455.0	-371.0	-269.0	-219.0
31.05.02 17:15		-524.0	-427.0	-301.0	-232.0
01.06.02 17:00				-305.0	-238.0
02.06.02 17:00				-323.0	-246.0
03.06.02 14:00		-327.4	-362.3	-301.6	-245.8
04.06.02 15:45		-438.0	-368.0	-259.0	-219.0
06.06.02 15:00	-134.7	-115.6	-134.3	-122.0	-149.0
10.06.02 13:00	-277.0	-244.0	-201.0	-165.0	-156.0
11.06.02 10:00			-222.0	-185.0	-168.0
12.06.02 11:00			-210.0	-187.0	-176.0
13.06.02 17:00	-250.0	-293.0	-248.0	-207.0	-183.0
14.06.02 17:00	-359.0	-323.0	-267.0	-223.0	-192.0
15.06.02 17:00			-281.0	-236.0	-203.0
16.06.02 17:00		-309.0	-275.0	-233.0	-232.0
17.06.02 17:00		-344.0	-294.0	-245.0	-211.0
18.06.02 18:15		-359	-306	-253	-216
19.06.02 11:00			-304	-255.5	-218.5
20.06.02 11:20			-305.2	-261.3	-220.5
21.06.02 09:00			-329.6	-280.5	-229.5
24.06.02 09:00	-36.5	-94.5	-231.1	-273.6	-226.7
24.06.02 17:00	-175.5	-239	-203	-220.5	-211.5
25.06.02 17:00	-369	-310	-284	-225.0	-198.0
26.06.02 15:30	-364.5	-324	-292	-249.5	-206.5
27.06.02 17:00	-376	-315	-307	-268	-223.0
28.06.02 18:15	-105	-69	-107	-112	-127.0
29.06.02 16:00	-253	-165	-155	-141	-138.0
30.06.02 16:00	-246	-194	-184	-166	-152.0
01.07.02 15:30	-220.5	-193	-178	-168.5	-153.5
05.07.02 10:00	-179.5	-178	-179	-176.5	-167.5
12.07.02 10:00	-227.5	-209	-199	-190.5	-177.5
18.07.02 13:00	-201.5	-160	-145	-137.5	-137.5
23.07.02 13:00	-176.5	-158	-152	-157.5	-155.5

On plot 4

Time	H [hPa] 10 cm Depth	H [hPa] 20 cm Depth	H [hPa] 40 cm Depth	H [hPa] 60 cm Depth	H [hPa] 85 cm Depth
14.05.02 18:00	-240.5	-231.0	-172.0	-159.5	-150.0
15.05.02 09:30	-273.5	-264.0	-209.0	-187.5	-157.0
16.05.02 19:30	-293.5	-280.0	-235.0	-201.5	-179.0
17.05.02 18:15	-304.0	-288.5	-255.5	-220.5	-202.0
18.05.02 16:45	-21.0	-71.5	-146.5	-183.5	-193.0
19.05.02 17:00	-256.0	-241.5	-201.5	-187.5	-178.0
20.05.02 18:15	-319.0		-257.5	-224.5	-197.0
21.05.02 17:30			-272.5	-245.0	-212.0
22.05.02 19:00	-363.0	-347.5	-299.5	-254.0	-217.0
24.05.02 13:00	-253.0	-219.5	-206.5	-185.0	-194.0
25.05.02 18:00	-335.0	-314.5	-274.5	-243.0	-211.0
26.05.02 18:00			-273.5	-246.5	-207.0
27.05.02 18:15	-303.0	-293.5	-277.5	-253.5	-221.0
28.05.02 18:15		-353.5	-286.5	-239.5	-208.0
29.05.02 17:00		-390.5		-267.0	-224.0
31.05.02 17:15		-408.5	-360.5	-291.0	-235.0
01.06.02 17:00		-419.5	-368.5	-301.0	-238.0
02.06.02 17:00		-432.5	-380.5	-308.0	-246.0
03.06.02 14:00			-286.5	-282.0	-254.0
04.06.02 15:45	-362.0	-362.5	-302.5	-257.0	-223.0
06.06.02 15:00	-49.0	-71.9	-87.7	-107.0	-141.3
10.06.02 13:00	-286.0	-235.5	-185.5	-168.0	-164.0
11.06.02 10:00	-324.0	-267.5	-221.5	-194.0	-178.0
12.06.02 11:00				-193.0	-182.0
13.06.02 17:00	-267.0		-235.5	-210.0	-193.0
14.06.02 17:00	-295.0	-275.5	-249.5	-221.0	-201.0
15.06.02 17:00		-288.5	-260.5	-226.0	-212.0
16.06.02 17:00			-264.5	-238.0	-218.0
17.06.02 17:00		-296.5	-269.5	-243.0	-217.0
18.06.02 18:15		-309.5	-282.5	-252.0	-225.0
19.06.02 11:00				-248.5	-218.0
20.06.02 11:20				-259.5	-223.0
21.06.02 09:00			-292.5	-274.9	-232.4
24.06.02 09:00		-7.9	-166.2	-245.5	-222.3
24.06.02 17:00	-26.5	-107.5	-141	-188.5	-204
25.06.02 17:00	-364	-312.5	-254.5	-220	-199
26.06.02 15:30	-406.5	-337.5	-287	-241.5	-204
27.06.02 17:00			-315.5	-270	-233
28.06.02 18:15	-35	-68.5	-102.5	-112	-133
29.06.02 16:00	-239	-192.5	-152.5	-143	-141
30.06.02 16:00	-308	-250.5	-192.5	-176	-164
01.07.02 15:30	-258.5	-229.5	-187	-173.5	-161
05.07.02 10:00	-179.5	-188.5	-190	-186.5	-177

4.2. Soil Water Retention

On plot 1
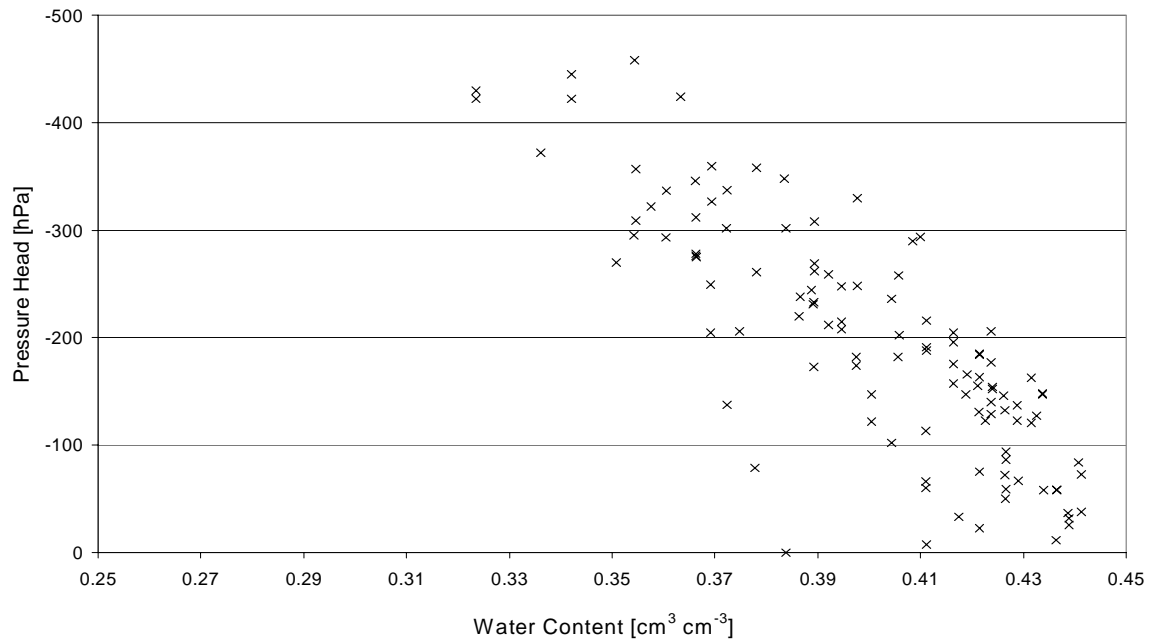
On plot 4: measured data (points) and adjusted Van Genuchten model (line; VAN GENUCHTEN, 1980)
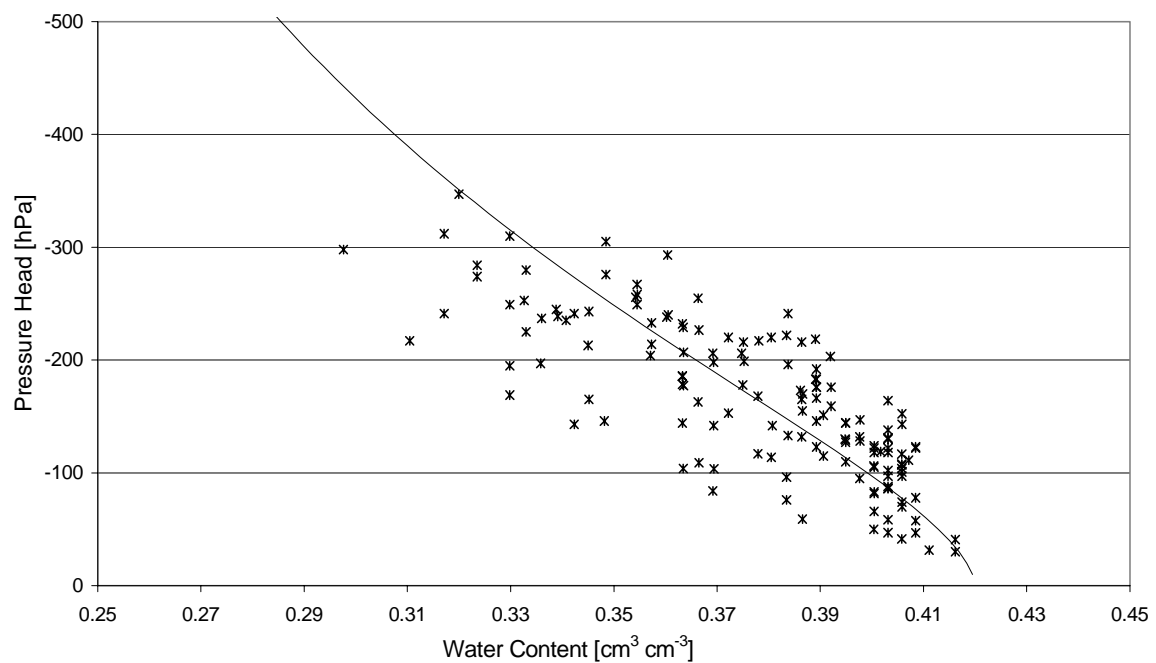
(for plot 3 see Ch. 4)

4.3. Chemical Concentration in the Unsaturated Zone in 2001

Atrazine in suction cups at different depths on plot 1
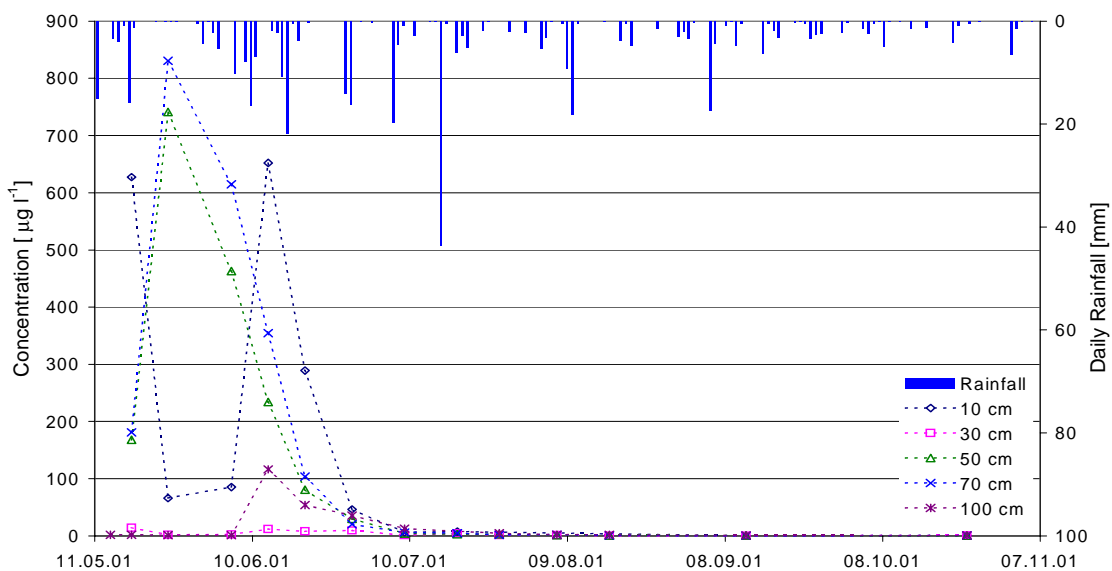
Atrazine in suction cups at different depths on plot 2
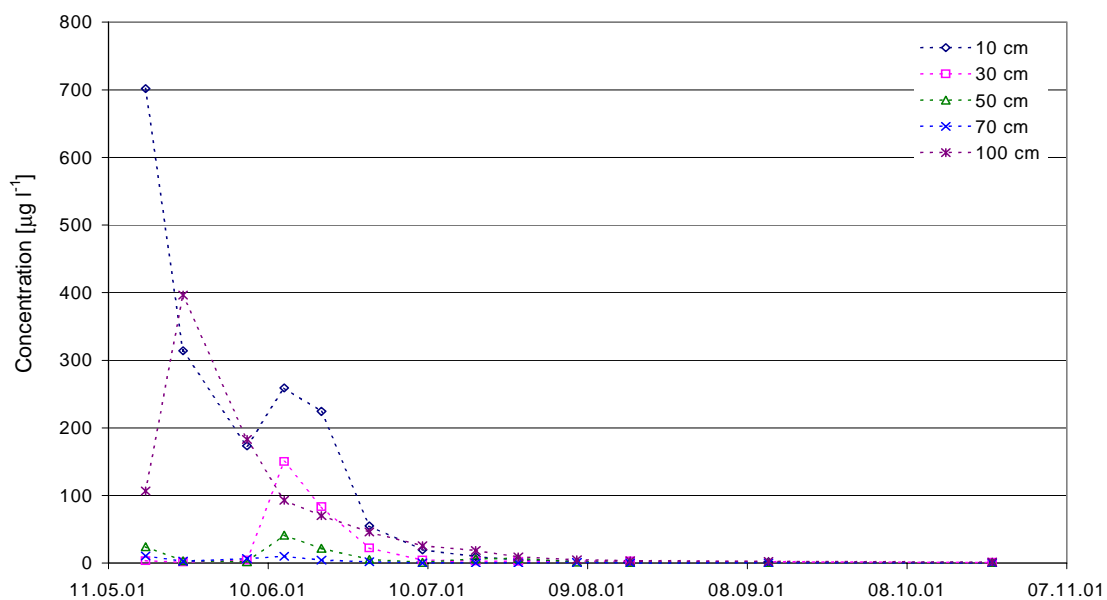
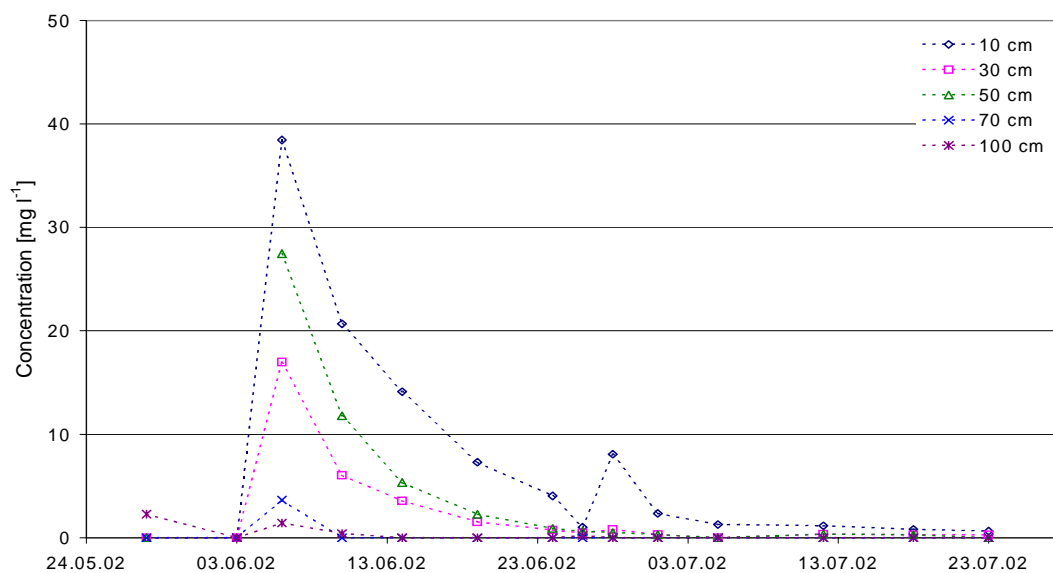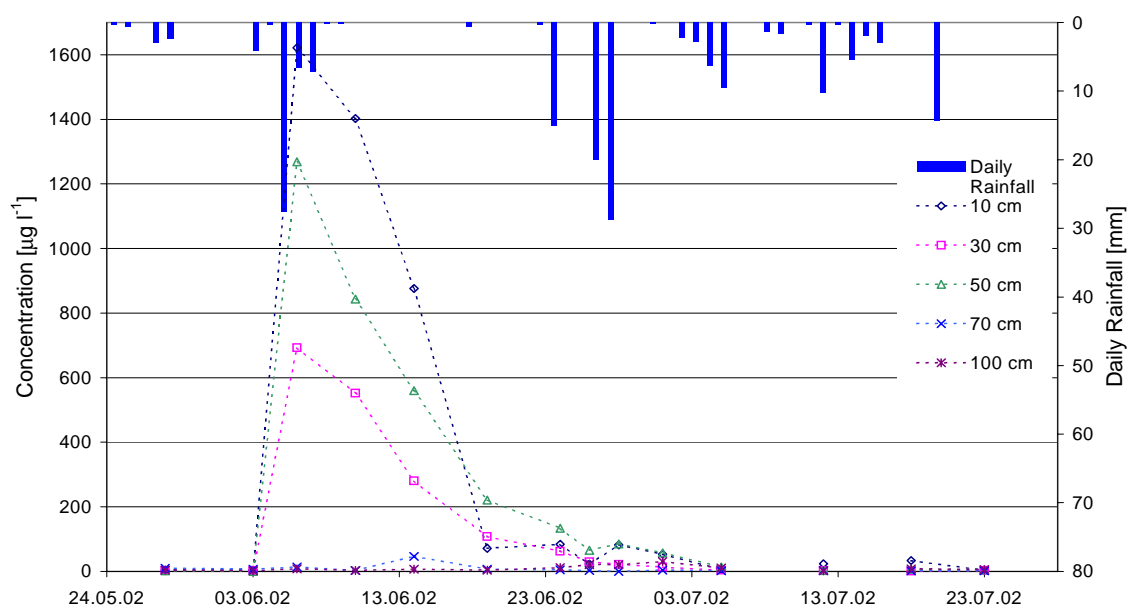## Atrazine in suction cups at different depths on plot 3
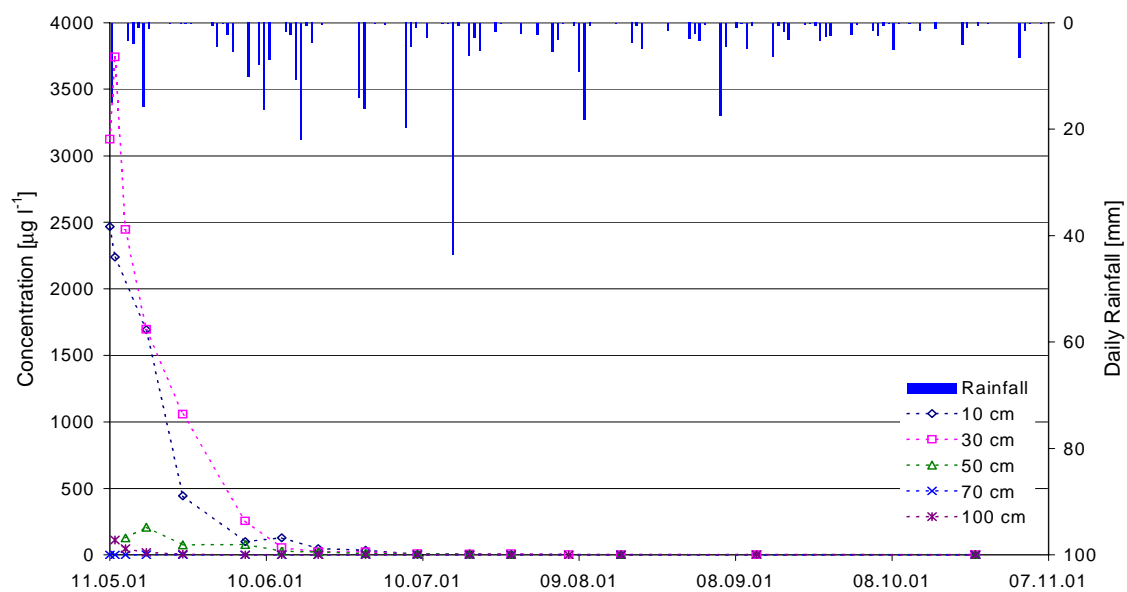
(for atrazine on plot 4 see Ch. 4)

Isoproturon in suction cups at different depths on plot 1
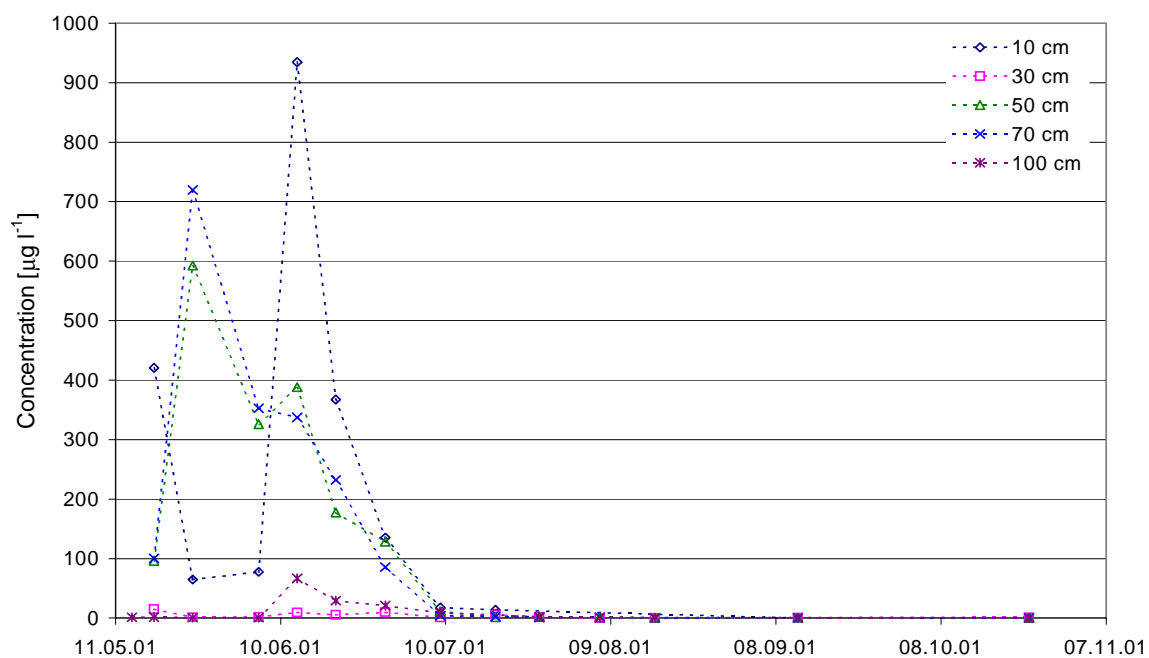
Isoproturon in suction cups at different depths on plot 2
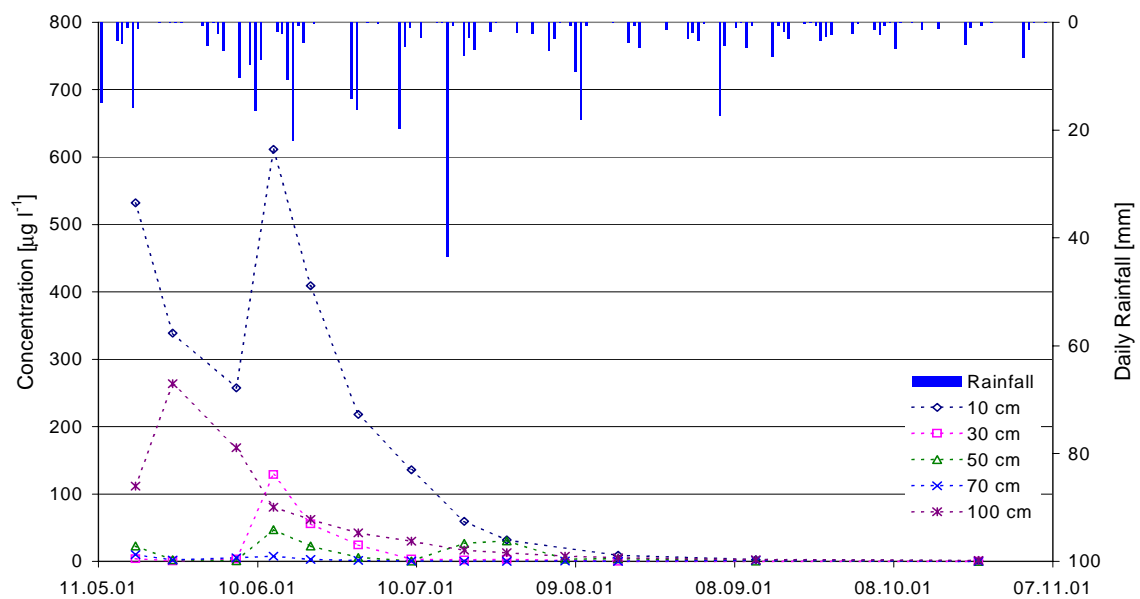
Isoproturon in suction cups at different depths on plot 3
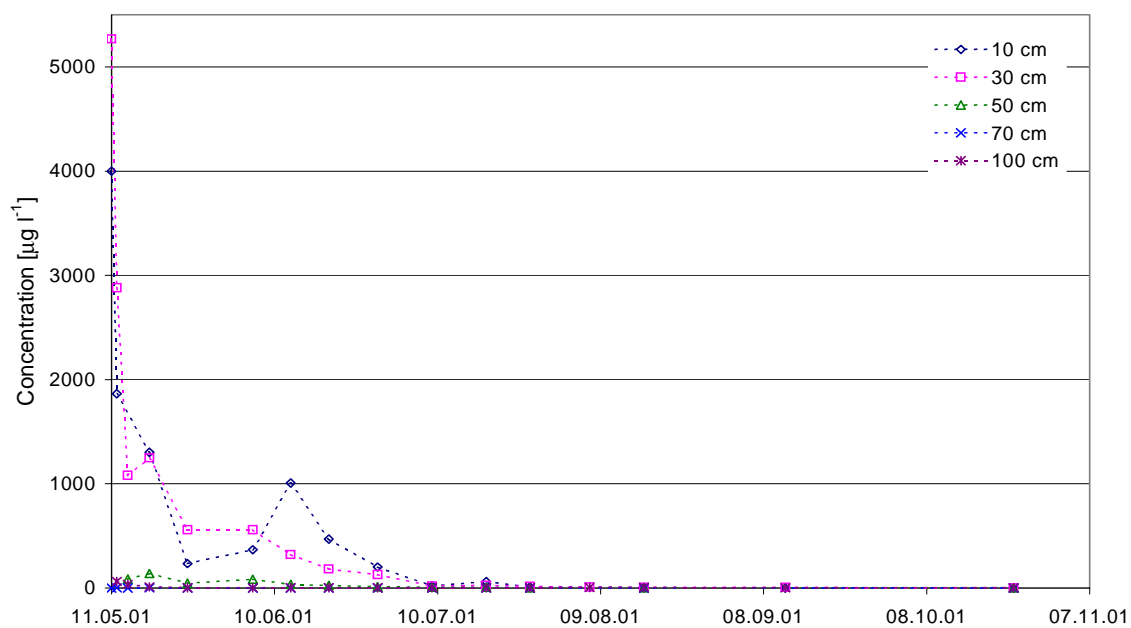
(for isoproturon on plot 4 see Ch. 4)

Bromide in suction cups at different depths on plot 1
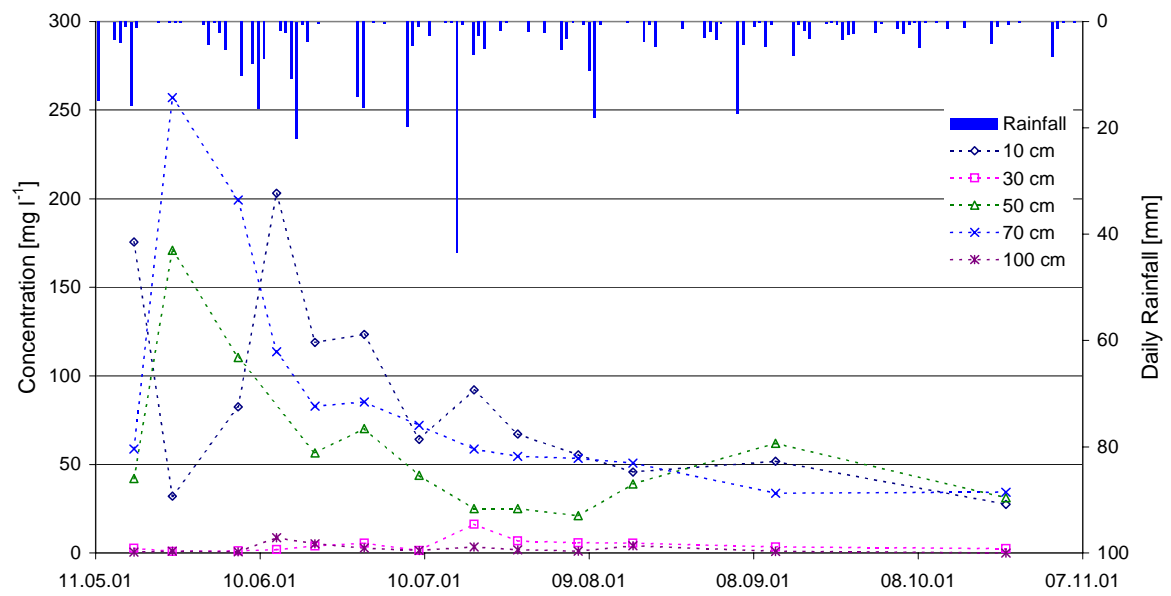
Bromide in suction cups at different depths on plot 2
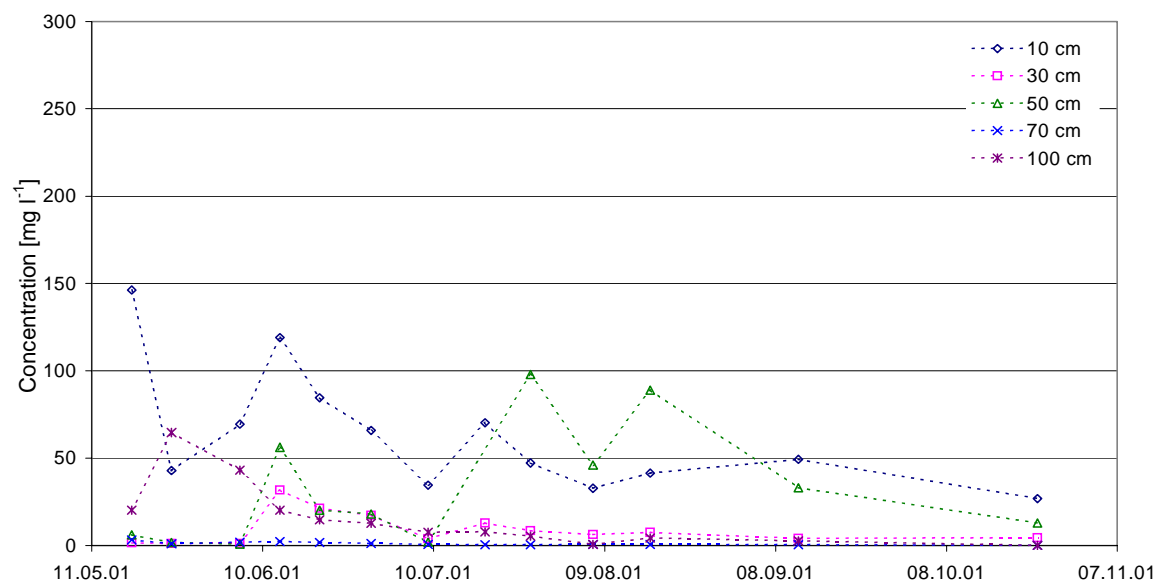
Bromide in suction cups at different depths on plot 3
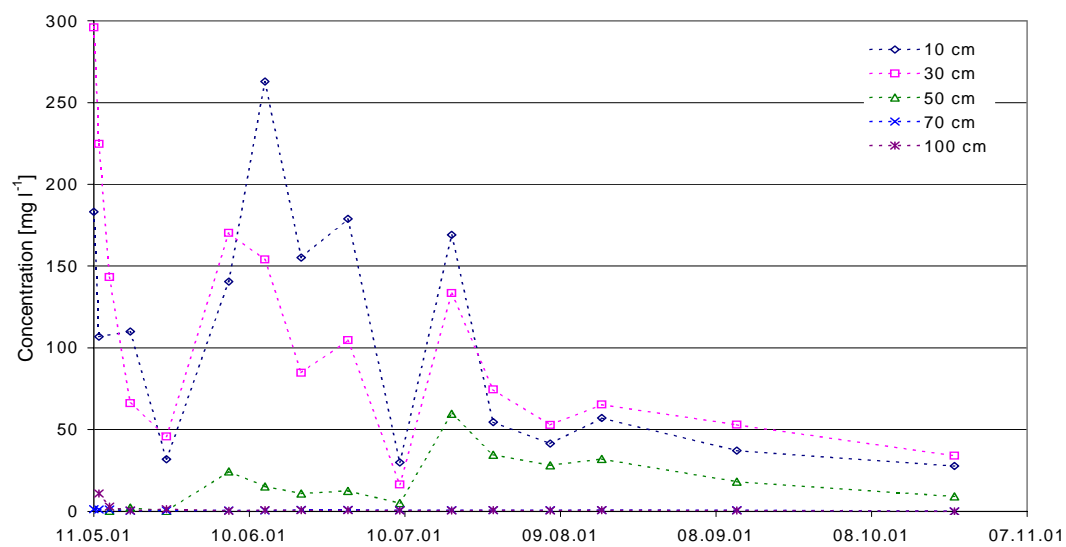
Bromide in suction cups at different depths on plot 4
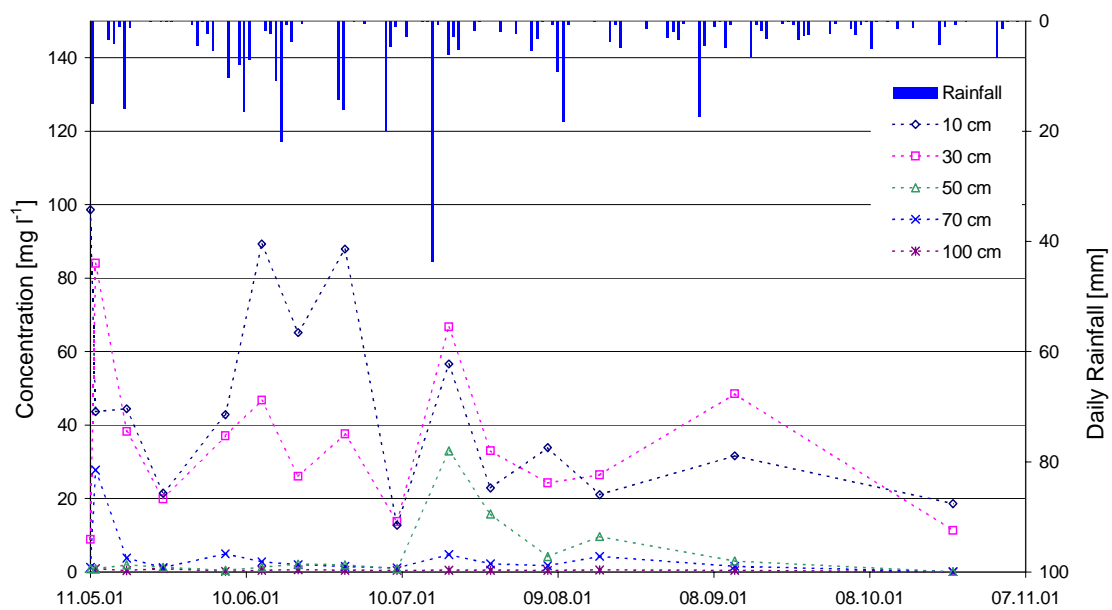
4.4. Chemical Concentration in the Unsaturated Zone in 2002

Iodide in suction cups at different depths on plot 3

Atrazine in suction cups at different depths on plot 3

Isoproturon in suction cups at different depths on plot 3
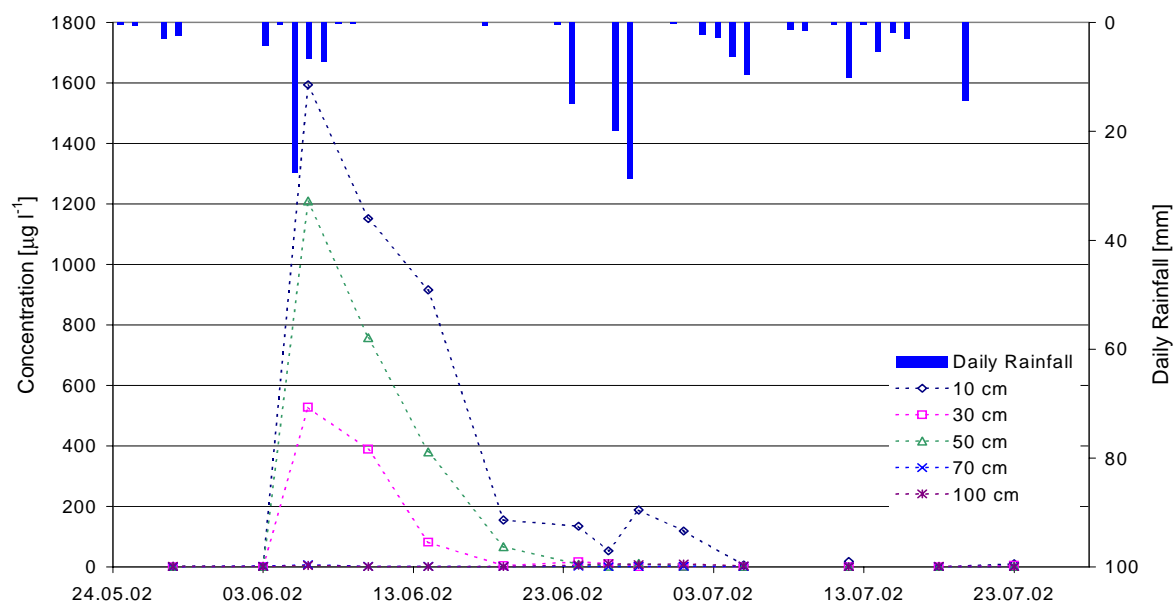
(for concentrations on plot 4 see Ch. 4)

4.5. Chemical Concentration in the Saturated Zone in 2001

On plot 3
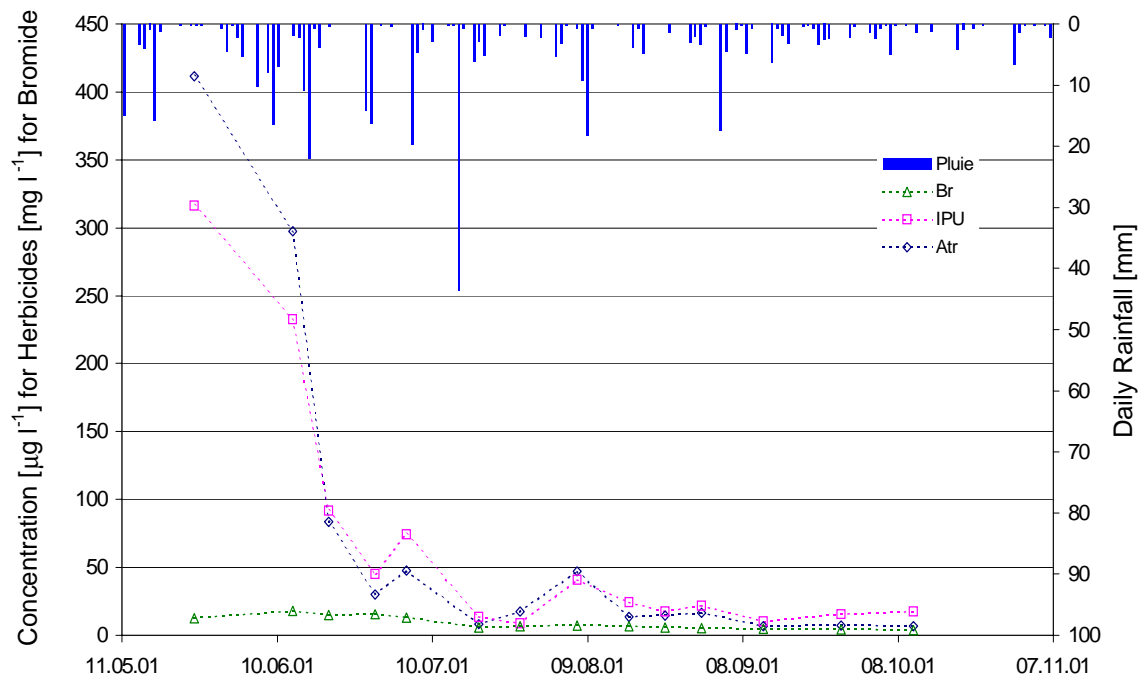
(for concentration on plot 4 see Ch. 4)

4.6. Chemical Concentration in the Saturated Zone in 2002

On plot 3
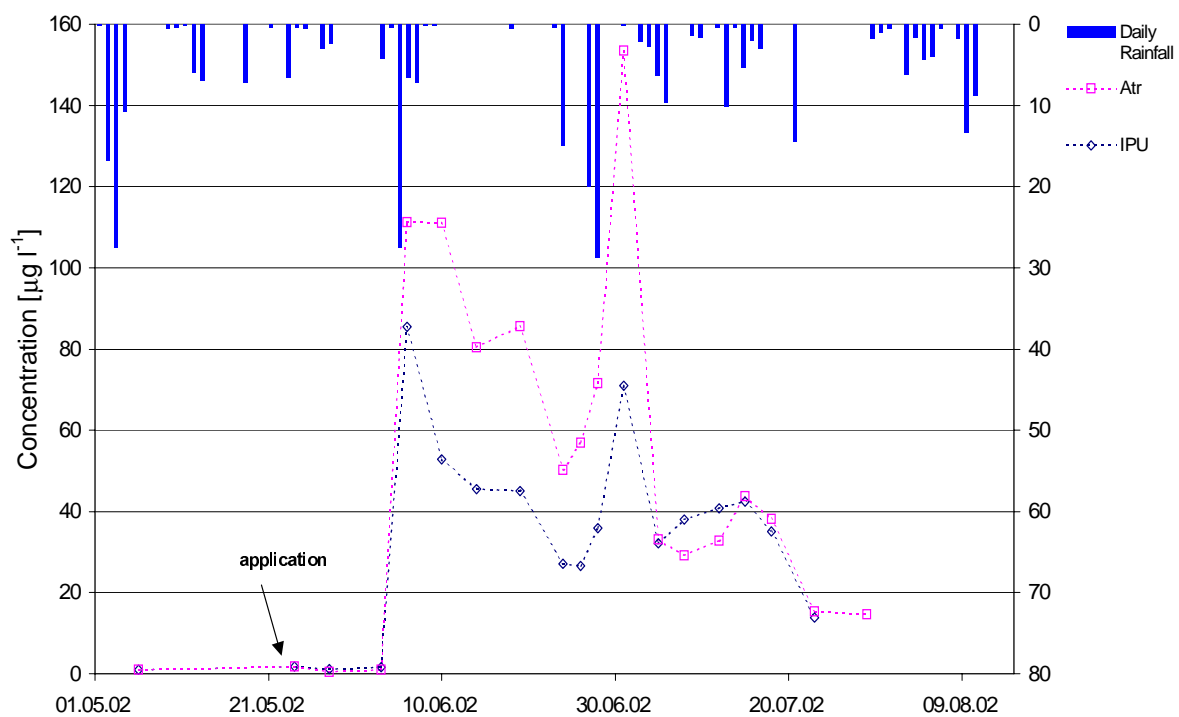
(for concentration on plot 4 see Ch. 4)

4.7. Mass Balances in 2001

On plot 3
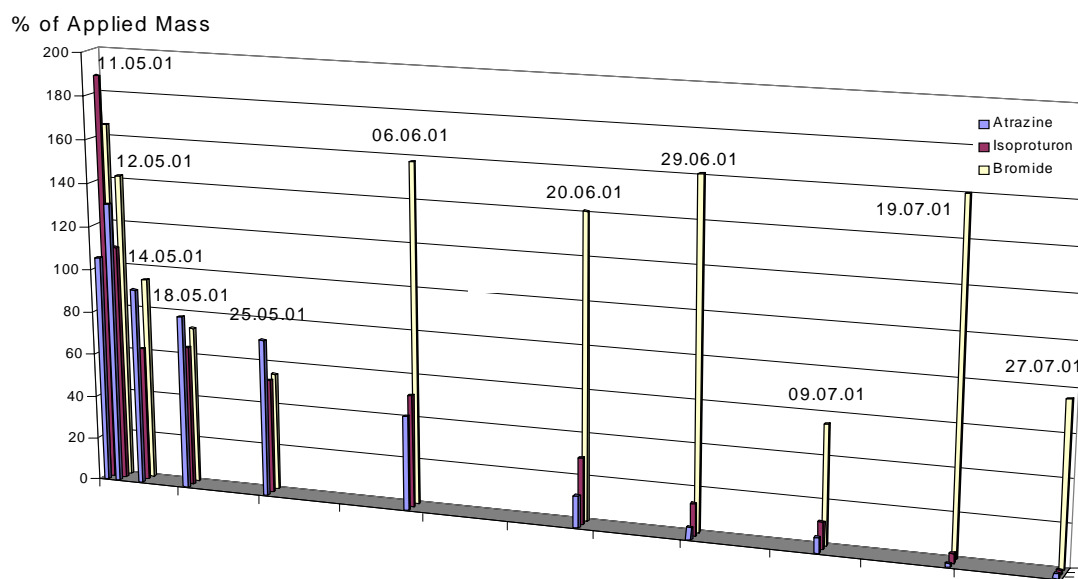
On plot 4
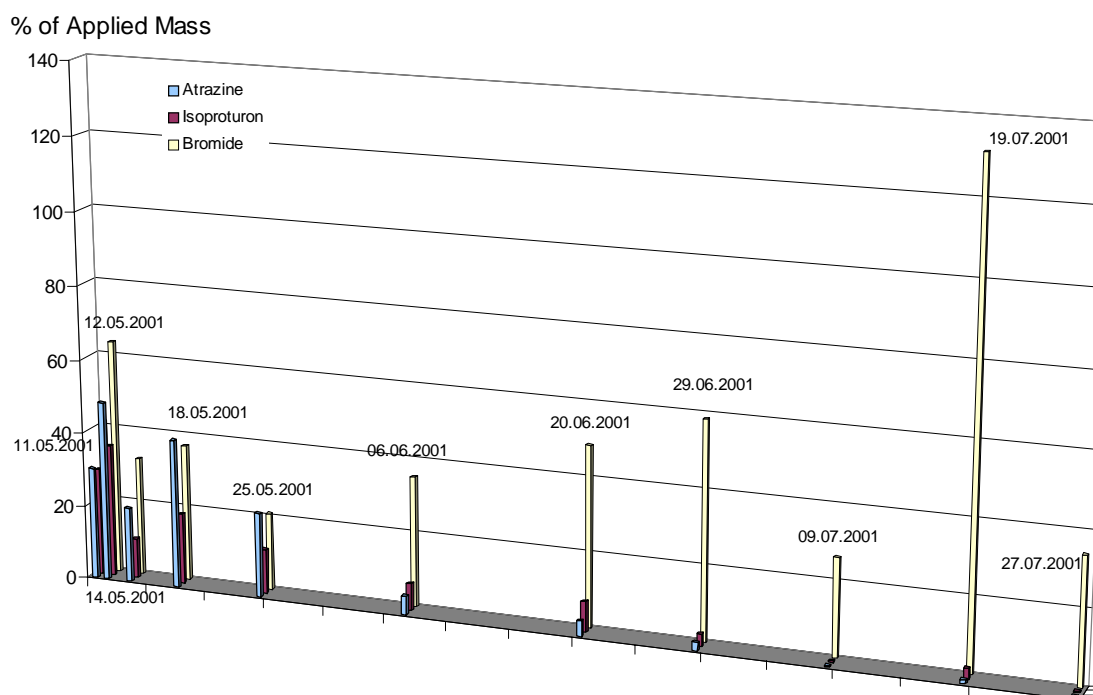
4.8. Mass Balance in 2002

On plot 4
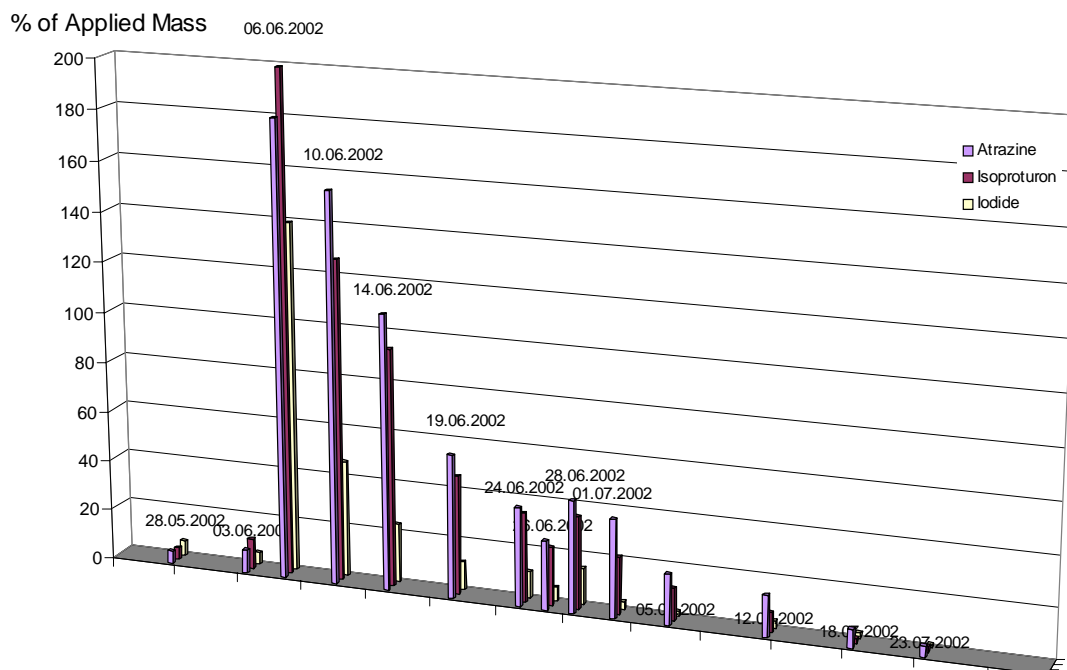
For different depth segments on plot 4
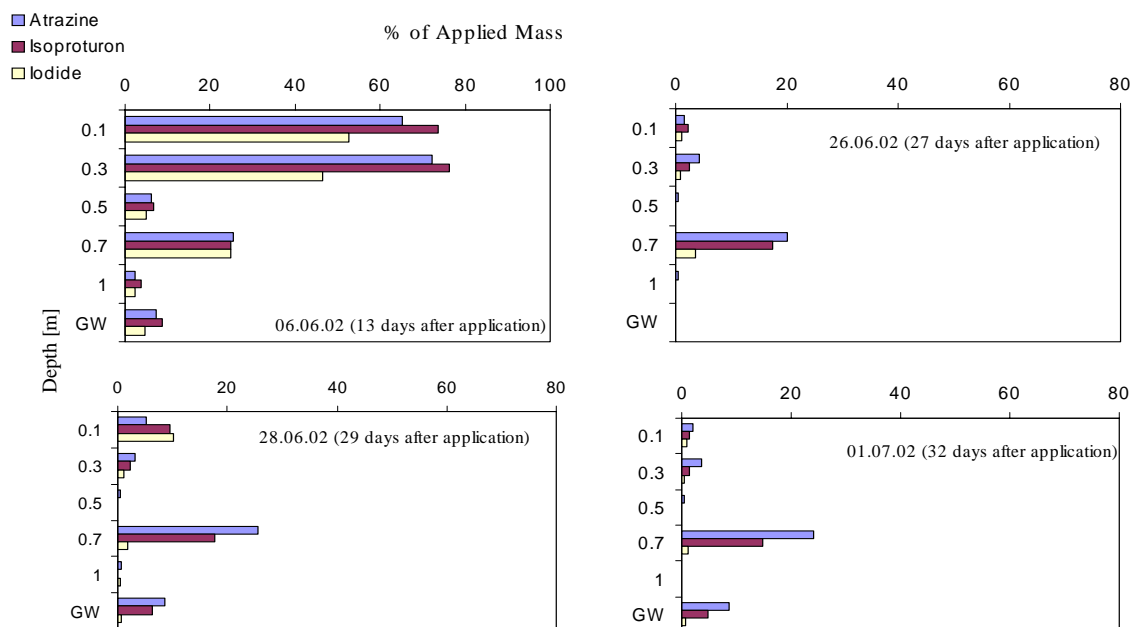
(for mass balance on plot 3 see Ch. 4

5.1. Residual Errors of the Inverse Calibration

Approach 1

		Soil Water Pressure Head					Water Content					GW
	Depth [cm]	10	20	40	60	90	10	20	40	60	90	Position
Plot 3	ME	1549.95	2012.89	1623.74	815.98	991.94	0.04	0.02	0.05	0.02	0.02	0.00
	RMSE	-40.90	-39.77	-40.98	-31.34	-39.07	5.47	3.33	5.73	2.02	1.75	0.00
	CD	1.76	3.22	2.80	3.52	2.81	0.07	1.20	2.13	1.11	0.54	1.00
	EF	0.57	0.38	0.30	0.48	0.30	-9.71	0.64	0.31	0.41	-0.95	1.00
	CRM	0.05	0.08	0.13	0.05	-0.10	-0.02	-0.02	-0.04	-0.01	0.00	0.00
Plot 4	ME	2324.78	1935.04	1366.89	866.01	754.01	0.06	0.04	0.01	0.02	0.02	0.00
	RMSE	-35.78	-30.64	-23.38	-20.56	-18.46	10.89	7.28	2.25	3.21	3.28	0.00
	CD	1.93	1.86	2.07	2.25	2.37	0.52	0.49	1.42	0.18	0.03	1.00
	EF	0.48	0.46	0.52	0.57	0.58	-0.90	-1.01	0.30	-5.10	-30.66	1.00
	CRM	-0.05	0.06	0.04	0.03	-0.03	-0.08	-0.06	-0.01	0.03	0.03	0.00

Approach 2

		Soil Water Pressure Head					Water Content					GW
	Depth [cm]	10	20	40	60	90	10	20	40	60	90	Position
Plot 3	ME	2398.04	2998.69	2208.25	1198.48	753.56	0.04	0.05	0.07	0.02	0.02	374.33
	RMSE	-72.38	-67.88	-71.33	-55.77	-46.54	6.76	9.61	10.64	5.20	3.20	14.66
	CD	1.18	0.95	0.80	1.20	2.38	0.11	0.88	1.31	1.13	0.47	0.50
	EF	-0.30	-0.69	-0.84	-0.24	0.40	-5.05	-0.33	-0.24	0.13	-1.03	0.32
	CRM	0.31	0.35	0.34	0.24	0.11	-0.02	-0.05	-0.06	-0.02	-0.01	0.05
Plot 4	ME	2673.23	3075.25	1623.39	994.95	559.14	0.07	0.05	0.03	0.01	0.01	511.50
	RMSE	-41.00	-42.61	-35.30	-30.33	-24.03	13.55	10.67	4.89	0.67	1.48	17.57
	CD	5.35	2.17	1.54	1.65	2.07	0.34	0.22	0.26	0.84	0.13	0.41
	EF	0.32	-0.04	-0.10	0.03	0.29	-1.95	-3.36	-2.32	0.76	-6.93	-0.22
	CRM	0.13	0.25	0.24	0.21	0.14	-0.13	-0.10	-0.05	0.00	0.01	0.11

5.2. Calibration Results on Plot 3 - Graphical Analysis
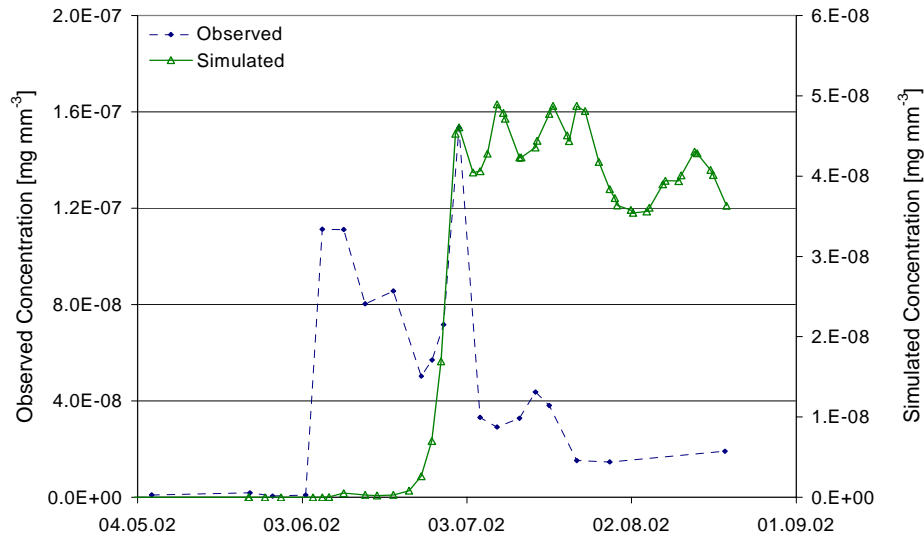
Approach 1
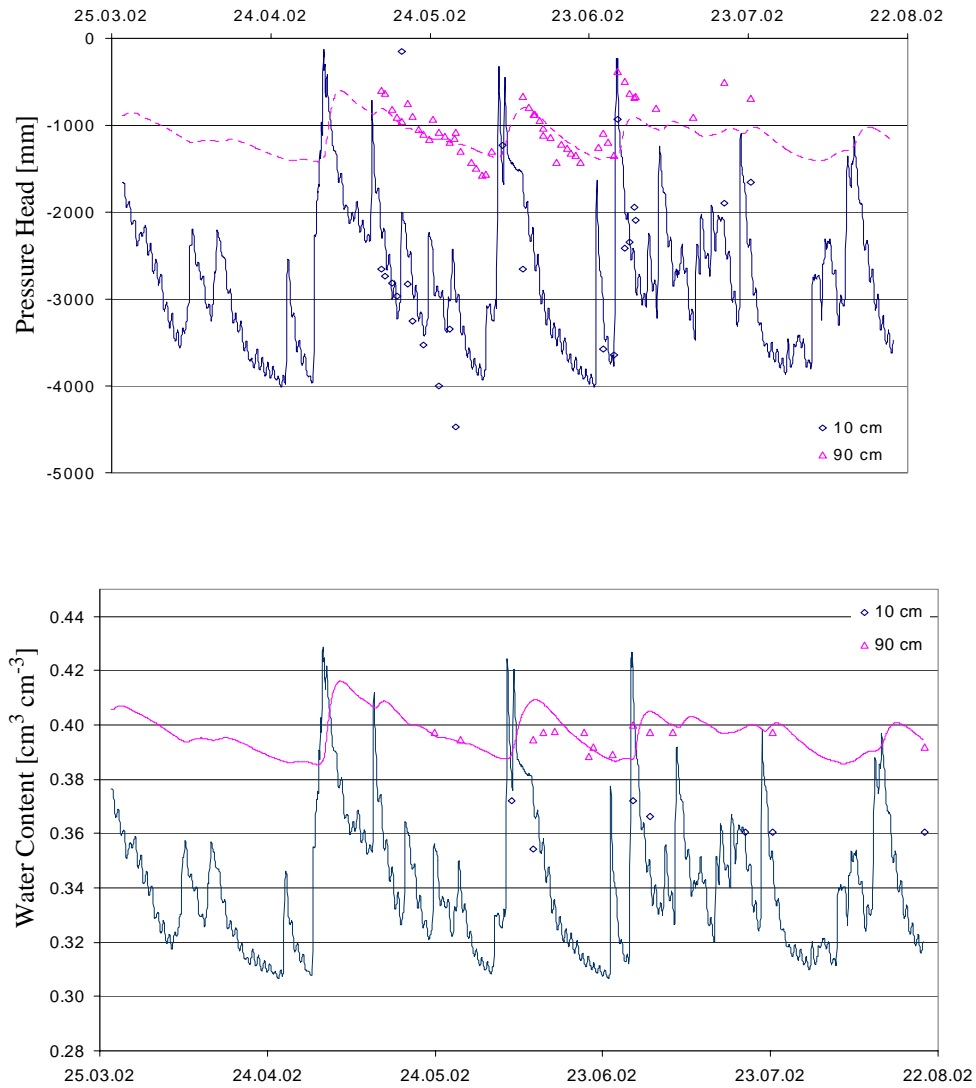
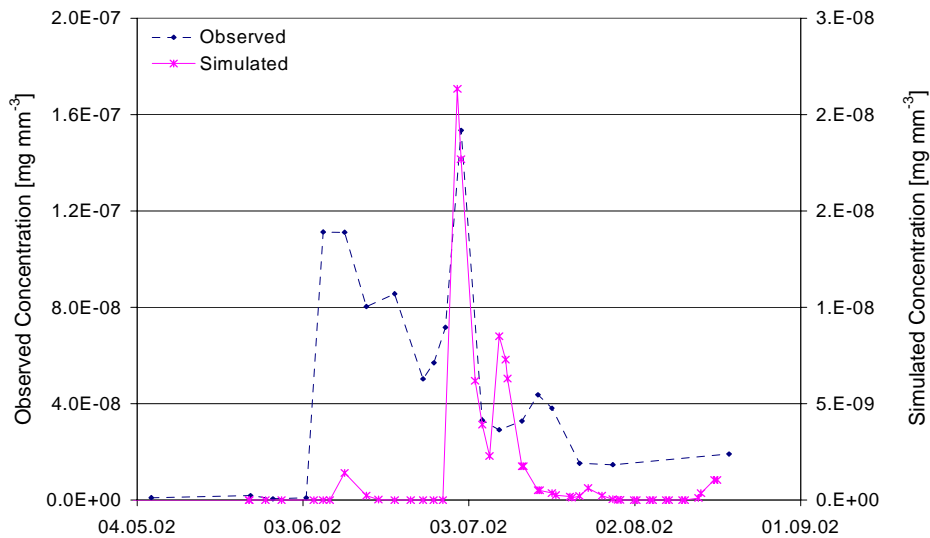## Approach 2
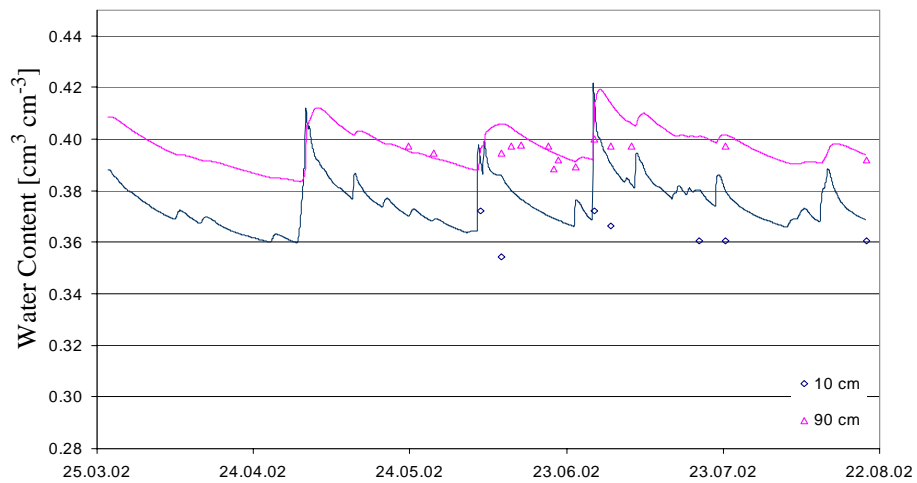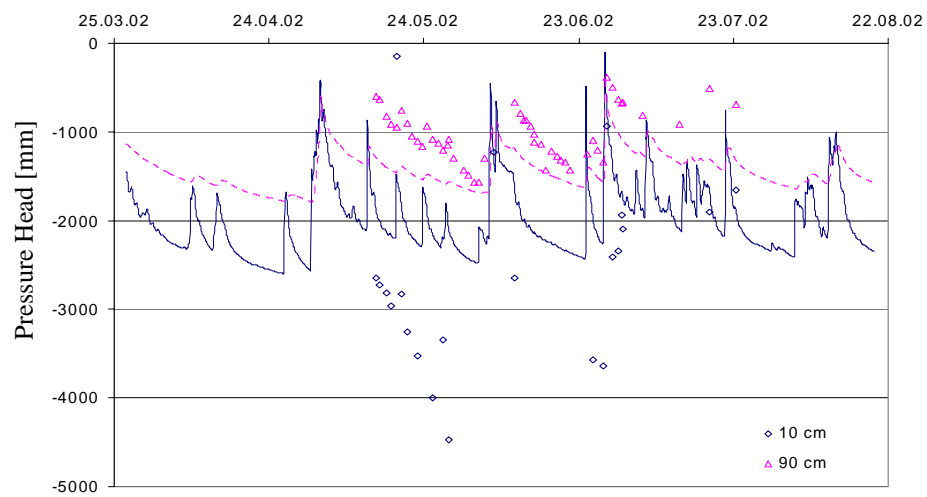
GW Level
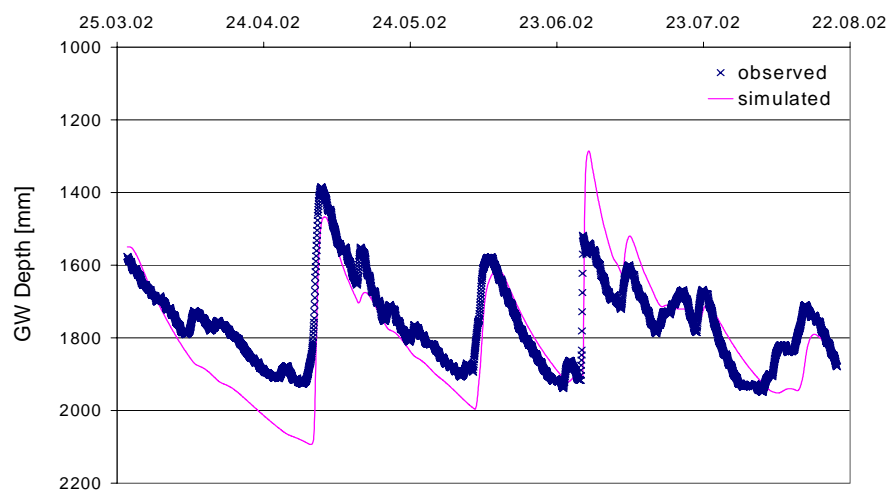
(for plot 4 see Ch. 5)

5.3. Simulated and Observed Atrazine Concentration in the GW in 2002, Plot 3
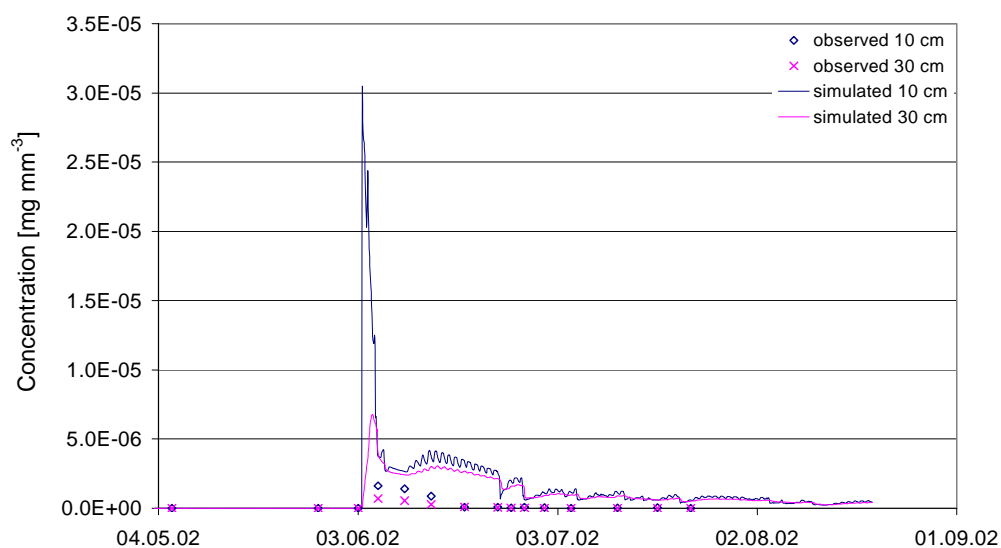
Approach 1
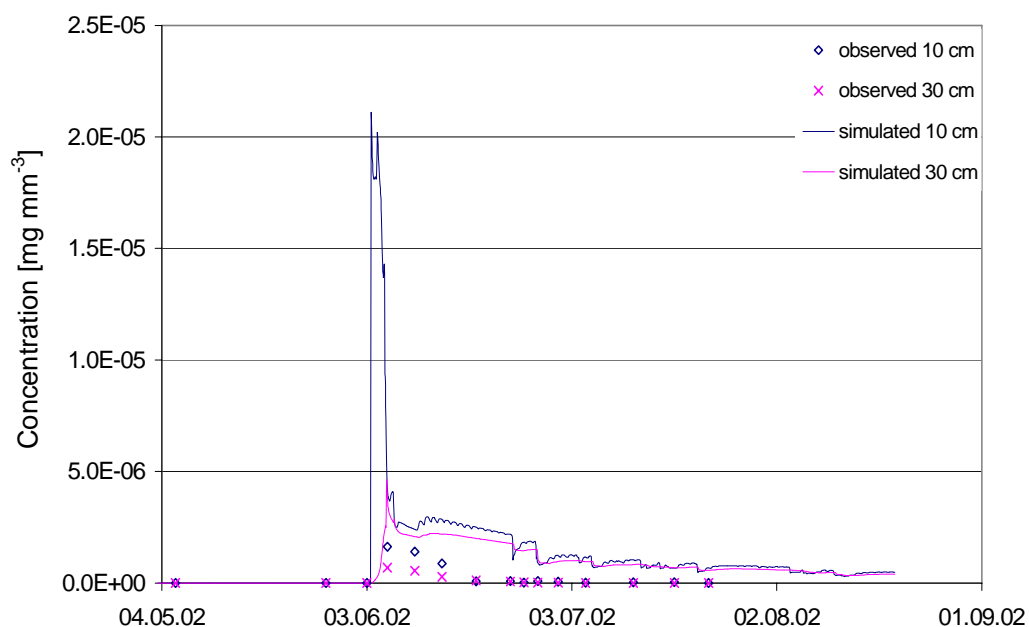

Approach 2

(for plot 4 see Ch. 5)

5.4. Simulated and Observed Atrazine Concentration in the Unsaturated Zone in 2002, Plot 3

Approach 1

Approach 2

(for plot 4 see Ch. 5

Appendix 5.4.

6.1. Soil Use and Agricultural Practices at the Piezometer Locations

Piezo-meter	Field Use	Herbicide	Irrigation
MAR1	pasture, few walnut trees	no herbicide application	never
MAR2	corn	atrazine in June	never
A21	apple trees	glufosinate end of May and sometimes again in August, glyphosate in November	freezing prevention second half of April: in 1998 approximately 10 times, in 1999 once, in 2000 and 2001 not at all no summer irrigation
Z17	apple trees	glyphosate + simazine after freezing season, in 2001 early May	freezing prevention: mid April until late May, fom midnight till 10 a.m. during freezing, not in 2001 summer irrigation: generally during one week in July 30 mm twice (before harvest)
Y19	apple trees	no information	no information
Y25	pasture, cows	no herbicide application	never
MAR4	apple and pear trees	glyphosate	freezing prevention: in April, not in 2001 on this field no summer irrigation needed
MAR3	pasture, sheeps	no herbicide application	never
Y08	pear trees	diuron in March/April, sometimes Glufosinate in July/August	freezing prevention: in April and early May, sprinkler irrigation, no quantification no summer irrigation
Lm9b	apple trees	no information	no information
Z12	apple trees	terbutylazine + diuron May 14, 2001 April 29, 2002	freezing irrigation: in April, not in 2001 nor in 2002 (1 sprinkler per 324 m2, 4 bar pressure, 4.5 mm valves) last summer irrigation: April 29, 2000 during 10 hours
X03	apple trees	no information	no information
X09	apple trees	no information	no information

6.2. Water Table Contour Lines and Hydraulic Gradients in the Observation Area in 1999
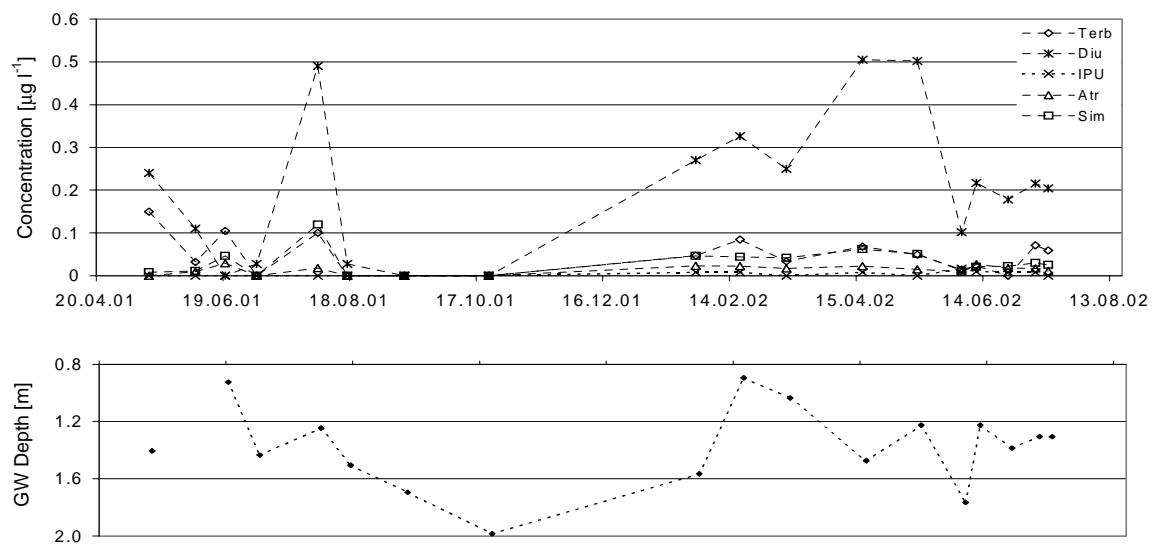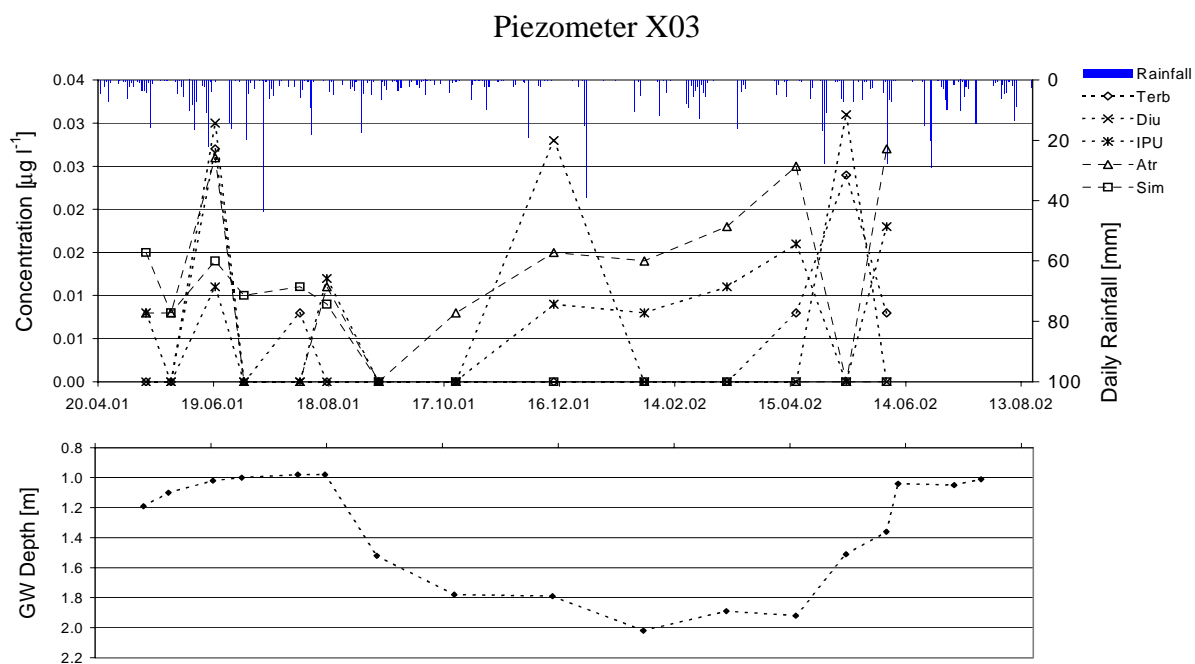
High Water Level,
July 1999
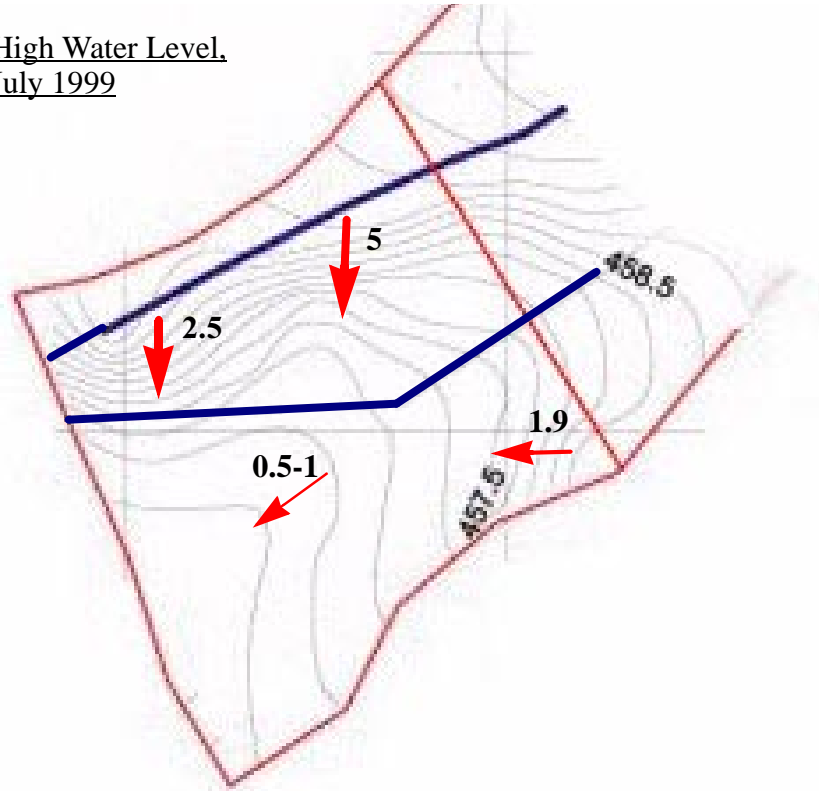
Low Water Level,
March 1999
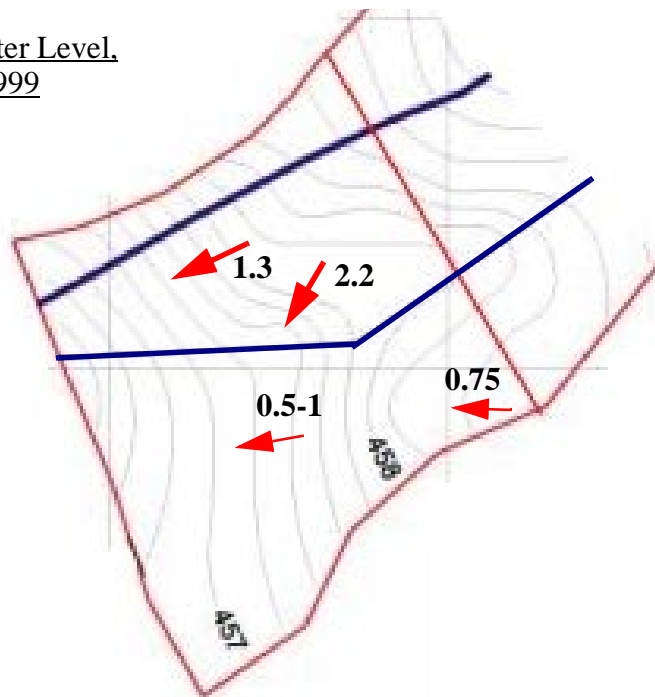
6.3. Herbicide Concentrations and GW Depth in the Piezometers
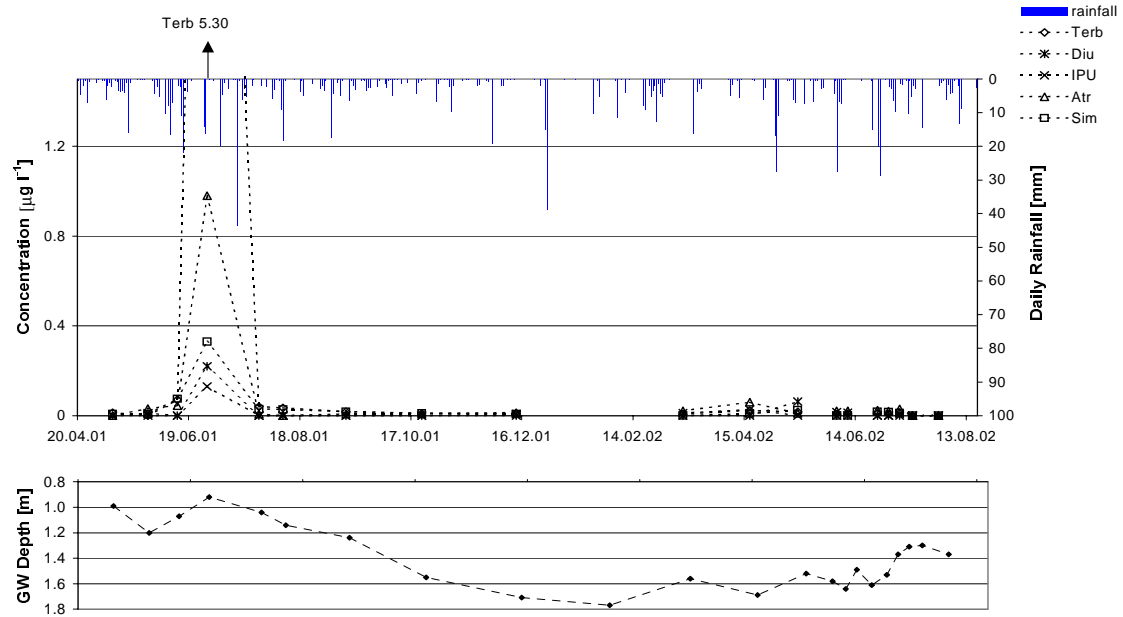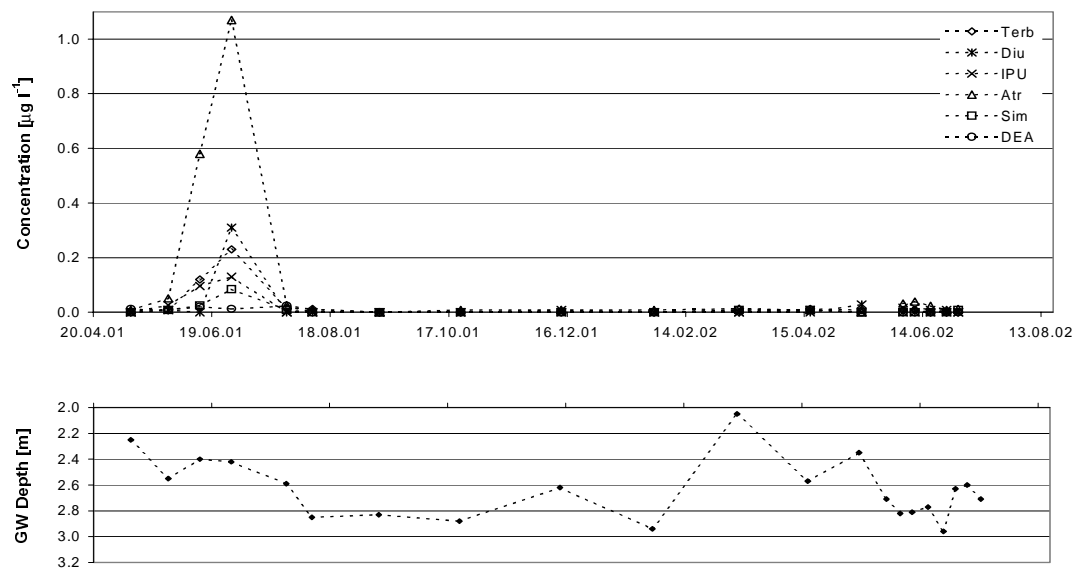
Piezometer X09
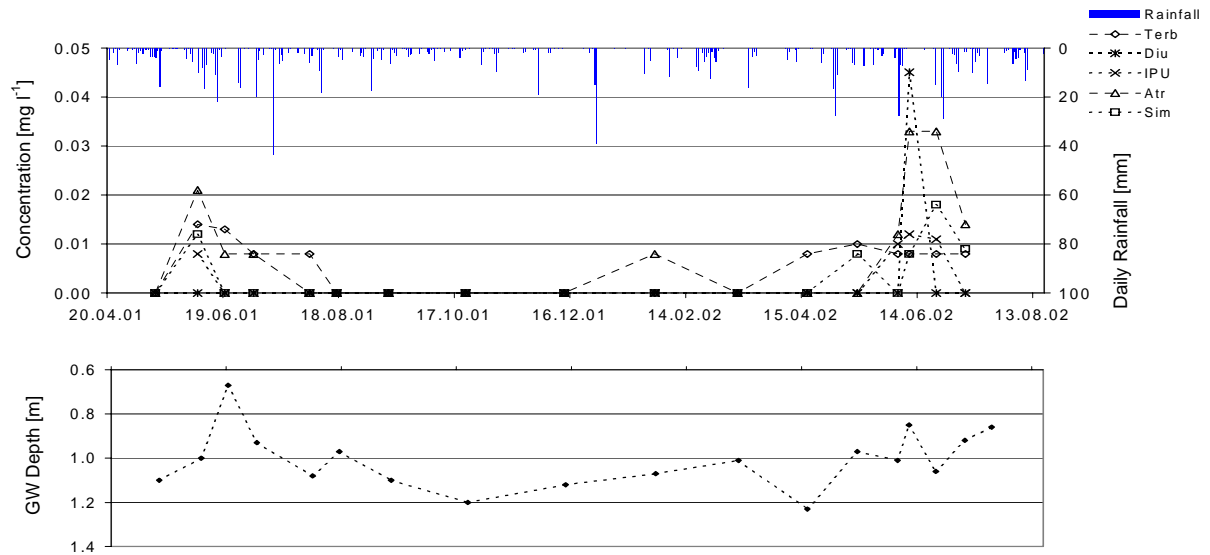
Piezometer Y08

Piezometer X03

Piezometer MAR4

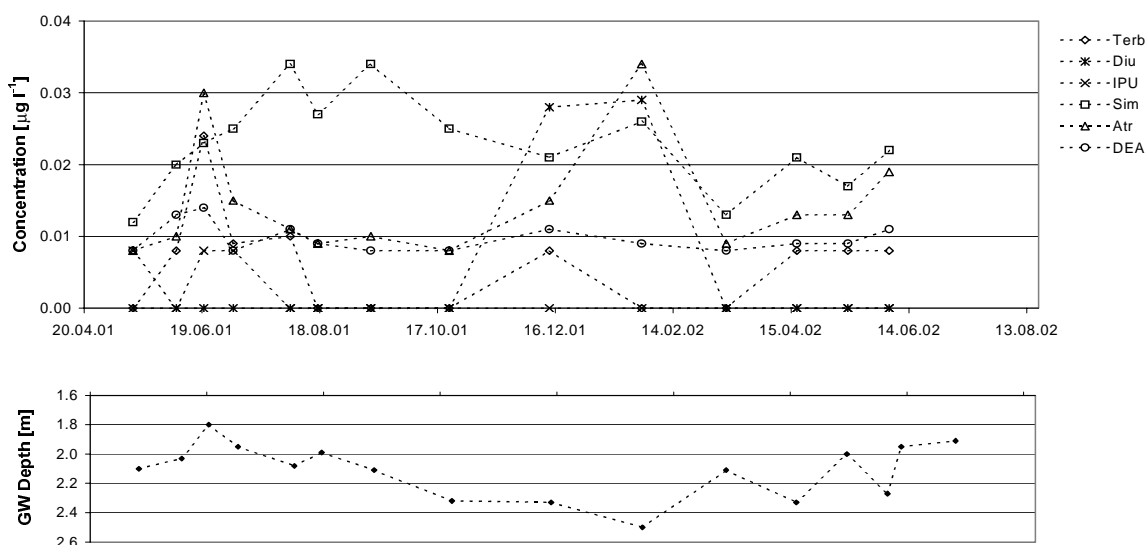The herbicide concentration exceeded the detection limit only once: 0.04 µg l^{-1} diuron on december 13, 2001.
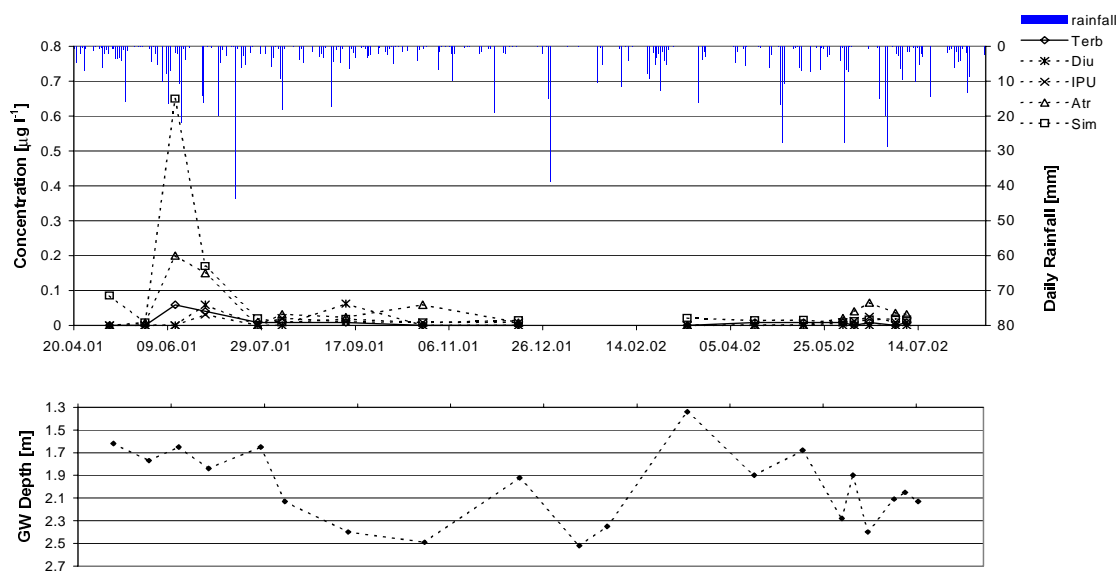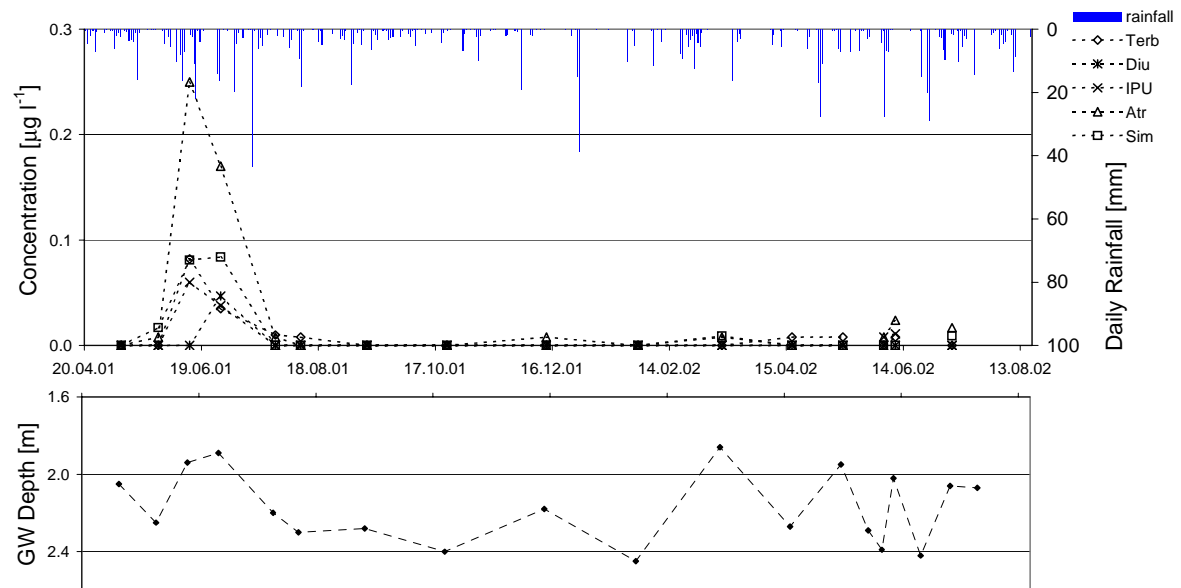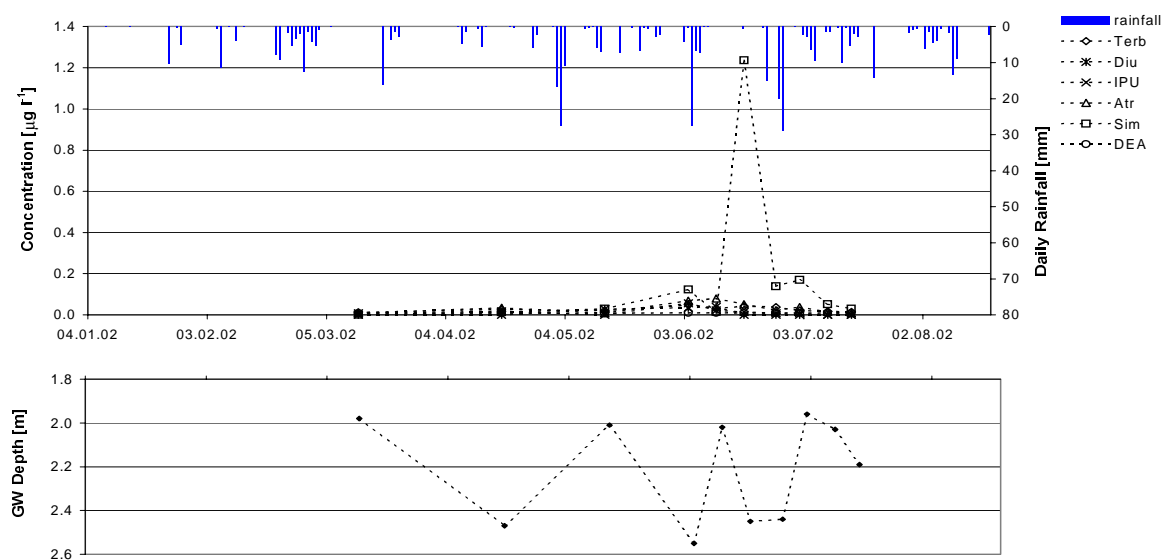
Piezometer MAR1

Piezometer MAR2

Piezometer MAR3

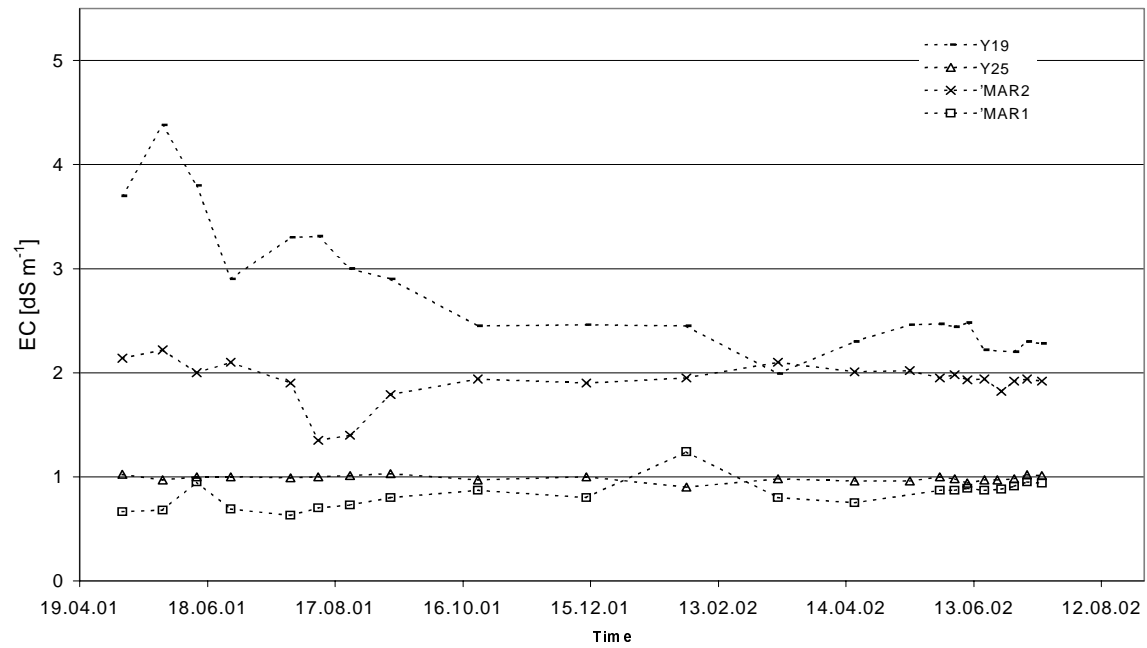## Piezometer Y19

Piezometer A21

Piezometer Lm9b

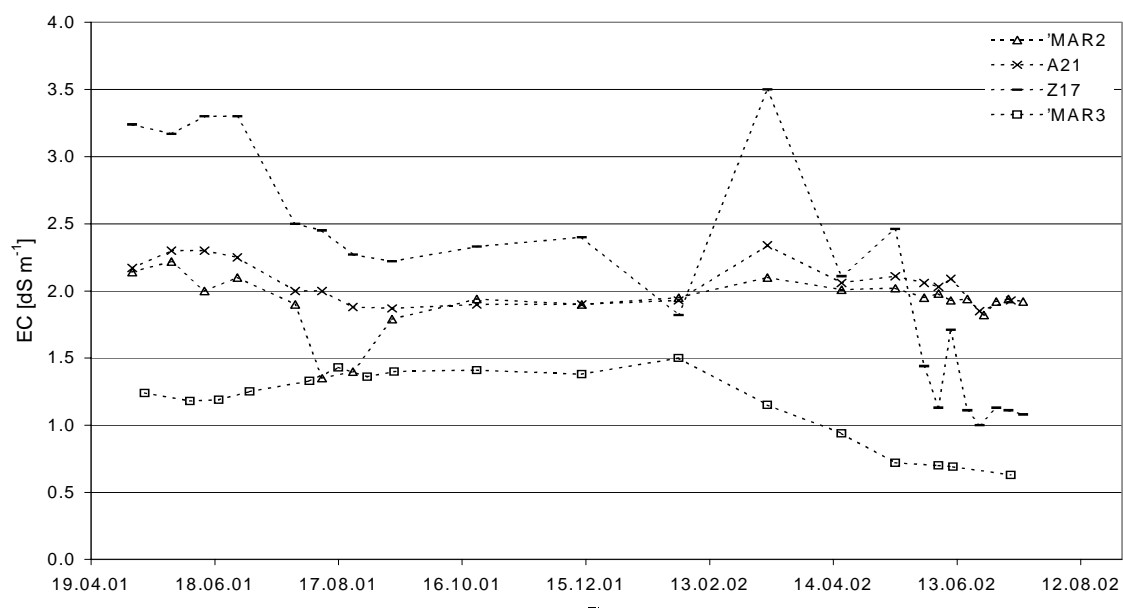(for piezometers Z12, Y25, and Z17 see Ch. 6)

6.4. Electrical Conductivity (EC) in the River-Influenced Zone
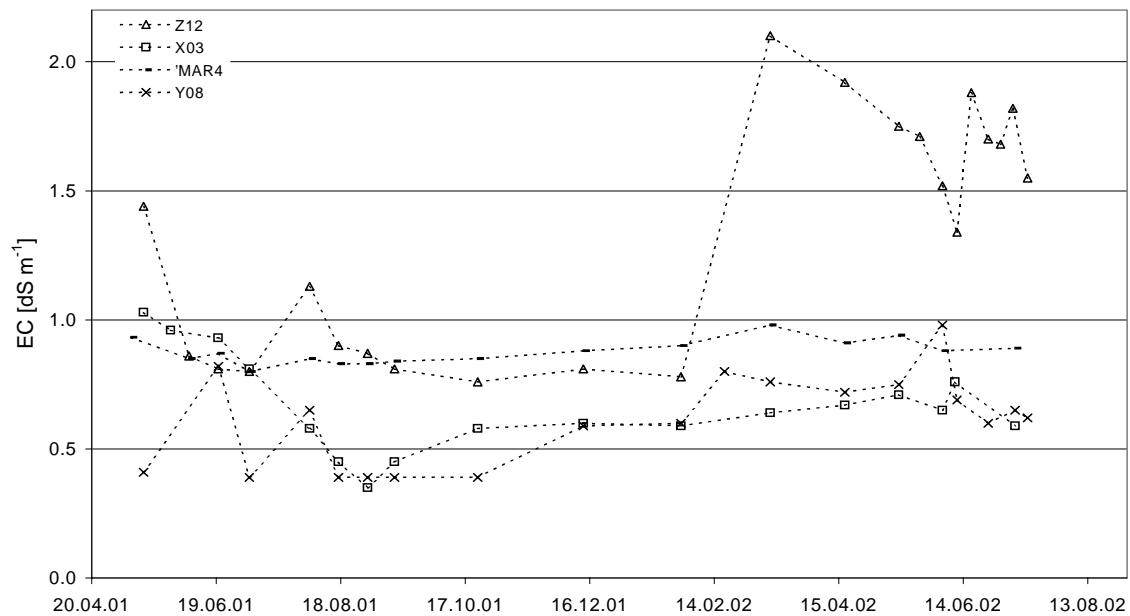
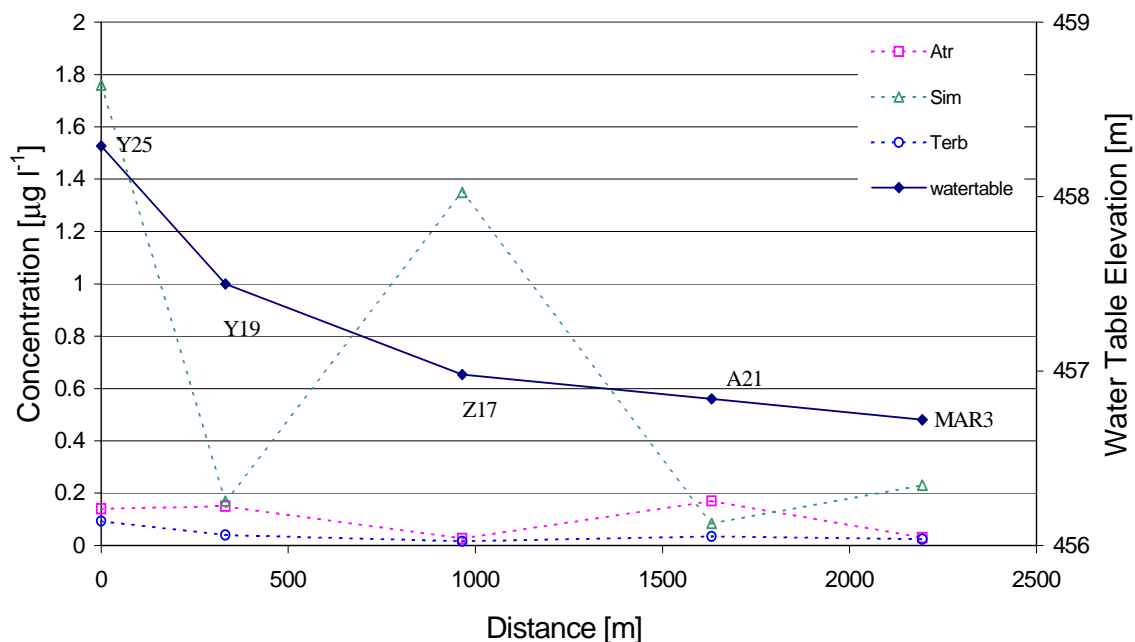# 6.5. EC in the Slope-Influenced Zone
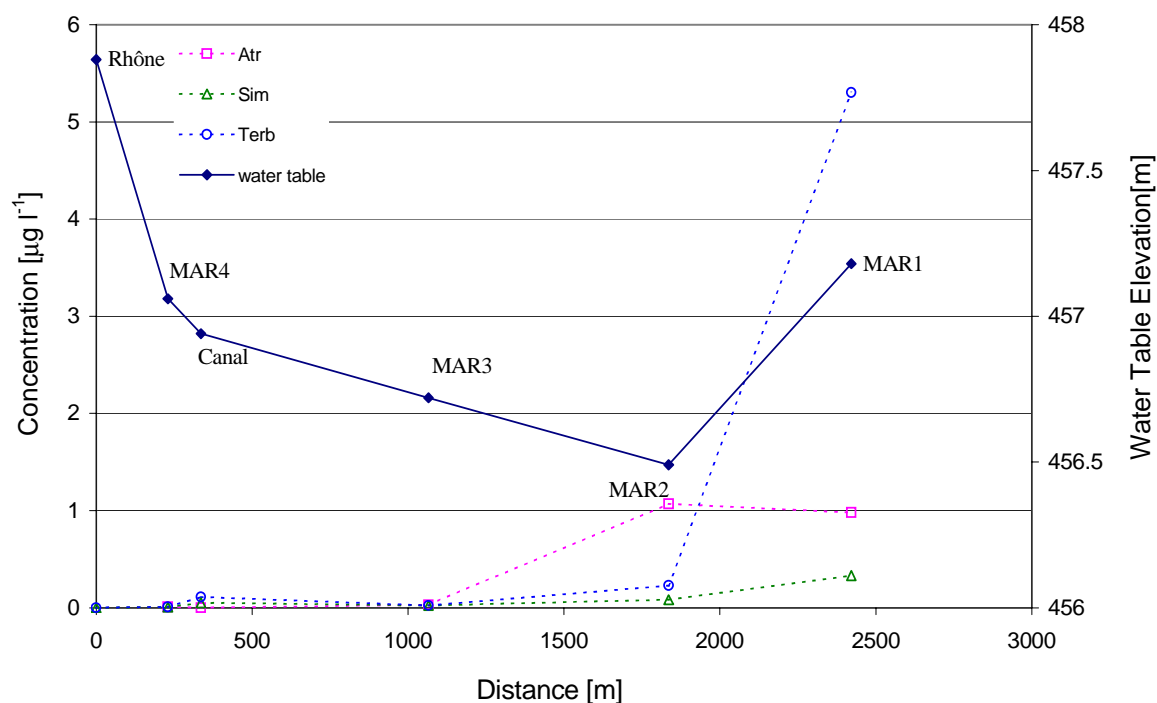
6.6. EC within the Plain

6.7. Hydraulic Gradients and Herbicide Concentration along Transects in 2001

Transect 2 in late June 2001

Lower boundary transect in late June 2001

(for transect 1 and 4 see Ch. 6)

Appendix 6.7.

Curriculum Vitae

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Education

09/1998 - 09/1999	French diploma (DEA) "Hydrologie, Hydrogéologie, Géochemie, Géostatistique" University of Paris VI, France
10/1991 - 02/1998	Study of Geology, Diploma University of Bremen, Germany, and University of Liege, Belgium

Professional Experience

07/2000 - 09/2003	Assistant Swiss Federal Institute of Technology, Department of Sciences and Environmental Engineering, Lausanne, Switzerland
03/1999 - 09/1999	Internship "Ecole des Mines de Paris" and "Commissariat à l'Énergie Atomique", Paris, France
04/1998 - 07/1998	Freelance Engineering office GeoC, Kiel, Germany
12/1995 - 02/1997	Chemical Assistant Department of Hydrogeology and Geochemistry, University of Bremen, Germany

Publications and Conferences

Meiwirth, K. & Mermoud, A. (2002): Local and regional study of the transport of herbicides in an alluvial zone. - In: Water Resources and Environmental Research Proceedings of ICWRER 2002, Dresden, Germany. Editor: Schmitz, G. H.

Meiwirth, K. & Mermoud, A. (2001): Transfer de pesticides en milieu alluvial. - Dans: Transfer des produits phytosanitaires, diagnostic de pollution et solutions correctives. Actes du XXXIe congrès du Groupe Français des Pesticides. Lyon, May 15-17, 2001.

Meiwirth, K., Kruse, L., Wachtendorf, S., Wienberg, M., Zabel, M. & Schulz, H.D. (1996): Schwermetall-Anreicherungen in Ostsee-Sedimenten (Kieler Bucht) - Frühdiagenese und anthropogener Eintrag. - Z. dt. geol.Ges., 147/1: 137-144, 4 fig.; Stuttgart